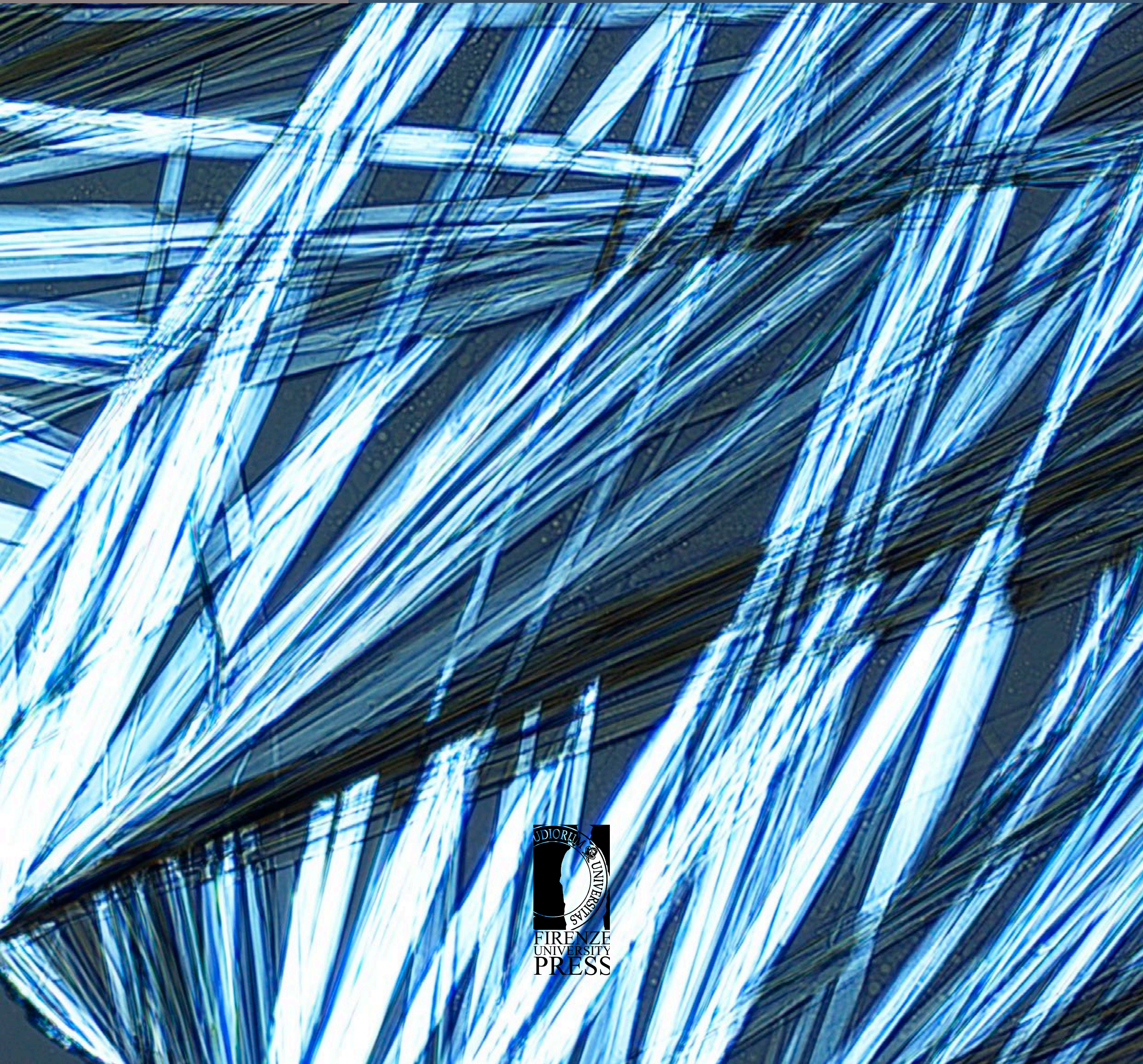
September 2017
Vol. 1 - n. 2

2532-3997

Substantia

An International Journal of the History of Chemistry



FIRENZE UNIVERSITY PRESS

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Vol. 1, n. 2 - September 2017

Firenze University Press

***Substantia*. An International Journal of the History of Chemistry**

Published by
Firenze University Press – University of Florence, Italy
Via Cittadella, 7 - 50144 Florence - Italy
http://www.fupress.com/substantia

Direttore Responsabile: **Romeo Perrotta**, University of Florence, Italy

Cover image: **Optical micrograph under crossed polarizers of a hydrated lamellar phase of ascorbyl-6-O-dodecanoate.**

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The Editorial that introduces this second issue of Substantia *focusses on a critical issue, the assessment of the quality of scientific research.*

An everlasting question that is currently debated in several institutions is: how can we measure and evaluate the performance of individual researchers? This is a terrifically concrete and overwhelming process that affects and afflicts most of scientists in their career, and ultimately the progress of Science. The outputs of Science are not manufacturing industrial products. We need to speak out about the use of more or less obscure algorithms whose final result becomes a judgment on the quality of research. The use of algorithms does not guarantee impartial neutrality, as claimed. It is typical of those who cannot really and deeply evaluate, and therefore must rely on numbers: impact factors, h indexes, citations, etc. This Editorial tries to contribute to the current international debate by presenting the case of the Italian National Agency ANVUR.

I also recommend you to read a nicely acute and amusing paper written by Gregory A. Petsko for Genome Biology *in 2008, entitled "Having an impact (factor)". Not only for fun, but for your thoughtful consideration.*

24/09/2017

Pierandrea Lo Nostro

Editorial

How do we recognize a good scientist?

On June 11, 2010 before actually starting its activities, ANVUR - Agenzia Nazionale per la Valutazione del Sistema Universitario e della Ricerca (*National Agency for the Evaluation of the University and Research System*) had raised positive expectations in Italy. It was quite clear to everyone, inside and outside the academic community, that it was useful to carefully check the quality of both teaching and research activities, respectively in all Italian universities and Research Institutes.

In these seven years, ANVUR has released several reports, and has often expressed its assessments of the quality of both University education and scientific research. However, there is no longer a general support of evalutation. ANVUR's practical activity has aroused consensus, as well as criticism, both inside and outside the academic world.

Several people criticized the way in which assessments have been used. Indeed, the Italian governments of the last seven years, have allocated remarkable "reward shares" out of the scarce FFO (Fondo di finanziamento ordinario – *Ongoing Financing Fund*) to those universities which had been the best, according to ANVUR's judgement. This has meant a flow of funds from the Universities of Southern Italy up to those of the Centre and North of the country. As a consequence, the University system of the most economically depressed area of Italy has been further weakened, whereas the richer northern areas have taken advantage of it. In turn, fewer young people have enrolled in the South. Also, many boys and girls from the South moved towards the universities of Central and Northern Italy. Many other youth did not enroll at all. However, ANVUR cannot be blamed for this usage of the evalutation of university system. Nor the idea of evalutation itself can be blamed. In fact, this is a political responsability.

This choice does not concern Italy only: it is actually a general problem. The idea is spreading all around Europe and the whole world, that research is an enterprise like any other, and that human and financial resources should be concentrated in a few centres and universities of excellence, which can "compete and win" on the International market for the production of knowledge and education. From this perspective, most research institutes and universities only fulfil residual tasks.

This choice is a direct attack against both democracy and knowledge, as well as against the effectiveness of scientific research. It is indeed an attack against the democracy of knowledge, since it involves the fact that only a chosen few can get access – as researchers, lecturers or students – to universities and centres of excellence. In the case of students, there is a clear inequality. In several countries – from the United States to the United Kingdom – the tuition fees for universities of excellence are so expensive (tens of thousands euros a year for foreign students in some British universities) that only the children of very rich families can enrol. On the other hand, education is not a "rival" good, which diminishes as it is used. Quite the opposite: the more it is used, the more it grows. This was clear to

Substantia. An International Journal of the History of Chemistry 1(2): 5-6, 2017
ISSN 2532-3997 (online) | DOI: 10.13128/substantia-22

Vannevar Bush, as he wrote his report to the US President in 1945 – *Science, the Endless Frontier*, the "manifesto" of modern science policy. In it, Bush stated the need to enlarge the recruitment of "brains" necessary for the scientific development, by opening the university doors to the children of all US families, because intelligence does not belong to one social class only, but is rather transversal by definition. During the Second World War, the U.S. were planning to take – thanks to scientific research too – the economic and cultural leadership of the planet. In the same way, the whole world needs the intelligence of everyone.

Another kind of criticism has been made by a section of the Italian accademic community, and concerns ANVUR's method of evalutation. Indeed, they say ANVUR uses in an excessively overriding and rigorous way the typical parameters of bibliometry when assessing the research quality of a university: namely, the number of published papers; the impact factor of journals in which they are published; and, finally, the number of quotations of each paper.

This type of criticism has a wider significance. Indeed, many people all over the world are wondering whether the bibliometric method may indeed be considered the best evalutation method for research, or even for researchers.

It is true that, in a world where several millions people devote their lives to science, in the framework of a growing number of International projects, it is convenient to find a universal evalutation method for research activity. However, it is also true that, if we reduce evalutation to the mere analysis of bibliometric parameters, this may produce misleading results.

Indeed, bibliometric analysis has its own inherent limits, as pointed out by an endless scientific literature. We cannot analyze them in detail here. We'll just consider its main limits, since they can steer the evolution of the International research and Higher Education system in undesiderable directions.

In bibliometric analysis, research quality and quantity tend to match. Normally, quality is assessed by measuring quantity. Now, the number of papers published in International scientific journals, as well as quotations obtained, are significant indicators of a researcher's talent. However, they are not the only indicators, and probably not the main ones.

In any case, the evalutation of quality as based esclusively on bibliometry is not only incomplete: it is also misleading.

Young people, in particular, pay a high price for this evaluation system. First of all, even geniuses are penalised, because they have had no time as yet to publish a lot of papers and get quotations. Secondly, this leads to a vision of scientific activity as based upon the "publish or perish" principle, rather than upon good ideas.

Bibliometric evaluation, when used in the wrong way, may become a levelling-out power in the research community, for more than one motive.

First of all, the "publish or perish" principle tends to eat away at scientific creativity, in favour of Thomas Kuhn's "normal science". Even the search for a high number of quotations may become a levelling-out element, because it leads to join "fashionable" schools of thought, rather than look for originality, which is one of the five values considered by Robert Merton as the bases of scientific enterprise.

The exclusively quantitative pressure becomes a levelling-out power, not only for individual researchers, and for small groups of researchers, but also for large Institutes and broad areas of science. Indeed, both financial and human resources tend to be concentrated in those Institutes and areas which are better assessed. As a consequence, small – but promising – institutes and areas suffer from a worse assessment – as in the case of the flow of students from Southern to Northern Universities in Italy. As a result, we may get a world scientific system constituted by a sea of mediocrity and a few islands of excellence, where many papers are published and lots of quotes are made, where as Kuhn's "dominating paradigms" are not challenged.

It would be something of a paradox that an age so rich in scientists – the world has never had so many of them – also becomes an age poor in groundbreaking scientific ideas.

Hence the need, which is also felt ouside academia, to get past the bibliometric method and look for a satisfying answer to the difficult question, which the German physicist Reinhard Werner recently posed in *Nature*: «How do we recognize a good scientist?»

However, the pooling of human and financial resources in few "knowledge firms" competing on the International market, together with the wrong method of evaluation of research quality can lead to the end of science itself. This has already happened in the past: Hellenistic science, for instance, was "forgotten" with the Romans conquering the Mediterranean area. It took Europe a millennium and a half in order to go back to its own true nature. In the same way, if science resorts to seeking – like any other firm – immediate results which may increase its competitiveness; if it entrenches itself smugly in a few fortresses; if it promotes uniformity rather than innovation, it risks dying out.

Therefore, the urgent question now is: "How do we recognize and save a good science?

Pietro Greco

Substantia
An International Journal of the History of Chemistry

Firenze University Press
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Citation: H. Kragh (2017) On the Ontology of Superheavy Elements. *Substantia* 1(2): 7-17. doi: 10.13128/substantia-25

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declared that no competing interests exist.

Research Article

On the Ontology of Superheavy Elements

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Abstract. The study of so-called superheavy elements with atomic numbers $Z > 102$ has for several decades been a major research field in nuclear physics and chemistry. Presently all elements up to and including $Z = 118$ have been discovered and assigned official names by IUPAC. To speak of "discovery" is however unfortunate since the elements are in reality produced, manufactured or created in the laboratory. They are not found in nature. Moreover, it is not obvious that they exist in the normal sense of the term or that they can be called elements at all. Apart from sketching the history of transuranic and superheavy elements, the paper focuses on some of the philosophical issues which are relevant to the synthesis of very heavy elements at the end of the periodic table. In addition, the relationship between superheavy elements and exotic atoms (such as anti-atoms and muonic atoms) are briefly considered.

Keywords. Superheavy elements, nuclear chemistry, transuranic elements, discovery, periodic table.

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1. INTRODUCTION

For more than half a century the synthesis and study of very heavy chemical elements have attracted much attention not only scientifically but also in the public sphere. What are known as superheavy elements, commonly abbreviated SHEs (SHE in the singular), are investigated in a few large and very expensive research facilities currently located in Russia, the United States, Germany, and Japan. Whereas the transuranic elements up to $Z = 100$ were produced by means of neutron capture or irradiation with alpha particles, since the late 1960s the basic method of synthesis has been heavy-ion collisions where a target of a heavy element is bombarded with accelerated ions of a lighter element. For example, in 1981 a few atoms of element 107 (bohrium) were produced in the nuclear reaction

$$^{54}_{24}\mathrm{Cr} + {}^{209}_{83}\mathrm{Bi} \rightarrow {}^{262}_{107}\mathrm{Bh} + {}^{1}_{0}n$$

In so far that SHE research is concerned with the formation of new atomic nuclei and relies crucially on advanced accelerator and detection technology, it is a branch of nuclear physics rather than chemistry. On the other hand, in the identification of new nuclides methods of nuclear chemistry are indispensable.

More importantly, SHEs are about elements and there is a long historical tradition that everything concerning new elements belong to the domain of chemistry. The responsibility of recognizing new elements still belongs to IUPAC (the International Union of Pure and Applied Chemistry) and not to the physicists' sister organization IUPAP (the International Union of Pure and Applied Physics). The distinction between physics and chemistry in modern SHE research is in some way artificial as workers in the field rarely consider themselves as either physicists or chemists. Nonetheless, the relationship between the two sister sciences in this research area has often been characterized by controversy rather than harmony.[1]

While the scientific literature on the synthesis and properties of SHEs is dauntingly large, there is no comprehensive history of SHE research. What has been written is limited to reviews from the perspective of the scientists participating in the development.[2] Next to nothing has been written on the subject from a proper historical perspective and even less from a philosophical perspective. And yet, as Eric Scerri points out, the synthesis of SHEs "has raised some new philosophical questions regarding the status of the periodic law."[3] The subject is indeed of considerable interest from the point of view of history, philosophy and sociology of science.[4]

In this paper I focus on the crucial notion of what constitutes a chemical element. Can one reasonably claim that superheavy elements exist in the same sense that the element oxygen exists? After all, they are created in the laboratory and not discovered in nature such as has been the case with most elements. Apart from this ontological question, SHE research also involves the epistemic question of how knowledge of a new SHE is obtained and what the criteria for accepting discovery claims are. And, what is equally important, *who* are responsible for the criteria and for evaluating discovery claims? The latter questions are relevant to the paper, but not what it is primarily about. They deserve a fuller treatment.

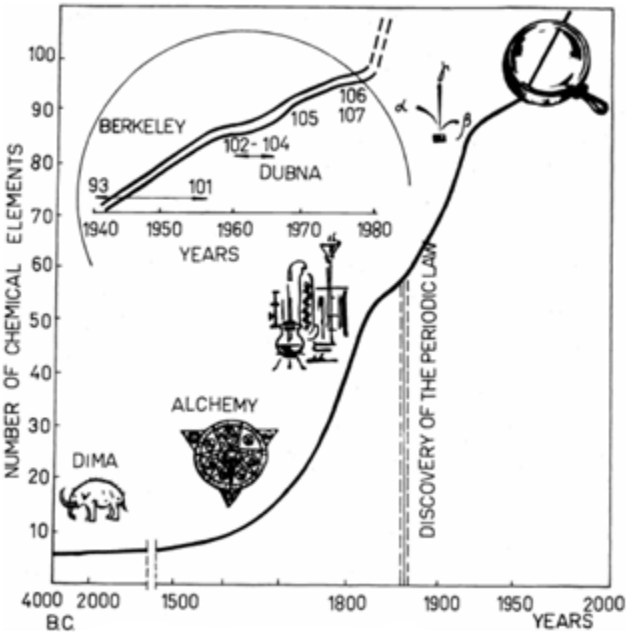

Figure 1. A version of the history of element discoveries according to two leading Dubna scientists. Source: G. N. Flerov, G. Ter-Akopian, *Pure Appl. Chem.* **1981**, *53*, 909, on p. 910. © IUPAC.

The synthesis and scientific study of SHEs, not to mention the historical development of the field, may not be well known to the majority of chemists and historians of chemistry. For this reason I start with two introductory sections offering a brief historical account of how the early attempts in the 1930s to produce transuranic elements in the post-World War II era grew into the modern research area which may be best characterized as a hybrid between high energy physics and nuclear chemistry.

2. ARTIFICIAL CHEMICAL ELEMENTS

The periodic table consists presently of 118 elements, starting with hydrogen of atomic number $Z = 1$ and ending with oganesson of $Z = 118$. About a quarter of the elements does not exist in nature or only exist in miniscule amounts. Twenty-six of the elements are transuranic, meaning that they have atomic numbers larger than the $Z = 92$ for uranium, the heaviest of the naturally occurring elements. The name "transuranic" (German "Transurane") may first have been used by the German physicist and engineer Richard Swinne in a paper of 1926 dealing with the periodic system.[5] On the basis of Bohr's atomic theory Swinne proposed detailed electron configurations for elements with $92 < Z < 108$.

Although speculations concerning transuranic elements can be found as early as the late nineteenth century,[6] it was only with the development of nuclear physics in the 1930s that laboratory synthesis of the elements became a realistic possibility. Famously, Enrico Fermi and his research group in Rome thought for a short while to have obtained the elements 93 and 94 by bombarding uranium with slow neutrons:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Ao} + \beta^- \rightarrow {}^{239}_{94}\mathrm{Hs} + 2\beta^-$$

The supposed but premature discovery of two new elements – provisionally called ausenium (Ao) and hesperium (Hs) – was part of the reason for awarding Fermi the Nobel Prize in physics in 1938.[7] It soon turned out that the announcement was a mistake. Only in 1940, when investigating fission fragments from neutron-irradiated uranium, did Edwin McMillan and Philip Abelson at the Berkeley Radiation Laboratory succeed in detecting element 93, soon to be named neptunium. The more important discovery of element 94 (plutonium) made by Glenn Seaborg, Arthur Wahl and Joseph Kennedy followed a year later. Due to the war it was only announced in public in a paper of 1946.

However, the first artificial element ever produced in the laboratory was sub-uranic and a result of Fermi's group in Rome. In 1937 Emilio Segré and his collaborator Carlo Perrier analyzed plates of molybdenum irradiated with deuterons and neutrons from the Berkeley cyclotron. They were able to identify two isotopes of element 43, for which they proposed the name "technetium" ten years later. There had earlier been several unconfirmed claims of having detected the element in natural sources, as reflected in names such as "masurium" and "illinium," but Segré and Perrier soon became recognized as discoverers.[8] Segré is also recognized as the co-discoverer, together with Dale Corson and Kenneth MacKenzie, of element 85 which was produced in Berkeley in 1940 by bombarding Bi-209 with alpha particles. In 1947 they suggested the name astatine for it. Tiny amounts of astatine exist in nature, and also in this case there were previous claims of having identified the very rare element.[9]

The early history of transuranic elements was completely dominated by a group of Californian chemists and physicists led by Seaborg and Albert Ghiorso. Elements 95 and 96 were first identified in 1944 at the Metallurgical Laboratory in Chicago and named americium (Am) and curium (Cm), respectively.[10] After the war followed the discovery of $Z = 97$ (berkelium, Bk) and $Z = 98$ (californium, Cf) which were announced in 1950. In 1951, at a time when six transuranic elements had been added to the periodic system, Seaborg and McMillan were awarded the Nobel Prize in chemistry "for their discoveries in the chemistry of the transuranium elements." Elements 99 and 100, named einsteinium (Es) and fermium (Fm), were first identified in late 1952, not in a planned experiment but in the fallout from a test of the American hydrogen bomb (the discovery team led by Ghiorso only published its findings in 1955, a delay caused by orders from the U.S. military). Also in 1955, the discovery of element 101 (mendelevium, Md) was announced by the Berkeley group using its cyclotron to irradiate a tiny sample of the einsteinium isotope Es-253 with alpha particles.

The Californian dominance in the synthesis of new transuranic elements was first challenged in connection with element 102. An isotope of this element was claimed discovered by experimenters in Stockholm in 1957 and some years later also by the Russian physicist Georgii Flerov and his group at the new Joint Institute for Nuclear Research (JINR) in Dubna outside Moscow. Founded in 1956, the Dubna institute soon became a most important centre for nuclear physics and chemistry.[11] Much of the later research in the synthesis of heavy transuranic elements was marked by an intense rivalry between the two research centres, one American (LBNL, Lawrence Berkeley National Laboratory) and the other Russian (JINR).

Although transuranic elements are artificial there is a faint possibility that some of their isotopes have a long life-time and are not exclusively the products of nuclear laboratories. Since about 1970 there have been numerous searches for heavy transuranic elements in nature, but so far not a single atom has been found. The exception is neptunium and plutonium which, strictly speaking, do occur naturally. However, the trace amounts found of these two elements are not of primordial origin but owe their existence to nuclear reactions in uranium such as neutron capture followed by beta decay. The two elements exist in nature in extremely low concentrations only, such as illustrated by the amount of plutonium in the uranium mineral pitchblende (largely UO_2), which is about one part to 10^{11}.

Several of the transuranic elements have been made in visible quantities and a few of them, such as long-lived isotopes of curium and americium, have even found applications in science and industry (many household smoke detectors contain the americium isotope Am-241). Plutonium is unique by being the only synthetic element produced in very large quantities, primarily a result of its use in nuclear weapons. It is estimated that today the world stockpile of the element is about 500 tons.[12] The long half-life of plutonium (2.4×10^4 years for Pu-239) means that the element is not just an ephemeral visitor on Earth but will remain with us for thousands of years to come. The heaviest isotope detected in nature is Pu-244 with a half-life of 81 million years.

3. A BRIEF HISTORY OF SUPERHEAVY ELEMENTS

The term "superheavy element" for the heaviest of the transuranic elements has no precise meaning but often refers to the transactinide elements with Z ranging from 103 to 120. The name owes its origin to the American physicist John Wheeler, who in the 1950s examined theoretically the limits of nuclear stability. However, it can be found even earlier, perhaps first in a 1938 review paper on possible transuranic elements.[13] On the basis of the liquid drop model of nuclear structure Wheeler suggested that atomic nuclei twice as heavy as the known nuclei might be ascribed "experimental testable reality."[14] With this phrase he implied that the nuclei should have a lifetime greater than 10^{-4} second. The first scientific paper with "superheavy elements" in the title appeared in 1966 and fifty years later the cumulative number of such papers had grown to approximately 2,000.

Much of the impetus for SHE research derives from theories of nuclear structure and in particular from predictions based on the shell or independent-particle model developed in the late 1940s independently by Maria Goeppert Mayer in the United States and Hans Jensen and collaborators in Germany.[15] According to Mayer, nuclei with 2, 8, 20, 50, 82, and 126 protons or neutrons were particularly stable. These were "magical numbers" representing closed shells in the nucleus, an idea which mineralogists had anticipated much earlier. The first anticipation of magical numbers dates from 1921 and was due to the Swiss mineralogist Paul Niggli.[16]

The theoretical possibility of a relatively stable element of $Z = 126$ seemed remote from laboratory physics, but in the late 1960s more sophisticated nuclear models indicated that $Z = 114$ rather than $Z = 126$ was a magic number. The region around $(Z, N) = (114, 184)$ – a "doubly magical" nucleus – was expected to represent nuclei with a relatively long half-life and therefore accessible to experimental study. The region became known as an "island of stability," a term that may first have appeared in the physics literature in 1966.[17] The hope of the experimenters was to reach the fabled island, if it existed, either by manufacturing the nuclides or by finding them in nature. As a leading SHE physicist recalled, the predictions from nuclear theory "immediately stirred up a gold-rush period of hunting for superheavy elements in natural samples."[18]

Indeed, from about 1970 many researchers began looking for evidence of SHEs in cosmic rays, meteorites, terrestrial ores, or even samples of lunar matter.[19] The favoured method was to look for tracks due to spontaneous fission, a process which is exceedingly rare in nature but is the dominant decay mode for SHEs (the probability of spontaneous fission is roughly proportional to the parameter Z^2/A). The first searches for natural SHEs were reported in 1969 by research groups from Berkeley and Dubna, and a decade later the search had grown into a minor industry. The search is still going on, but without any convincing evidence of naturally occurring SHEs.[20] Interesting as this chapter in SHE history is, in the present context there is no need to cover it.

One of the problems of reaching the island of stability is that by and large the half-lives of the longest-living nuclides decreases with the atomic number. While the half-life for Sg-269 ($Z = 106$) is 3 minutes, it is 14 seconds for Ds-281 ($Z = 110$), 2 seconds for Fl-289 ($Z = 114$), and 0.7 milliseconds for Og-294 ($Z = 118$). Another problem is the very low production rate, which typically is of the order of a few atoms per day and in some cases even lower. In spite of these and other problems all SHEs until and including element 118 have now been discovered and are officially recognized as citizens of the periodic kingdom.

The elements with Z ranging from 103 to 109 were synthesized in the two decades from 1965 to 1985, in all cases by means of heavy-ion fusion reactions where a target of a heavy element is bombarded with medium-sized ions. The elements were produced in a competitive race between scientists from Dubna and Berkeley, and since the mid-1970s also involving a third party in the form of the GSI (Gesellschaft für Schwerionenforschung)

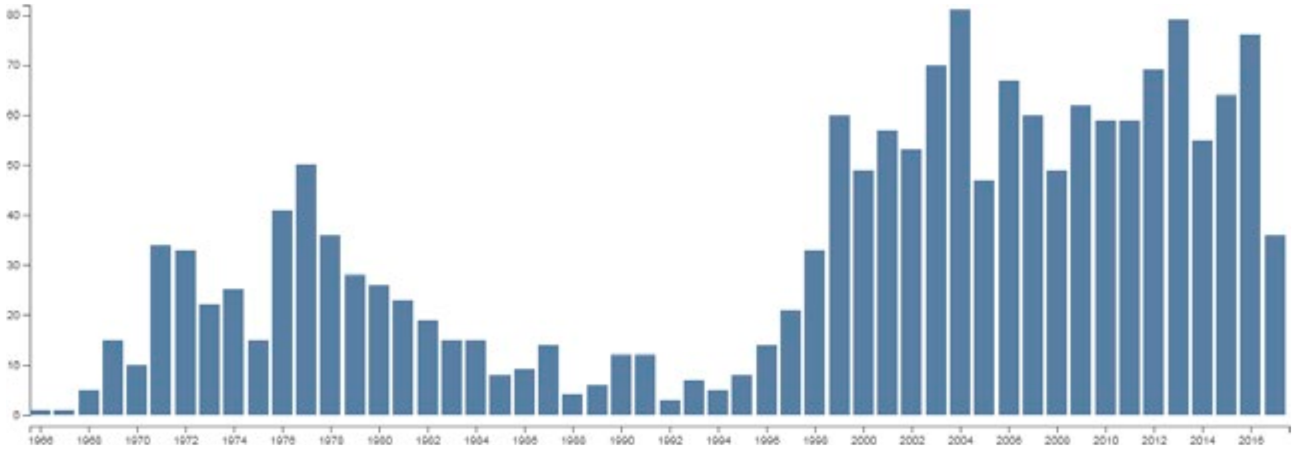

Figure 2. Number of scientific papers including the term "superheavy elements" in the title. Source: *Web of Science*.

in Darmstadt, Germany, established in 1969. In the present context there is no need to go into detail or to dwell on the many controversies between the research groups concerning priority and names.[21] Elements with atomic numbers 110, 111 and 112 were produced by the Darmstadt group in the years 1995 and 1996 and eventually named darmstadtium (Ds), roentgenium (Rg) and copernicium (Cn). The even heavier elements 114 and 116 (flerovium and livermorium) were first synthesized in Dubna by a Russian-American collaboration including scientists from LLNL, the Lawrence Livermore National Laboratory.

The most recent newcomers to the periodic table are the elements with atomic numbers 113, 115, 117 and 118, which all received official recognition in 2016. The first atoms of element 113, named nihonium (Nh) were produced in 2003-2005 by a team at the RIKEN Nishina Center for Accelerator-Based Science in Japan. Elements 115 and 117 were synthesized in experiments from 2010 by the Dubna-Livermore collaboration extended with scientists from the Oak Ridge National Laboratory in Tennessee. While element 115 was named moscovium (Mc), element 117 was assigned the name tennessine (Ts).

Element 118 was another product of the successful Dubna-Livermore collaboration led by the Dubna physicist Yuri Oganessian, a highly esteemed veteran in SHE research. In experiments of 2006 the team observed three decay chains arising from the fusion of Ca-48 and Cf-249, which was interpreted as due to the formation of the A = 294 isotope of element 118, namely

$$^{48}_{20}\mathrm{Ca} + {}^{249}_{98}\mathrm{Cf} \rightarrow {}^{294}_{118}\mathrm{Og} + 3\,^{1}_{0}n$$

The results obtained in 2006 were confirmed and improved in subsequent experiments, but it took until 2016 before the discovery was officially recognized and the new element was named oganesson (Og) in recognition of the leader of the discovery team.[22] Although no atoms of oganesson have ever been studied experimentally, calculations predict that its electron shell structure is

$$2, 8, 18, 32, 32, 18, 8,$$

and that it thus belongs to the group of noble gases. Remarkably, this is the very same structure that Bohr suggested back in 1922.[23]

4. CRITERIA FOR DISCOVERIES

The history of discoveries and discovery claims of SHEs differs from the earlier history of most element discoveries. The reason is that short-lived SHEs are produced artificially and in a small number of atoms only, sometimes one by one, and that the atoms can only be identified indirectly according to certain criteria of nuclear physics and chemistry. Moreover, new SHEs need to have the characteristics of ordinary elements in order to be placed in the periodic table alongside other elements. The organization responsible for accepting or dismissing discovery claims is IUPAC, which also authorizes the names and symbols of the elements. Bureaucratically speaking, an element is only an element when it has been officially approved by the IUPAC Council. The names of the transuranic elements were first considered at the 15th IUPAC conference in 1949, when the Commission on Nomenclature of Inorganic Chemistry (CNIC), a branch under IUPAC, officially adopted the proposed names for elements 93 to 96.[24]

During the first decades of the twentieth century there were two basic criteria for recognizing the discovery of a new element, namely the optical spectrum and the atomic weight of the claimed element. Since the mid-1920s the main criterion became the element's characteristic X-ray spectrum which directly reveals the atomic number.[25] The first element identified and recognized in this way was hafnium, Z = 72. However, for several of the superheavy elements none of these criteria are relevant since they have no definite atomic weight and also no spectrum based on electron transitions between different energy levels. Besides, X-ray spectroscopy requires amounts of matter much greater than the few atoms often produced in SHE reactions. The method could only be used indirectly, to determine the characteristic X-rays emitted by atoms of the daughter nuclide after the decay of the parent SHE nuclide.

The confusing number of discovery claims for new SHEs through the 1960s and 1970s inevitably caused reconsideration of the old question, what does it mean to have discovered a new element? Scientists engaged in SHE synthesis agreed that the atomic number was the defining parameter of an element, but they shared a concern over the confusion caused by missing operational criteria for SHE discoveries.

In 1971 Flerov and his Dubna colleague, the Czechoslovakian nuclear chemist Ivo Zvára, wrote a memorandum in which they pointed out that the concept of element belonged to chemistry and atomic physics and not to nuclear physics. "If the atomic number is established by chemical means or by techniques of atomic physics (Roentgen spectroscopy, etc.)," they stated, "then even without a nuclear-physics identification the work should be considered a discovery."[26] The following year two nuclear chemists at the Lawrence Berkeley Laboratory similarly suggested that chemical methods to the identification of atomic numbers would be essential or at least complementary to methods of nuclear physics.[27]

On the proposal of the Dubna group, in 1974 IUPAC in collaboration with IUPAP appointed an ad hoc group of nine neutral experts, three of which were from the United States and three from the Soviet Union. According to the American members of the group, its purpose was "to consider the claims of priority of discovery of elements 104 and 105 and to urge the laboratories at Berkeley (USA) and Dubna (USSR) to exchange representatives regarding these experiments."[28] However, the initiative was a failure as the committee never completed its work or issued a report. Indeed, it never met as a group.[29] According to Roger Fennell, a historian of IUPAC, "In 1977 IUPAP said it had lost interest as the existence of the two elements was doubtful anyway."[30]

In a paper of 1976 a group of Western SHE specialists pointed out that lack of definite discovery criteria "has contributed significantly to the competing claims for the discovery for these [transuranic] elements."[31] In discussing various ways of identifying new elements, some chemical and other physical, the authors emphasized proof of the atomic number as essential. The 1976 article was general in nature and did not apply the proposed discovery criteria to the ongoing priority controversies. But several years later three of the American co-authors published a detailed investigation of the discovery claims of elements 104 and 105 which was largely based on the 1976 criteria.[32]

The leading GSI physicist Peter Armbruster joined the debate in early 1985, expressing his wish of an international physics-chemistry commission taking care of the many controversies over names and discoveries. He proposed that "a name should be accepted only if the experiment claiming the discovery is reproducible." Moreover, "An isotope is defined by its mass and atomic number, its fingerprints are its decay modes and its half-life."[33] Armbruster's paper most likely inspired IUPAP's president, the Canadian-American nuclear physicist Allan Bromley, to suggest a working group of physicists to investigate priority questions related to the transfermium elements ($Z > 100$). The result was the Transfermium Working Group (TWG) established jointly by IUPAP and IUPAC in 1985 and consisting of two scientists nominated by IUPAC and seven by IUPAP. To secure neutrality, none of the members were from USA, USSR or West Germany, the three nations with SHE facilities. The responsibility of the group, headed by the distinguished Oxford nuclear physicist Denys Wilkinson, was to formulate criteria for when an element was discovered and to evaluate discovery claims accordingly.[34]

In a report published in *Pure and Applied Chemistry* in 1991 the TWG investigated systematically and thoughtfully criteria for recognizing the existence of a new chemical element. Of interest in the present context is the summary definition formulated by Wilkinson and his fellow TWG members: "Discovery of a chemical element is the experimental demonstration, beyond reasonable doubt, of the existence of a nuclide with an atomic number Z not identified before, existing for at least 10^{-14} s."[35] With regard to the requirement of a minimum lifetime of the nuclide it was introduced to make the formula more chemical and in accord with the standard view of the term element. "It is not self-evident," the authors wrote, "that 'element' makes sense if no outer electrons, bearers of the chemical properties, are present." It takes about 10^{-14} second for a nucleus to acquire its electron system and thus to become an atom with certain chemical properties.

The same requirement was mentioned in the earlier mentioned report of 1976. "We suggest," the authors wrote, "that composite nuclear systems that live less than about 10^{-14} second … shall not be considered a new element."[36] So-called quasi-atoms of very high Z are formed transiently in heavy-ion collisions, but they exist only for about 10^{-20} second. Consequently they do not qualify as nuclides of new elements. However, there seems to be no consensus among nuclear physicists of when a nucleus exists. Some take the definition of an atomic nucleus to be limited by the time scale 10^{-12} second, and according to others "If a nucleus lives long compared to 10^{-22} s it should be considered a nucleus."[37]

The definition of an element did not change as the atomic number Z was still considered the defining property, as it had been since the early 1920s. On the other hand, the TWG report of 1991 pointed out that "The exact value of Z need not be determined, only that it is different from all Z-values observed before, beyond reasonable doubt." That determination of the atomic number was still important is shown by the competing claims for having found element 113. When an IUPAC-IUPAP joint working party decided to attribute the discovery to the RIKEN team and not to the Dubna team, it was primarily because the first team provided solid evidence for the atomic number. The Dubna measurements, on the other hand, "were not able to within reasonable doubt determine Z."[38]

The TWG was disbanded in 1991 but later on followed by other ad hoc inter-union groups of experts, generally referred to joint working parties or groups. For example, a five-member joint working party was established in 2011 to examine claims of having discovered elements with $Z > 112$ and another working party reported in 2016 on element 118. The discovery definition of TWG mentioned above was adopted by all the later working parties and can thus be ascribed an authoritative status.

5. DISCOVERED OR CREATED?

The various working groups established by IUPAC and IUPAP were concerned with the *discoveries* of new elements, a term used consistently in their reports. The press release issued by IUPAC on 30 December 2015 announced "the verification of the discoveries of four new elements" (namely $Z = 113$, 115, 117, and 118).[39] But although SHE scientists agree that their synthetic elements have been discovered, clearly this is in a different sense than the one we associate with the discoveries of, for example, gallium, argon and hafnium. Whereas the latter elements were found in nature, SHEs and artificial elements generally were *created* or *invented*, in largely the same way that a statue is created or a technological device invented. They belong to what the ancient Greeks called *techne* (human-made objects or imitation of nature) and not to *physis* (nature). To Aristotle and his contemporaries, *techne* denoted primarily a kind of craft or skill that could bring forth an artefact from the material nature.

Interestingly, Seaborg insisted that the transuranic elements he and others had found were created rather than discovered. "After all," he said, "you can't discover something that doesn't exist in nature any more than Michelangelo discovered his David inside a block of marble."[40] And yet Michelangelo did not think of his famous sculpture as just imposing form onto a lifeless block of marble, but rather as releasing a form that was imprisoned in the block. He reputedly said that he just cut away everything that wasn't David.[41] By contrast, it makes no sense to say that a transuranic element is imprisoned in the nuclear reactants out of which it eventually emerges.

The creation of synthetic and yet in a sense natural objects did not start with the work of Segré and Perrier in 1937, for at that time there already was a long tradition in organic chemistry of synthesizing chemical compounds. The first such compound without a counterpart in nature may have been William Perkin's famous discovery (or manufacture) of the aniline dye mauveine in 1856. The discovery initiated the synthetic revolution in chemistry, a revolution which has resulted in millions of man-made molecular compounds. In a sense the synthesis of transuranium elements is a continuation of the tradition in synthetic organic chemistry, only at a more fundamental level.

When Mendeleev and his followers predicted from the periodic table that certain missing elements actually existed, they implicitly relied on a version of the so-called principle of plenitude.[42] According to this metaphysical principle as expounded by Leibniz and others, what can possibly exist does exist. Nature abhors unactualized possibilities. Or, in its modern version, if a hypothetical object is not ruled out by laws of nature it (most likely) will exist and thus be a real object. According to Leonard Susskind, a physicist and cosmologist, there are planets made of pure gold, for "they are possible objects consistent with the Laws of Physics."[43] In this line of reasoning it is presupposed that existence refers to nature, but the situation with respect to SHEs is different as these elements are possible and yet not realized in nature. The potential existence is turned into actual existence not by finding a SHE in nature, as ordinary elements like gallium and germanium were found, but by creating it in the laboratory. The classical plenitude principle, expressing a belief in nature's richness and continuity, does not seem applicable to the artificial world created by chemists and physicists.[44]

Whereas plutonium may be said to be a technological product, not only because it is man-made but also in so far that technologies are always purposeful and oriented towards social practices, this is not the case with most of the SHEs. They have been produced in minute amounts only and serve no social or economic purposes. The business of SHE research is fundamental science with no aim of contributing to technological and economic progress. It is science for the sake of science.

In a recent interview Yuri Oganessian justified his research field by saying that "it is about tackling fundamental questions in atomic physics." Foremost among the questions is the prediction of an island of stability. According to Oganessian: "Theorists predict that there should be some superheavy atoms, with certain combinations of protons and neutrons, that are extremely stable … but we are still far from the top of the island where atoms may have lifetimes of perhaps millions of years. We will need new machines to reach it."[45] Other leading SHE scientists have expressed a similar *l'art pour l'art* attitude. The GSI veteran Sigurd Hofmann refers to the "sense of the excitement which has motivated workers in this field" and suggests that the motivation for study SHEs is "because we are curious."[46]

But of course one may always fall back on the mantra, as two SHE nuclear chemists did in 1972, that "practical and useful applications would be forthcoming eventually, as is always the case with basic research."[47] They were referring to the possibility that long-lived SHEs might be discovered in nature. Should this be the case, unlikely as it is, these hypothetical elements would have been discovered in the traditional sense (or perhaps in the sense that technetium was discovered). But the short-lived isotopes below the island of stability would still belong to created and not discovered elements.

6. ONTOLOGICAL STATUS OF THE HEAVIEST ELEMENTS

As mentioned, SHE isotopes have short life-times and thus, in several cases they have been produced only to disappear again almost instantly. The elements have been produced and detected in nuclear processes and thus *did exist* at the time of the detection. But strictly speaking they *do not exist* presently any more than dinosaurs exist. The existence of SHEs is ephemeral or perhaps potential, which is quite different from the existence of ordinary elements whether radioactive or not. Can we truly say that the element oganesson *exists* when there is not, in all likelihood, a single atom of it in the entire universe? Sure, more atoms or rather nuclei of element 118 could be produced by replicating or modifying the Dubna experiments, which makes the element different from the long-time experiment of living nature known as the dinosaurs. But within a fraction of a second the re-created oganesson atoms would disappear again.

One may object that particles with even shorter lifetimes are known from high energy physics without physicists doubting that they really exist. For example, the neutral pion π^0 decays into two gamma quanta with a lifetime of about 10^{-16} seconds. The particle was first detected in nuclear reactions in Berkeley in 1950, but contrary to the nuclides of the SHEs it was also found in nature, namely in cosmic rays. The neutral pion thus exists and is not exclusively a laboratory product.

The same is the case with the antiproton, another exotic particle first produced in accelerator experiments, in this case in 1955, and only subsequently detected in the cosmic rays. Incidentally, in 1959 Owen Chamberlin and Emilio Segré – the co-discoverer of the elements technetium and astatine – were awarded the physics Nobel Prize for the antiproton experiment. The antiproton can be brought to combine with a positron and thus form anti-hydrogen according to

$$\overline{p} + e^{+} \rightarrow \overline{\mathrm{H}}$$

This exotic atomic system has been produced in the laboratory and studied experimentally.[48] Anti-hydrogen atoms can under laboratory conditions survive for as long as 15 minutes. In 2011 an international collaboration of physicists reported observation of 18 events of artificially produced anti-helium $^{4}\overline{\mathrm{He}}$ consisting of two antiprotons and two antineutrons.[49] No anti-helium atom has been detected so far. Anti-hydrogen has in common with SHEs that it is element-like and only exists when manufactured. But contrary to the SHEs, there is no place for anti-hydrogen or other anti-elements in the periodic system.

There is also no place in the periodic system for other exotic atoms where the constituent protons and electrons are replaced by elementary particles such as positrons and muons. Positronium, a bound system of an electron and a positron, was discovered experimentally in 1951 but had been hypothesized almost twenty years earlier.[50] Sometimes described as a very light isotope of ordinary hydrogen or protium, the short-lived positronium has been extensively researched and its chemistry studied for more than half a century.[51] The positron can be replaced by a positively charged muon (μ^{+}) in which case one obtains muonium with an atomic mass $A \cong 0.11$ between positronium and protium. First detected in 1960, muonium has a half-life of about 2×10^{-6} second.

If only a historical curiosity, ideas of exotic chemical "elements" had much earlier been entertained by a few chemists suggesting that the electron was such an element. This was what Janne Rydberg, the Swedish physicist and chemist, proposed in 1906, assigning the symbol E for the electron and placing it in the same group as oxygen.[52] Two years later, the Nobel laureate William Ramsay independently made a similar proposal, again using the symbol E.[53] But nothing came out of these speculations and when the atomic number was introduced in 1913, they were relegated to the graveyard of forgotten chemical ideas.

In 1970 the distinguished Russian nuclear chemist Vitalii Goldanski wrote a paper on SHEs and exotic atoms in which he suggested that Mendeleev's table remained unaffected by the discovery of the latter kind of atoms. He wrote as follows:

> *The replacement of electrons with other negative particles (for example, μ^{-} or π^{-} mesons) does not involve a change in the nuclear charge, which determines the position of an element in the periodic system. As to the replacement of a proton with other positive particles, for example, a positron (e^{+}) or μ^{+} meson, such a replacement leads to the formation of atoms which in the chemical sense can be considered as isotopes of hydrogen. … On the basis of the value of the positive charge [positronium and hydrogen] occupy one and the same place in the periodic table.*[54]

Goldanski's view is remarkable but also problematic, to say the least. Two widely different elements in the same box of the periodic table? Although muonium does not count as an ordinary chemical element it does have chemical properties and has even been assigned a chemical symbol (Mu). The analogy between muonic atoms and SHEs is underlined by the fact that the nomenclature of the first kind of atoms and their chemical compounds has been considered by IUPAC.[55]

A related question is whether short-lived transfermium elements really count as *elements* in the traditional meaning of the term. Elements consist of atoms and it is the atoms and their combinations which endow elements with chemical properties. An isolated atomic nucleus has no chemistry. This is what Wilkinson and his TWG stated in its 1991 report and more recently two nuclear chemists elaborated as follows: "The place an element occupies in the Periodic Table is not only defined by its atomic number, i.e. the number of protons in the nucleus, but also by its electronic configuration, which defines its chemical properties. Strictly speaking, a new element is assigned its proper place only after its chemical properties have been sufficiently investigated."[56] To phrase the point differently, although a chemical element is defined by its atomic number, not everything with an atomic number is an element.

The point is worth noticing as nuclear scientists commonly refer to an atomic nucleus or a nuclide as were it an element. For example, the 1991 TWG definition stated that a chemical element had been discovered when the existence of a *nuclide* had been identified. However, the term nuclide, coined in 1947, refers to a species of nucleus and thus emphasizes nuclear properties. By contrast, the corresponding and older term *isotope* denotes an atomic concept and emphasizes chemical properties. The difference between the two terms is more than just a semantic detail, but unfortunately the terms are often used indiscriminately.

Not only is the number of produced transfermium atoms extremely small, what are directly formed are nuclei and not atoms. Under normal circumstances a bare atomic nucleus will attract electrons and form an atom, but the circumstances of SHE experiments are not normal and the few atoms may only exist for such a small period of time that they cannot be examined experimentally. No atoms are known for the heaviest of the SHEs of which only atomic nuclei have been produced and studied. To this date, some 35 nuclei of livermorium ($Z = 116$), all with half-lives less than 50 milliseconds, have been observed.[57]

Despite the elusive nature of SHEs nuclear scientists have succeeded in measuring some of their chemical and physical properties. Ionization potentials have been measured up to lawrencium ($Z = 103$) and even an element as heavy as flerovium ($Z = 114$) has been the object of experimental study. Much is known also about other SHEs, but for some of them the knowledge is exclusively in the form of theoretical predictions, extrapolations and estimates.[58] For example, in the case of tennessine, element 117, its oxidation states have been predicted to be +1, +3, and +5; the electron structure and radius of the atom have been calculated and so have the boiling point and density of the element as well as of hypothetical compounds such as TsH and TsF_3. But there are no empirical data and none are expected to come in the foreseeable future. Of course, the situation is different for the less heavy transuranic elements and especially for plutonium. Even some of the transactinides such as rutherfordium and dubnium have a real chemistry.[59]

Consider again the heaviest of the elements, oganesson, which is presently known only as one nuclide with an extremely small lifetime. To repeat, very few of the nuclei have been produced and none of them exist any longer. Oganesson has received official recognition from IUPAC and entered the periodic table alongside other and less exotic elements. And yet one may sensibly ask if oganesson is really a chemical element in the ordinary sense of the term. Perhaps its proper status is better characterized as a potential element, somewhat along the line recently suggested by Amihud Gilead, an Israeli philosopher of science.[60]

I am not arguing for an anti-realist position with regard to the SHEs at the end of the periodic table. Nuclides of these elements undoubtedly exist, or rather they existed at the time of their detection, but it is questionable if they exist or existed as proper chemical elements.

7. CONCLUSION

The study of the present state and historical development of SHEs is not only of interest to the historian of modern chemistry and physics but also raises questions of a more philosophical nature. Besides, in so far that much of the modern development of modern SHE research has taken place within the framework of a few competing nuclear laboratories and been evaluated by working groups established by IUPAC and IUPAP, it is also of interest from the perspective of sociology of science.

As pointed out in this paper, SHEs are not discovered in the normal sense of the term but are man-made objects the existence of which is entirely due to artificial nuclear reactions. The short-lived nuclides of SHEs are ephemeral visitors to our universe, which calls into question the meaning of their existence. Although they have been officially recognized as chemical elements and designated places in the periodic table, it is far from evident that they can be properly characterized as elements. The old question of what constitutes a chemical element appears in a new light when seen through the lens of SHE research.

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Substantia
An International Journal of the History of Chemistry

Firenze University Press
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Research Article

Summary of the Nature and Contents of "The Origin of Rocks and Mineral Deposits – Using Current Physical Chemistry of Small Particle Systems"

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Citation: J. Elliston (2017) Summary of the Nature and Contents of "The Origin of Rocks and Mineral Deposits – Using Current Physical Chemistry of Small Particle Systems". *Substantia* 1(2): 19-62. doi: 10.13128/substantia-26

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declared that no competing interests exist.

Abstract. The book referred to in this title is a comprehensive interdisciplinary scientific treatise that introduces revolutionary new knowledge achieved by competent use of the scientific method. The research on which it is based has been more thoroughly and critically reviewed than is usual for scientific works and the international edition has recently been published.

However, correct statements and advertising of the publisher and booksellers are disbelieved because many scientists assume the author is claiming to have discovered the origin of rocks and mineral deposits. Millions of dollars are spent each year on research endeavouring to understand the formation of ore deposits. It is a preposterous misconception that any one scientist could discover the origin of rocks and mineral deposits.

The book definitely does not introduce a new geological theory or revise an existing one. Using the basic scientific method of logical conclusions from direct observation it reinterprets geological phenomena and processes using currently established physical chemistry of small particle systems. The title of this book *"The Origin of Rocks and Mineral Deposits – using current physical chemistry of small particle systems"*[1] is not a boastful or exaggerated claim. It summarises the results of over 50 years of systematic industrial research that actually achieved an understanding of how modern surface chemistry now explains the otherwise puzzling features and textures we see preserved in the rocks and the release of ore minerals in various geological environments. It is the culmination of the work of many outstanding scientists guiding and mentoring a highly competent and successful mineral exploration team.

THE OUTSTANDING SCIENTISTS

Professor A. E. Alexander

Professor of Physical Chemistry, University of Sydney, 1957 to 1970,

Co-author, Alexander and Johnson, *"Colloid Science"*, 1950, Oxford University Press.

He identified mysterious large banded chert nodules in specimens of porphyroid from the Black Angel prospect in Tennant Creek as colloidal accretions in 1959. This initiated the many years of research into the origin of mineral deposits based on the properties and behaviour of colloidal particles in natural sediments.

Professor P. G. H. Boswell

No picture is available of Professor P. G. H. Boswell, OBE, Geology Department, Liverpool University, UK. He is the author of *"Muddy Sediments"*, Heffer, Cambridge, 1961. Professor David Williams from Imperial College in London presented this book to Geopeko after his visit to Tennant Creek in 1962. It was our first authoritative introduction to the rheological and surface properties of natural sediments.

Dr Ralph K. Iler

We have no picture of Dr Ralph K. Iler, of DuPont de Nemours & Co, Wilmington, Delaware, USA. After several brief consultations during his visit to Australia in 1984, his comprehensive treatise *"The Chemistry of Silica"*, John Wiley and Sons, New York, 1979, provided the essential information on the solubility, polymerisation, and surface properties of silica particles in natural sediments.

The late Professor S. W. Carey

The late Professor S. W. Carey, AO, DSc, (1911-2002) was certainly the most highly qualified Earth scientist in Australia in recent times. His qualifications include two Honorary Doctorates, Fellow of Australian Academy of Science, Honorary Life Fellow of seven learned societies, five medallists and numerous Chairmanships and Presidencies. After his first visit to Tennant Creek in 1962 he recognised the significance of Geopeko exploration company research and immediately convened an international symposium at the University of Tasmania with field visits to Tennant Creek entitled *"Syntaphral Tectonics and Diagenesis"*[2]. This was to create wider interest in understanding how the physical chemistry of small particle systems now explains so many otherwise puzzling geological phenomena. Professor Carey became guide and mentor to this series of ongoing research projects until he died in 2002.

The late Professor T. F. W. Barth

Professor T. F. W. Barth from Oslo University in Norway was a visiting Fellow to the Australian Academy of Science in 1965. He is the author of several books including *"Theoretical Petrology"*, John Wiley & Sons, New York, 1962, and *"Feldspars"*, John Wiley & Sons, New York, 1969.

With some difficulty, Professor Carey prevailed on Professor J. C. Jaeger, member of the Australian Academy of Science at that time to alter Professor Barth's schedule of visits to Australian universities so the he could accept Sir John Proud's invitation to visit Tennant Creek. Professor Barth accepted and arrived in Tennant Creek on the afternoon plane of Monday 8th November 1965.

Professor Carey had arrived two days earlier to assist in hosting the visit of this world authority on feldspars. It was a busy but very successful visit. Professor Barth was at first rather reserved about the way our new approach using principles of current colloid and surface chemistry seemed to explain so much. However, after a week inspecting mines, drill cores, outcrops, and in-depth discussions and technical presentations each evening, he became keenly interested and enthusiastic. On the evening prior to his departure from Tennant Creek, Professor Barth's remark became a legend in company history and a turning point for Geopeko exploration and research. In his best Norwegian accent he said:

> *They told me in Canberra I was coming on a wild goose chase, but now I know where the gooses are!*

Professor T. F. W. Barth was on the organising committee of the International Geological Congress and recognising the importance of Geopeko research he invited papers to be presented at the 23rd International Geological Congress in Prague in August 1968. By 1968, the application of advanced geophysics and understanding the origin of the mineral deposits had found and brought into production four new mines at Tennant Creek and Geopeko drilling had located high-grade mineralisation at the Explorer 1 prospect that was to become the Gecko Mine. These successes justified a three-month trip to Europe for John Elliston and his wife to present the invited papers prepared for the 23rd IGC and to visit mines prospects and outcrops on the pre and post Congress excursions.

Professor Zdenék Pouba

Professor Zdenék Pouba from Charles University in Prague led the pre-Congress excursion to the Silesian mines in Poland. The Congress opened in grand style with some 5,000 delegates on Monday 19th August 1968 and the first paper entitled *"Retextured Sediments"*[3] was successfully presented. The more important paper *"The*

Professor A. E. Alexander

The late Professor S. W. Carey

The late Professor
T. F. W. Barth

Professor Zdenék Pouba

Professor Richard L. Stanton

Distinguished
Professor Ross Large

Emeritus Professor
Thomas W. Healy

Sir John Proud

genesis of some epigenetic type ore deposits" was scheduled for presentation later in the congress. However, the Russians invaded Czechoslovakia and their tanks arrived in Prague in the early hours of Wednesday 21st August. Congress was disrupted and abandoned. Professor Pouba arranged the evacuation from Prague and recognising the significance of the new research in *"The genesis of some epigenetic type ore deposits"*, he had this paper published by the Czech Geological Society (Organ. Czech. Soc. of Min. and Geol., 14(2): 129-139.). He found that the Russian authorities would not permit return of Congress manuscripts that had not been presented for them to be published elsewhere.

Professor Richard L. Stanton

Professor Richard Stanton was head of the Geology Department, University of New England, Armidale, NSW. His very significant and fundamental research is completely independent of the industrial research projects that have established the origin of rocks and mineral deposits. He corresponded for some years pointing out its complimentary nature and confirmation of the origin rocks and mineral deposit using the physical chemistry of small particle systems.

In 1989, Professor Stanton concluded that a wide range of metamorphic, gneissic and porphyry-like rocks had developed their texture by crystallisation of ordered sedimentary diagenetic gels [Stanton, R. L., *"The precursor principle"*, 1989, Phil. Trans. Royal Society of London, A 328: 529-646 (p. 638)]. His conclusions are based on mineralogy and direct measurement of the chemical composition of the substances crystallising with a microprobe analyser. Stanton's establishment of the precursor principle agreed with and confirmed the conclusions reached in the systematic investigation of the origin of rocks and mineral deposits using the physical chemistry of small particle systems.

Distinguished Professor Ross Large

Ross Large is a Distinguished Professor of Economic Geology at the University of Tasmania. He was the foundation Director of the Australian Research Council Centre of Excellence in Ore Deposits (CODES). He joined the University of Tasmania in 1984 and was the Director of CODES for over 20 years until recent retirement. Prior to his work at the University of Tasmania Ross large worked for Geopeko in the Northern Territory, gained his PhD at the University of New England in 1973, undertook a Post Doctoral Fellowship at the University of Toronto in 1974 and worked for Geopeko in the difficult to access area at Elliot Bay south of Macquarie Harbour in Tasmania.

Together with Kim Wright, former General Manager, Earth Resources Foundation, University of Sydney, Ross Large organised the highly successful symposium *"Syntaphral Tectonics and Diagenesis – 44 years on"* at CODES in November 2007. The Australian preview edition of *"The Origin of Rocks and Mineral Deposits – using current physical chemistry of small particle systems"* was printed for that occasion and discussion, presentations and papers contributed recognised the exciting new knowledge it contained.

Emeritus Professor Thomas W. Healy

Thomas W. Healy, AO, FRACI, FAA, FTSE, Emeritus Professor Physical Chemistry at the University of Melbourne is a world leader in colloid science. During the period from 1991 to 1999 he was Director of the Advanced Mineral Products Special Research Centre of the Australian Research Council (ARC), and in 2000 was appointed Deputy Director of the Particulate Fluids Processing Centre, also a Special Research Centre of the ARC.

He was consultant to Geopeko Limited from 1967 to 1977. He attended the company technical seminars and provided the essential guidance and information to ensure our application of the physical chemistry of small particle systems and nanotechnology to interpret geological phenomena was correct. He wrote 14 reports for the company the most comprehensive of which is *"Physicochemical Processes in the Diagenesis of Sediments"*, April 1972. He attended and contributed to the symposium *"Syntaphral Tectonics and Diagenesis – 44 years on"* in Hobart in November 2007. His review of the preview edition of *"The Origin of Rocks and Mineral Deposits"* contains the statement **"The colloid science in the book is impeccably correct."** Other leading colloid scientists in Australia who have examined the preview edition, Associate Professor Robert J. Hunter, University of Sydney and Emeritus Professor Barry W. Ninham, Australian National University, agree.

Sir John Proud

John Seymore Proud, a mining engineer, joined the board of Peko (Tennant Creek) Gold Mines NL on 26th September 1952. The company changed its name to Peko Mines NL in 1954 and John Proud became Chairman of the Board and CEO when the company merged with the Newcastle Wallsend Coal Company to become Peko-Wallsend Limited in 1961. John Proud set up the subsidiary company, Geopeko Limited later that year and appointed John Elliston, as Managing Geologist to develop much needed additional resources to sustain operations. Ore reserves at the small Peko Mine were rapidly depleting.

John Proud consistently supported maximum exploration effort and encouraged the research and development of more advanced technologies to achieve it. Geopeko's exploration was highly successful. Five new mines were developed on the Tennant Creek field from the first 15 prospects drilled. By 1975 significant new resources had also been discovered at King Island in Tasmania, the Ranger uranium deposits in the Alligator Rivers Province and prospective economic mineralisation identified at Parkes in NSW. A management consultant firm was commissioned by one of Geopeko's competitors to make a comparative study of the results of 13 successful Australian exploration companies in the period 1960 to 1975. By application of a developing understanding of the way that mineral deposits are formed Geopeko's expenditure on exploration (including substantial expenditure on research) was found to be 320% more cost effective. This record remains unsurpassed and is due to Sir John Proud's support and encouragement for research and technological development.

THE SCIENTISTS AND LEADERS OF AUSTRALIA'S MOST SUCCESSFUL EXPLORATION TEAM

Mr Lewis A. Richardson

Lew Richardson worked on the Tennant creek field for the Australian Geological and Geophysical Survey of Northern Australia in 1936 to 1939. He had done the detailed magnetic surveys of a number of the mines and prospects on the field including Peko, Black Angel, Orlando and the 'Mantle-piece Anomaly' (later to become the Juno Mine). He was geophysical consultant to Peko Mines NL, Peko-Wallsend and Geopeko Limited from 1954 until he died in 1971.

He was meticulous and accurate. He developed a technique for accurately modelling the buried bodies of mineralisation that gave rise to the magnetic anomalies measured on the surface. Patiently with mechanical hand calculators he modelled them as having elliptical shapes with variable axial inclination and dimension. The Peko magnetic anomaly was pear shaped. In 1961 mining and drilling had revealed the shape, dimensions and magnetic susceptibility of the main mineral body. Lew Richardson subtracted the effect of this magnetic body from the larger pear-shaped anomaly he had measured in 1936 to reveal the Peko No. 2 mineral body. Under ground drilling defined ore lenses in this body that extended mine life by about five years. Lew Richardson's modelling of the small rich magnetic body that was to become the Juno Mine predicted within 2 feet where the discovery drill hole would enter this mineral body centred 600ft below the surface.

Mr John Love

John Love was a keen and enthusiastic observer and properly sceptical of the new concepts our research into the origin of the Tennant Creek porphyroids, granites and mineral deposits was establishing. He satisfied himself that our conclusions were correct based on the evidence for that field but represented such a radical departure from mainstream beliefs and teaching that he needed to ensure that they also applied to rocks and mineral deposits world-wide.

He therefore took unpaid leave from Geopeko for a two-year working tour round the world. From South Africa he sent back pictures of orbicular norite he had found in drill core at the Empress Nickel Mine in Gatooma, granite orbicules from Diana's Pool, Lundi River, Zimbabwe, accretions in the colloidal mud from a settling tank at the Nababeep Mine, South Africa, numerous pictures of the fluid folding and structures in the nearby Reitberg Granite, and matching patterns in fluid mud from the tank at Nababeep that he had been able to produce. While in Europe John Love visited the French Academy of Science in Paris to see the fossil echinoderm shell embedded in granite feldspar that Termier and Termier[4] had reported from the Atlas Mountains in Morocco. He studied the 'marker argillite' horizon in British Columbia. This is a narrow band of micro-granite in a sequence of thin sedimentary beds that extend over 100 miles. John Love[5] very carefully checked the petrology and wrote a paper about this granite crystallised from a sedimentary layer for Geoscript on his return. John Love was one of Geopeko's outstanding scientists.

Mr Alex Taube

Alex Taube was an outspoken critic of Geopeko research. He stoutly upheld classical volcanogenic models of mineral deposit genesis and loudly demanded extended and costly diamond drill hole patterns based on this model. His scepticism was of the right sort. He could not change his views based on observation of narrow carbonate dykes or ptygmatic quartz veins that he found in the Woodcutters drill core but after some years he became convinced that granite and related porphyroidal and metamorphic rocks had crystallised from hydrous precursor sedimentary pastes or "magmas" in its original meaning. Alex Taube was convinced by his own observation of a substantial limestone breccia dyke that was found within the large Ravenswood Granite Batholith some 2 kilometres from is boundary contact with surrounding rocks.

Mr Geoff Sherrington

Geoff Sherrington was Geopeko's Chief Geochemist. He designed and used a radon detection system for uranium exploration but his main contribution to Geopeko's exploration success was the monitoring system he set up for trace element detection, field sampling and assays. In mineral exploration the decision to continue investigating or follow up a higher geochemical reading often depends a single analytical result. The sample recording and assay monitoring system set up by Geoff Sherrington made a significant contribution to Geopeko's success in calculating ore reserves and developing new resources.

Mr Robert L. Richardson

Bob Richardson continued as company geophysicist in charge of L.A. Richardson Associates after his father died in January 1971. That consultancy was acquired by Peko-Wallsend on 7th November 1978 and Bob became Geopeko's Chief Geophysicist. Meanwhile he and his associates (Mike Palmer, Bruce Kirkpatrick and Albert Berkavicious) had designed, tested and flown in the Alligator Rivers province the world's first 256-channel airborne radiometric survey system for uranium exploration. They located many other uranium anomalies but drilling established very significant energy resources at

Mr Lewis A. Richardson

Mr John Love

Mr Alex Taube

Mr Geoff Sherrington

Mr Robert L. Richardson

Mr Brian Williams

Mr Rado Jacob Rebek

Mr George Roy Ryan

Mr Kim Wright

Ranger 68 before the Whitlam government policies had quashed Australia's opportunity to develop safe nuclear power generation. This was to be an alternative to the inherently unsafe light water reactors. Bob Richardson also designed a down-hole magnetic survey instrument and a vehicle mounted magnetometer.

When it became clear that the Australian government would no longer permit proper development of its nuclear energy resources, Bob Richardson offered his new aerial survey system for a national geophysical survey in Iran. Mohammad Reza Shah Pahlavi's policy at the time was: - *"We will buy the best technologies that the west can supply to secure this country's economic future when oil resources are depleted."* A US$16 million contract was successfully negotiated and Austirex Aerial Surveys Pty Ltd was set up as a subsidiary company of Geopeko to conduct an aerial geophysical survey of about one third of Iran. Work commenced on 17th June 1977.

Bob Richardson appointed the manager and technical staff and this survey was 85% complete when operations were disrupted by the revolution in Iran in December 1978. Aircraft, aircrews, Australian staff and copies of the data tapes recording the survey results were evacuated and successfully returned to Australia. Substantial financial losses were incurred by the cessation of work at this stage. However, maps were delivered in batches in response to very slow payments. Austirex finally recovered all but about A$1 million of the payments due for 85% of the work. This achieved a breakeven position but an impatient new Peko-Wallsend CEO abandoned collection of the million dollars that would have been profit. He terminated map deliveries and the recovery process. Bob Richardson had left Geopeko but he deserves great credit for his outstanding service to that company.

Mr Brian Williams

Brian Williams remained in charge of exploration and mine geology at Tennant Creek when other senior staff had moved to the new Geopeko headquarters in Merriwa Street, Gordon, in 1972. He did not report the discovery of high-grade gold ore at the Warrego Mine in August 1972 but he was also responsible for the continuing program of testing magnetic anomalies. He was promoted to Managing Geologist, Western Australia in 1975. He set up the field camp at Paterson range and supervised Western Australian exploration. He found oolites in the siliceous shale at the Explorer 12 prospect and large feldspars in the layered granite at Wilson's Promontory that contributed to Geopeko research.

Mr Rado Jacob Rebek

Jacob Rebek has given strong support for the extension of Geopeko research to establish that the basic principles are relevant to all geological environments and to mineral deposits generally. The management of CRA Exploration Limited and Sir Roderick Carnegie, Chairman of their parent company board at the time, commissioned management consultants, McKinsey & Company, Inc., New York, in 1975 to compare the results of 13 successful exploration companies in the period 1960 to 1975. The report identified Geopeko Limited as most successful and its exploration more cost effective that the average of the 13 successful companies by 320%.

This led to an offer of a confidential research contract after John Elliston had retired from Peko-Wallsend in 1984. The contract offered all facilities needed to complete the research and bring the CRAE exploration team "up to speed". Jacob Rebek was assigned the task of supervising the contract, ensuring results were valid and that their application could lead to improved success rates. He examined all progress reports, arranged visits to mines, exploration camps and drilling and study of outcrops. He recognised the importance of the research and its application to significantly improve exploration success rates. He became an enthusiastic supporter. He was promoted to Group Chief Geologist, Rio-Tinto Exploration Limited and after the CRAE-Rio Tinto research contract had finished he arranged a lecture tour to introduce the new concepts to the company's exploration geologists in Chile.

Mr George Roy Ryan

Rob Ryan worked for Peko Mines NL and Geopeko as mine geologist and for resource evaluation from 1959 to April 1962. His work was excellent but he left to join the Geological Survey in Western Australia as Party Leader for the Regional Mapping Division in the Pilbara district. He re-joined Geopeko in January 1966 as Managing Geologist to take charge of exploration in northern Australia. He established a base in Darwin from which they supervised the drilling at Woodcutters silver-lead deposit, did the mine geology at the Mount Bundey iron ore mine and exploration at Eva Valley and Brocks Creek. Early in 1969 Geopeko reconnaissance found uranium ore veins (pitchblende) in crystalline rocks of the Nanambu Complex north of the Oenpelli track and west of the South Alligator River. It indicated that the uranium mineralisation was related to disturbance of the uranium-bearing black shales of Nanambu age and not "unconformity related" as proposed by the official government surveys.

With our joint venture partner's agreement Rob Ryan applied for and was granted a very large exploration area extending westward from the Kombolgie Escarpment to the South Alligator River. Grey soil plains and light tropical vegetation largely cover this vast area but the Ranger radiometric anomaly was easily detected by the airborne total count scintillometer surveys in use at that time. Rob Ryan pegged the Ranger uranium deposit just before the wet season prevented access to that remote area in late 1969. He established a field camp and airstrip at Jabaru in 1970 and assembled a highly competent team of geologists and support staff, including Peter Kitto, Geoff Eupene, Mike Danielson and Andy Browne, to develop one of Australia's most significant energy resources. The Ranger 1 deposit was ready for production in 1972. Rob Ryan is one of the best exploration geologists in Australia.

Mr Kim Wright

Kim Wright joined Geopeko in June 1962 to continue work as mine geologist. He is a keen observer and over his first few years he collected an abundance of evidence that the ore and gangue minerals at Peko had been deposited from colloidal particles dispersed in the ore-forming brines. Kim Wright was responsible for the Peko underground drilling that that developed the No. 2 Orebody and associated ore lenses. His work on the Tennant Creek field found the features produced by unconsolidated sediment movements at the Plum Mine about 12 miles east of Peko. He presented a paper at the 1963 symposium recording these pelletoid, accretionary and concretionary structures. Kim Wright also presented a paper at the Meeting on Remobilization of Ores and Minerals convened by Professor Zaffardi at Cagliari University in 1969. Kim's paper[6] contained magnificent examples of colloform textures and evidence that minerals from the Gecko, Peko, Juno and Ivanhoe Mines had been deposited as a paste or sludge of colloidal precipitate. Kim Wright's work at Tennant Creek also included the development and mine geology of the Ivanhoe Mine.

He was promoted to Managing Geologist, Eastern Australia and moved to Sydney to organise building of the Geopeko headquarters in Merriwa Street, Gordon from which our geophysical, geochemical and ore reserve computation services could be supplied to all exploration bases. This was completed in 1973 and Kim was responsible for Geopeko exploration bases at King Island, Mount Morgan, the coal exploration team at Newcastle in 1971 and at Parkes in 1972. He established a new base at Devonport in Tasmania in 1973 and appointed Ross Large to run it. He set up a base in Townsville in 1974. He and his coal geologist, Paul LeMessurier, found a ptygmatic quartz vein in the coal seam at Pelton. He supervised the development of the Dolphin and Bold Head mines on King Island and Gary Jones successful exploration and development of the North Parkes porphyry copper mine. Kim Wright was one of Geopeko's keenest observers and competent exploration managers.

The idea that any one scientist could claim to have discovered the real origin of rocks and mineral deposits cannot be used to disregard the evidence presented in "The Origin of Rocks and Mineral Deposits" book. Readers and reviewers have simply to decide wether or not the physical chemistry of natural sedimentary particle systems set out in the book now adequately explain the geological features and phenomena illustrated.

Preparing the many progress reports, attending and organising seminars, conferences, field visits and preparing presentations, courses, lecture tours, etc. did involve study of thousands of textbooks and scientific papers over the years. However, the new knowledge introduced by this book clearly could not have been achieved without the advice and guidance of the outstanding academic scientists and the observations, competence and enthusiasm of Australia's most successful exploration team.

THE SCIENTIFIC METHOD

The new knowledge in this book has been achieved by the scientific method. Today scientists world-wide are dismayed by scientific reports and concepts that rely on surveys of opinion, exaggerated media reports, post-normal statistical assessments of likelihood, "it must be the way I think it is because I don't know of any alternative", "it is generally accepted that … therefore ….", etc. Intense competition for research grants has resulted in strong bias towards politically expedient investigations that are believed favoured by funding authorities. Once thriving geology departments have been downgraded to small divisions in Department of Geography, Department of Environmental Sciences, etc. Mineral exploration is difficult to finance and discovering new resources harder to achieve.

Since 1936 the 'scientific method' has been recognised by Australian law (Subsection 73B(1) of the Income Tax Assessment Act 1936) as:

> *Systematic investigative and experimental activities that involve testing a hypothesis (new idea) by deductive formulation of its consequences. These deductions must be rigorously tested by repeatable experimentation and logical conclusions drawn from the results of the experiments. The hypothesis must be based on principles of physical, chemical, mathematical, or biological sciences.*

This would include colloid science and current nanotechnology.

In 1970-74 Australian universities abandoned the procedure that had been used to that time for award of their highest degrees in science. DSc candidates were required to submit a doctoral thesis embodying an original research finding (details of a tested hypothesis). This was "peer reviewed" by two or more external scientists selected by the university as most appropriately qualified. It was recognised that a candidate who had tested an original hypothesis may be equally or better able to interpret the results than an external reviewer. Candidates were therefore entitled to a "right of reply" to the written report or comments of the universities' reviewers. In reply they could produce references or call on reviewers of their own selection. University authorities were able to fairly assess the candidate's new research finding and determine if it merited the award of their highest degree.

This procedure raised standards in all scientific disciplines to which it applied but by 1974 it was abandoned by all Australian universities as too tedious and time consuming to cope with the rapidly increasing number of candidates aspiring to higher degrees. With continuing rates of increase since 1970's, Australian universities now resemble production-line 'higher degree factories'! They quite rightly require higher degree candidates to meet very high standards but they are uniform standards requiring each candidate to conform to the limitations of the knowledge of his or her degree supervisor. Significant new discoveries cannot conform to what is currently "generally accepted".

All publicly funded research in Australia tends to digress, at least to some extent, from the scientific method toward the extreme case depicted in the American cartoon below (Figure 1). Competitive research proposals are written to get research grants rather than to advance our knowledge by resolution of long-standing problems. Researchers spend more time looking at computer screens than looking at rocks and mineral deposits!

THE CENTRAL HYPOTHESIS

Most people recognise that sediments are formed from tiny sediment particles and chemical precipitates and it is quite logical that sediments in the ancient oceans had the same physical, chemical and fluid properties as sediment accumulations in the oceans today. We are therefore able to assume that these ancient particle systems that have now consolidated to rocks containing mineral deposits, may have contained or been comprised of colloidal sediment particles like clays, colloidal silica and hydrous ferromagnesian particles. The total surface area of the billions of particles in every cubic meter of mud is about 60,000,000 square meters.

Therefore the central hypothesis that has been systematically tested is: -

If ancient sediments were particle systems containing or comprised of colloids, evidence of the former colloidal properties of these materials should be preserved in the rocks. We should be able to find evidence of former plasticity, diffusion, cohesion and fracture, mobilisation by shaking or movement (called thixotropy) caused by earthquake shocks or sliding and flow downslope, and sudden resetting where mudflows or intrusions were about to stop (called rheopexy). The

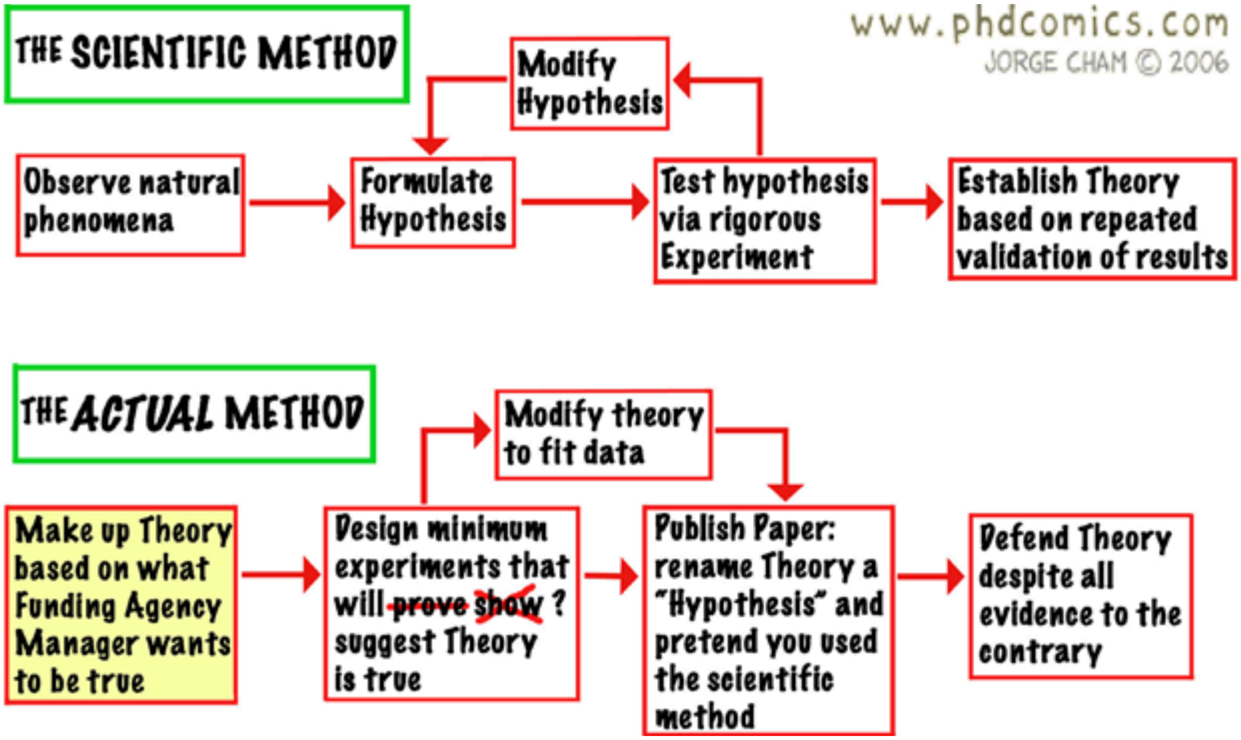


Figure 1. This cartoon by Jorge Cham, 2006, depicts the unfortunate trend from the scientific method to expediency in obtaining research grants.

Concretion in orbicular granite, Karu Finland **Slumped mobile Pb - Zn ore from Mt Isa, Qld.** **Ptygmatic (looped) quartz vein from Woodcutters** **Verde marble porphyry from AMP building** **Feldspar with shrinkage cracks, Great Western**

Figure 2. Five examples of the evidence that ancient sediments and mineral deposits contained or were comprised of colloidal particles.

rocks and mineral deposits should contain residual hydrous minerals and show aggregation or ‘clotting’ of the fine-grained components (called accretion). We should see spontaneous shrinkage cracks (called syneresis cracks) in aggregates and nodules, overgrowth and rimming structures (called concretion), bulbous ‘loopy’ vein intrusions (called ptygmatic), ordering patterns and enhanced crystal growth.

This hypothesis has been rigorously tested by repeated experimentation. The abundant evidence of the former colloidal properties of ordinary rocks and mineral deposits can be seen and recorded photographically or as observational data. The simple experiment can be repeated by anyone willing to look at the rocks and consider the observations from first principles including those now established in current colloid science.

Ordinary rocks and mineral deposits do contain this evidence in abundance (Figure 2).

Every picture in *“The Origin of Rocks and Mineral Deposits”* book or similar ones that can be recorded by others is a valid experimental test of the central hypothesis.

The whole research program is definitely interdisciplinary. It is dependent on current colloid and surface chemistry as much as on geological observations. The research began with one of the most puzzling observations relating to the porphyroids. In 1958 some geologists considered these to be “volcanics” and possibly the source of the ironstone and associated copper and gold ores that were being mined at Tennant Creek in central Australia.

THE INITIAL IDENTIFICATION OF ACCRETIONS

Government geologist, J. F. Ivanac, studied the geology and mineral deposits at Tennant Creek, Central Australia in 1954. He reported a most unusual variety of porphyroid associated with a gold prospect called Black Angel that was one of the largest ironstone masses known on the field at that time. Detailed mapping showed the unusual porphyroid to be intrusive and formerly mobile (Figure 3). The government geologists did not know what it was and they called it the “pigeons egg conglomerate”.

These irregular intrusive porphyroid lenses at the Black Angel Prospect in Tennant Creek contained large ovoidal chert nodules (Figure 4). Their internal concentric banding is similar to that found in much larger geodes but many of the ovoids were fragmented and randomly oriented pieces in the matrix showed the banding truncated at the margin of the angular fragments (Figure 5). The concentric banding appeared primary and not due to later weathering. The occurrence of chert ovoids instead of the usual ovoidal embayed quartz “phenocrysts” in most other porphyroids from the outcrops and drill cores at Tennant Creek was initially quite puzzling.

Chert was thought to be a hardened form of colloidal silica so advice on the possible origin of these ovoids was sought from a senior colloid chemist. Specimens of the Black Angel “pigeons egg conglomerate” together with a selection of so-called quartz “phenocrysts” from more typical Tennant Creek porphyroids and sheared porphyroids as illustrated in Figure 6 were taken to Professor A. E. Alexander of University of Sydney.

In 1958 Professor Alexander, author of Alexander and Johnson *“Colloid Science”*[7] was certainly the best colloid scientist in Australia and a world leader in this specialised branch of surface chemistry and particle interactions.

After examination of the specimens and particularly the concentrically banded chert ovoids in the Black Angel porphyroid he was completely confident of their origin. *“Mr Elliston, those are not concretions, they are accretions!”* Professor Alexander explained that quartz was not soluble in water including normal ground water and stream water in the cycle of erosion. It is transport-

WHAT ARE THE BLACK ANGEL PORPHYROID OVOIDS?

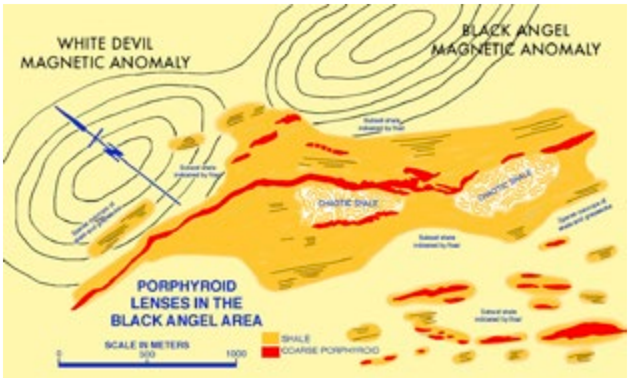


Figure 3. Map of the mysterious porphyroid lenses and magnetic anomalies at the Black Angel prospect, Tennant Creek.

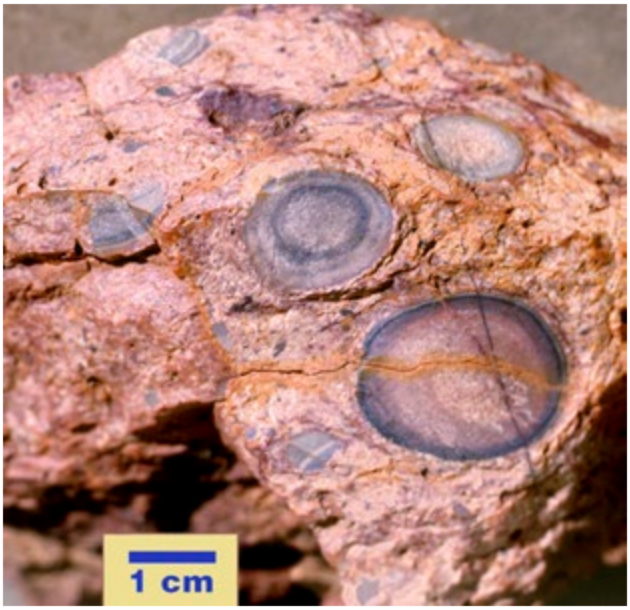


Figure 4. Chert ovoids in the Black Angel porphyroid have concentric internal diffusion (Leisegang) banding.

ed as gravel and sand grains and generated as sea sand. Quartz does not dissolve in seawater by dispersion of anions and cations as a solution but it does hydrolyse (react with water) in slightly alkaline seawater (pH 7.9 to 8.3). This process was later found to be "proton promoted dissolution"[8] as shown diagrammatically in Figure 7.

Professor Alexander explained that to form accretions in ordinary marine sediments such as the turbidite deposits at Tennant Creek the interstitial polymeric silica particles aggregate into large globules of silica gel if the mud at a certain stage of consolidation is reliquefied and able to flow.

Figure 5. Banding in Black Angel porphyroid chert ovoids was formed before some were broken in subsequent liquefaction of the matrix. The bands were not formed by exposure and weathering.

He pointed out that there is a critical concentration (distance between charged particles) at which "close packing" sets in and that this applies to all the charged particles or colloidal components of natural sediments. He was therefore confident that quartz ovoids from other porphyroid lenses in Tennant Creek that showed evidence of former shrinkage (syneresis), of having been soft or plastic or aggregates of smaller accretionary clusters were also accretions. This applied to all the colloidal components in the original sediment including the clays and hydrous ferromagnesian minerals that are the other major components of normal sediments.

There was obvious certainty about the Black Angel chert ovoid "porphyry" and clear evidence of its extension to other porphyroids in Tennant Creek that had been considered to be of volcanic or igneous origin. It was initially unclear how far the principles of particle aggregation (DLVO theory) [9,10,11] applied but a new and exciting new avenue of investigation was opened up. It was particularly relevant to the source of the ore deposits associated with the porphyroids. If the porphyroid

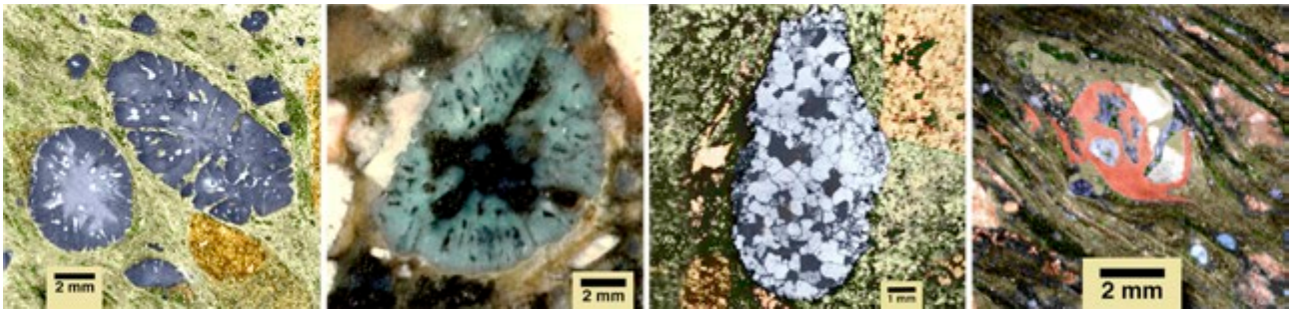


Figure 6. Quartz "phenocrysts" from the Tennant Creek porphyroids are typically rounded, embayed with crack patterns interpreted as due to syneresis shrinkage. Some show soft or fluidal contacts with feldspar, many are mosaics of smaller interlocking crystals and there are clear examples of colloidal silica (jasper, chert) aggregation.

"phenocrysts" had crystallised from accretions, syneretic desorption of critical clusters of insoluble sulphide and oxide ore and gangue minerals during their condensation was clearly the source of the ore.

THE SURPRISING VEHEMENCE OF OPPOSING VIEWS ON SIGNIFICANT DISCOVERY

The discovery that porphyroidal textures result from crystallisation of accretions in all sorts of sediments (including limestone) mobilised during diagenesis (the process of change between sediment and rock) is revolutionary. As the research was developed further, hundreds of textbooks and papers studied and specialist academic advice obtained, it became clear that a large majority of "middle ranking" academics remain stubbornly committed to historic concepts, existing old interpretations and ideas developed before the advent of current surface chemistry and nanotechnology. There is real apprehension about change.

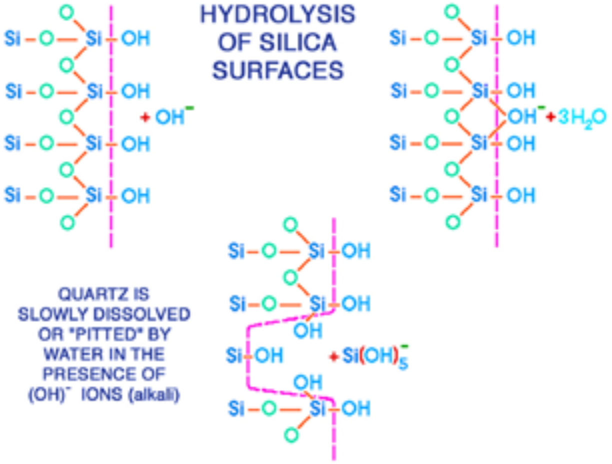


Figure 7. The molecular dispersion from crystalline silica in water as $Si(OH)_4$ is catalysed by hydroxyl ions of an alkali or base. Seawater is slightly alkaline and therefore silica (and most silicate surfaces) "disperse" by these surface reactions. In sea water and within marine sediments the small neutral $Si(OH)_4$ molecules polymerise to short chain polymeric silicic acids called "oligomers". (From Iler, 1979, fig. 1.11.)[8]

More thoughtful individuals, especially senior academics working to advance the frontiers of knowledge themselves, are prepared to consider the detailed observations and draw logical conclusions directly from the observational data. Professor S. W. Carey from the University of Tasmania came to Tennant Creek and after careful examination of the evidence, he fully accepted and became keenly enthusiastic about the new discoveries. He organised an international symposium in 1963 at the University with field visits to Tennant Creek to introduce the new concepts more widely.

Evidence such as the Black Angel porphyroid with chert ovoids should be conclusive. It was later shown that large concentrically banded geodes that lapidarists cut and polish for sale as ornaments also have an accretionary origin. The aggregation of smaller nodules of silica gel (now chert) and the Leisegang banding, central crystal cavity and fluid extrusion channels are shown in the cut section in Figure 8.

This and evidence for the accretionary origin of Tennant Creek porphyroids was accepted by some geologists working on the field, colloid chemists and a number of perceptive academic geologists. In addition to Professor S. W. Carey, Professor T. F. W. Barth from Oslo, Professors J. C. Jaeger and Anton Hales from Australian National University, Professor Beryl Nashar from Newcastle, Professor R. L. Stanton from University of New England, Professor T. W. Healy from PFPC at University of Melbourne and Assoc. Professors K. L. Williams and R. J. Hunter from University of Sydney have accepted and found the evidence for accretion and con-

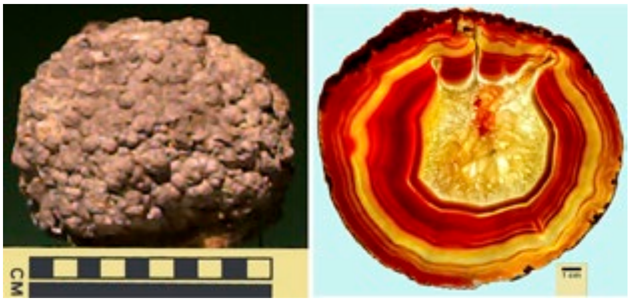


Figure 8. Following Professor Alexander's recognition that the concentrically banded chert ovoids in the Black Angel porphyroid were accretions, it was later found that much larger internally banded geodes are also aggregates of smaller polymeric silica nodules. Concentric (Leisegang) banding is due to different diffusion rates for ions and desorbed electrolytes that control precipitation of impurities [$Fe(OH)_3$].

cretion in rocks historically classified as "volcanics" and "igneous" to be clear and compelling.

In the long course of the systematic investigation many more earth scientists have assisted in assembling the great body of observational data (4,600 photographs of evidence of former colloidal processes preserved in the rocks) and recognised that the principles apply to all rocks and mineral deposits derived from natural sediments. Forty-eight senior scientists are listed in the book but since printing and distributing the Australian preview edition there are now many more.

Concretionary structures can only be formed by precipitation of charged particles diffusing to form concentric layers round nuclei that desorb ions and charged particles (synerectic). They are unique non-random structures that can only be formed in aqueous particle systems. They are conclusive evidence that the rocks in which they occur were lithified, crystallised or simply hardened by chemical dehydration reactions from aqueous particle systems. Concretions or orbicules have been found in siliceous shales at Tennant Creek, in porphyroids at Whip Spur, South Queenstown, Tasmania, and the variety of large concretions called orbicules are found in many granites worldwide. Orbicules have also been found in most other varieties of so-called igneous rocks, sediments, and "volcanics" except actual volcanic ejecta, ash and basalt.

Because concretions are such clear and compelling evidence of the former particulate and diffusive nature of the crystalline or lithified rocks in which they occur, during the course of the long investigation to establish the origin of rocks and mineral deposits using current physical chemistry of small particle systems, orbicules or concretions have been photographed or recorded in granite, diorite, rhyolites, norite, aplite, gabbro, dolerite, pyroxenite, peridotite, serpentine, chromite, kimberlite, dolomite, limestone, siliceous shale, carbonatite, latite, amphibolite schist, jasper, chert, quartz veins, and siliceous magnetite lodes.

All these examples are characterised by 23 features resulting from the particle system properties that give rise to them. The rounding, concentric rimming and former soft plastic and fractural condition are most obvious but most examples show only about seven or eight of the 23 characteristic features.

The physical and chemical processes by which orbicules and concretions generally are formed are set out in complete detail in the book *"The Origin of Rocks and Mineral Deposits – using current physical chemistry of small particle systems".*

A few examples concretions including those called orbicules are illustrated in Figure 9.

INCREDIBLY OBDURATE RESISTANCE

The revolutionary new hypothesis that ancient sediments were particle systems with the same rheological (ability to reliquefy) and physico-chemical properties as those now established for sediments accumulations of today remains a horrendous anathema to many academic geologists, editors and PhD graduates. They have abandoned the correct scientific method by which we should draw logical conclusions directly from factual observational data and measurements. The popular or majority view is considered more important and only papers and textbooks that conform to existing ideas and traditional interpretations are approved for publication in scientific journals.

Geology and other scientific disciplines to the extent that the correct scientific method is no longer used, are "stuck in a rut".

AusIndustry and Australia's most distinguished leaders in colloid science have ensured that our whole program is based on repeatable experimentation and that conclusions are based on sound principles of the physical chemistry of small particle systems and nanotechnology. However, the results of prolonged experimentation are still not "current knowledge" that is available in the public arena on a reasonably accessible worldwide basis.

The most significant new contribution to science from this research is that disturbance of wet sediment pastes allows colloidal particles in natural sediments to rearrange themselves into denser clusters called accretions so that surface energy is reduced. The large accretions that

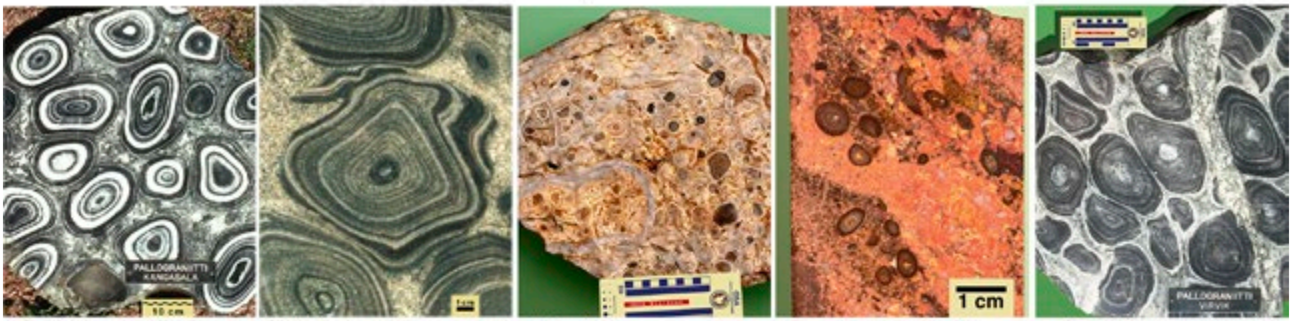
Orbicular granite from Separation Point, New Zealand.

Orbicule round schist fragment, Kangsaneimi Finland.

Dolomite orbicules round fragments, Gunpowder Creek, NW Queensland.

Orbicular diorite from Boogardie, Western Australia.

Small jasper concretions from Peko Mine lode, Tennant Creek, NT.



Orbicular granite from Kangasala, Finland.

Distorted and fragmented granite orbicules from Virvik, Finland.

Orbicular or concretionary chert from Roebourne, Western Australia.

Small iron ore oolites or concretions in granite, Olympic Dam Mine, SA.

Re-intruded orbicular granite from Virvik in Finland.

Figure 9. Examples of concretions include those called orbicules and oolites.

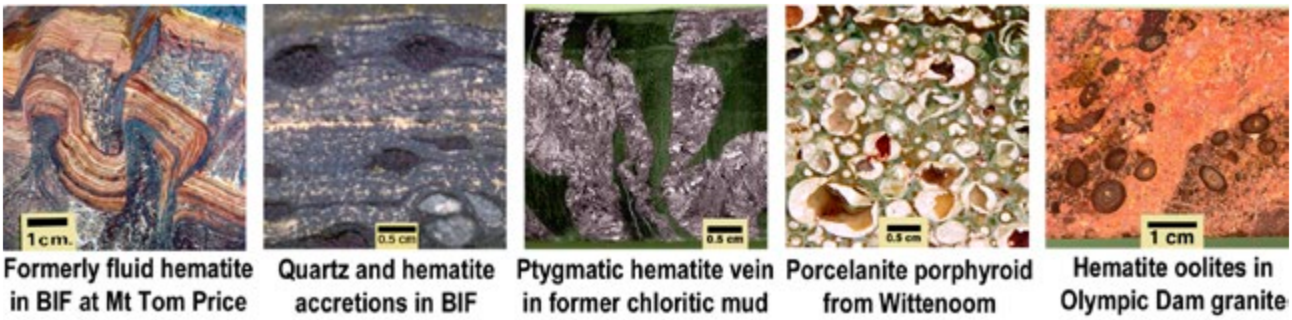
are formed during flow subsequently liberate colloidal ore metal sulphide suspensions into brines as they spontaneously divest surface adsorbed water (called syneresis). Rock masses are heated by chemical dehydration reactions as the pre-ordered particle aggregates finally crystallise.

It is clear that mineral deposits are not deposited from solution but from colloidal dispersions formed by successive synerectic desorption of critical clusters. Granitic, porphyroid and metamorphic minerals crystallise from precursor hydrosilicate accretions. These are formed by shear or viscous flow of mobilised semi-consolidated sediments. Syneresis of the accretions formed in large volumes of sediment mobilized during diagenesis desorbs ore and gangue minerals. Quartz veins, pegmatites, aplites, ferromagnesian mineral-rich rocks and massive intrusive iron ore accumulations are formed by rheological separation.

The vast majority of geologists still know very little or nothing about the way that the charged particles in natural sediments interact with each other and with the charged ions in fluids surrounding them. The main components of natural sediments are clays, polymeric silica particles and hydrous ferromagnesian minerals that carry a surface charge. The surface charges on natural sediment particles interact with those on adjoining particles, with polar water molecules and with the ions of any electrolytes dissolved in the pore fluids.

Many years of study and advice from world leaders in geology and in colloid and surface chemistry have determined the physicochemical processes by which many previously unknown geological textures and structures were actually formed. These include iron ore oolites, ptygmatic folding, granite orbicules, rapakivi textures, myrmekites, accretions, concretionary structures in mineral lodes, discordant folding and plastic deformation of minerals, etc. Several examples are illustrated in Figure 10.

The origin of these structures, of migmatites, porphyroids, granitic rocks and mineral deposits is still not current knowledge, information or experience. The scope of the core research and application of this book is extraordinarily wide. The principles of current surface chemistry apply to all rocks and mineral deposits that have been derived from natural sediments.



Formerly fluid hematite in BIF at Mt Tom Price

Quartz and hematite accretions in BIF

Ptygmatic hematite vein in former chloritic mud

Porcelanite porphyroid from Wittenoom

Hematite oolites in Olympic Dam granite

Figure 10. Former mobility of iron ore, accretions, ptygmatic folding, and concretions are now explained.

Those trained only in conventional geological principles must recognise the nature of any significant advance. It is new, unfamiliar, not yet accepted, and it must differ from traditional beliefs. Existing personal beliefs and traditional assumptions constitute the main impediment to the advance of science. The objective of this book is to present the primary data, the observations representing the experimental results and the details of the colloid and surface chemistry and rheology (fluid properties of clay, mud and gelatinous precipitates) that now explain the observations.

EXPLORATION SUCCESS RECORD

It has been demonstrated that an understanding of these processes can be used to achieve higher success rates and greater cost-effectiveness in mineral exploration.

For the first 26 years after Professor Alexander's advice that the chert ovoids in the Black Angel porphyroids were accretions, the research was developed in conjunction with an active mineral exploration programme in order to improve its effectiveness and success rate. It succeeded. This story of the successful application of the developing research is recorded in the book *"Australians Successfully Exploring Australia – and developing the science and technology to do it"*.

As soon as the origin of the mineral deposits at Tennant Creek was understood five new mines were discovered in different locations on that field with the first fifteen exploration holes drilled. In the period 1967 to 1984 before another company funded the ongoing research, a further mine was discovered on the Tenant Creek field, a new coalmine and three other significant mineral deposits developed elsewhere in Australia. A total of nine new metalliferous mines and 33 associated minable ore bodies established a record for the most successful mineral exploration group in Australia.

This has been confirmed by independent comparative studies commissioned by competitors. CRA Exploration Ltd commissioned McKinsey & Company Ltd, Management Consultants from New York in 1975 and Western Mining Corporation with a study of the *"Economics of the Australian Mining Industry"* led by Professor Brian Mackenzie in 1984. The record for exploration success using the new understanding of how rocks and mineral deposits were formed remains unsurpassed.

The long-running systematic investigation of the origin of rocks and mineral deposits including costs of highly qualified academic consultants, establishment of libraries, continuing access to world scientific literature, etc. was financed by the success in developing new resources.

PROGRESS REPORTS

In both the period of funding by Peko-Wallsend 1957 to 1984 and by CRA Exploration – Rio Tinto 1984 to 1996, hundreds of company reports relating to specific prospects and exploration or acquisition projects were prepared. In addition to these, scientific papers and presentations that record the progress of the new research could be summarised as: -

Papers published:	14
Public lectures, presentations and courses:	27
Company Research Progress Reports for Peko-Wallsend Limited:	19
Company Research Progress Reports for CRA Exploration – Rio Tinto;	66
Books:	3

The companies were keen to have the new scientific discoveries understood and applied to improve success rates and cost-effectiveness in developing new resources. Geopeko Limited, the exploration subsidiary of Peko-Wallsend Limited demonstrated this success.

From an initial misunderstanding that it would be easy for the much larger CRA Exploration team to be "brought up to speed" the progress reports for that company became increasingly detailed and authoritative.

Progress reports include contributions to the symposia held at the University of Tasmania in 1963 and its review in 2007, 14 consultant reports to the companies by Professor T. W. Healy on physico-chemical processes in the diagenesis of sediments and many of the later reports to CRA Exploration geologists. These are essentially substantive treatises based on numerous field observations that support their conclusions. AusIndustry has monitored all research for compliance with the prescribed scientific method since 1984.

Those prepared for CRA Exploration were released for publication on 27th September 1995. Each of these progress reports advances our knowledge of its topic by using current physical chemistry of small particle systems where this is relevant to the interpretation of the observations recorded. Figure 11 is a photograph of the progress reports relating to the long-running industrial research projects. The yellow introductory booklet contains the e-book on CD that was prepared for evaluation.

They are fundamental scientific papers explaining well-known problematic geological observations by using a wider range (interdisciplinary) of established physico-chemical processes.

Figure 11. Progress reports relating to the long-running industrial research projects include the yellow introductory booklet containing an e-book on CD. This was prepared for evaluation with direct links from the text to figures, glossary and references.

Some of the more significant titles of these early 1990's conclusive studies are illustrated in Figure 12.

THE COMPLACENCY OF CONSENSUS AND CONSTRAINTS OF CONVENTION

Science is the intellectual and practical activity encompassing the systematic study of the structure and behaviour of the physical and natural world through observation and experiment. This has largely been abandoned in modern times.

To be accepted into a University one has to provide the 'right' answers in exam papers. The 'right' answers are those considered to be in accord with present beliefs and rigorously maintained existing university standards. Students are brainwashed in University courses so that 'scientific correctness' prevails in geology.

To be successful in academic research one has to publish papers that present the 'right' answers to questions that are in accord with current beliefs and 'acceptable' theories. However logical, new conclusions from direct observation tend to be disregarded.

Academic training is constrained to orthodoxy and established lines of enquiry by its objectives in achieving highest technical standards, academic status, equivalence and uniformity in graduate levels, but above all by acceptance and recognition of its research, teaching, and graduates. The endeavour is for academic recognition and status rather than acquisition of new knowledge.

The academically oriented thinker is extraordinarily difficult to "teach", even by observations in the rocks themselves where they are clearly inconsistent with theory. This is because he or she attaches such great importance to "right" premises and pre-suppositions. Divergent views or "heresy" become for those in pursuit of an academic career a threat of excommunication or non-acceptance by peers.

Years ago Lowell wrote:

> *Is anything of God's contriving endangered by enquiry? Was it the System of the Universe or the monks that trembled at the telescope of Galileo? Did the circulation of the firmament stop in terror because Newton laid his daring finger on its pulse?*

When Professor S. W. Carey was first shown the evidence for aggregation of particles in remobilised dense mud and the way these close-packed clusters subsequently crystallised to textures that had previously been interpreted as "volcanic" or "igneous", he recognised the fundamental nature of this significant scientific discovery. In his 1963 symposium on gravity sliding of uncon-

THE TEXTURES OF ORE SOURCE ROCKS
by JOHN ELLISTON

THE HYDRATION OF SILICA AND ITS ROLE IN THE FORMATION OF QUARTZ VEINS

SILICEOUS ACCRETIONS AND THEIR FORMATION IN MOBILISED SEDIMENTS
by JOHN ELLISTON
Part 1 MAY 1992
Part 2 June 1992

THE GENESIS OF NON-ALLUVIAL OXIDE ORES
by JOHN ELLISTON

A REVIEW OF THE GEOLOGY OF THE IRON ORE PROVINCES
by JOHN ELLISTON
MAY 1991
REVISED AND UPDATED
MAY 2008

THE FORMATION OF CLAY ACCRETIONS AND THEIR CRYSTALLISATION TO FELDSPAR
by JOHN ELLISTON

FRAMBOIDS, AND THEIR SIGNIFICANCE AS AN INDICATION OF THE ENVIRONMENT IN WHICH THEY ARE FORMED
by JOHN ELLISTON

THE ORIGIN AND MOVEMENT OF METAL SULPHIDE SPECIES IN BASIN SEDIMENTS
by JOHN ELLISTON

Figure 12. Some of the more significant progress reports detail the features of ore source rocks, the aqueous chemistry of silica, the formation of siliceous accretions, the origin of non- alluvial oxide ores, the geology of the iron ore provinces, the formation and crystallisation of clay accretions, the formation of framboids and the origin of metal sulphide species that accumulate as mineable ores.

solidated sediments towards the deeper parts of the sedimentary basins he wrote:

> *These proposals frankly shocked me, because once these new premises and processes are granted I cannot see any discontinuity short of profound revision of many of our cherished concepts on ores and a wide group of "igneous" rocks."*

The evidence presented at the symposium convinced most of the geologists attending. However, most were left wondering how far the new principles applied and three or four attendees revealed their strong emotional commitment to existing interpretations and traditional assumptions made before the properties and surface chemistry of charged particles were known. It emphasised the reality of Professor Carey's edict. For many otherwise competent scientists: - *"We are blinded by what we think we know."*

However, the outcome was years of study of examples and accurate recording of observational data. The central hypothesis is established as correct but appropriately fair and competent refereeing remains extraordinarily difficult for academic geologists committed to historic assumptions and existing university teaching and "cultures".

Initial studies of mine openings and drill cores at Peko Mine found the quartz-magnetite lode contained oolites (fish-egg sized concretions) as illustrated in Figure 13. To understand the ore forming processes it was clearly necessary to understand how these concretions could form and then crystallise to quartz-magnetite.

This was achieved and first published in *"The genesis of some epigenetic type ore deposits"*, 23rd Session of Int. Geol. Congress, Prague, August 1968. Published in Organ. Czech. Soc. of Min. and Geol., 14(2): 129–139. The study of concretions extended to orbicular structures in granites was published as *"Orbicules: an indication of the crystallisation of hydrosilicates",* 1., Earth-Science Reviews, 20: 265–344 in 1984.

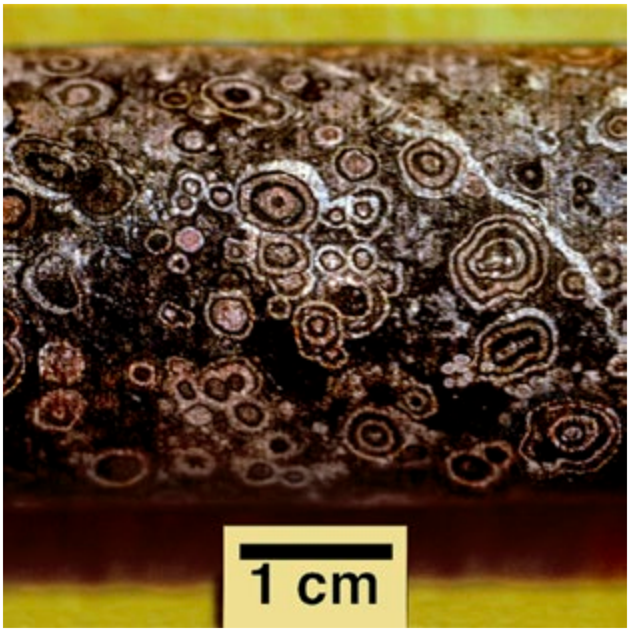


Figure 13. Fish-egg sized concretions or oolites were found in the quartz-magnetite lode at Peko Mine, Tennant Creek.

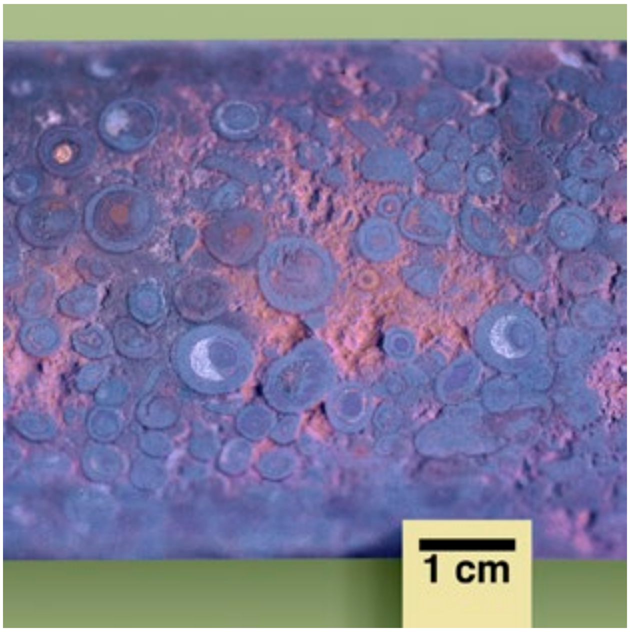


Figure 14. Oolitic hematite oolites in the hematite lode at the Olympic Dam Mine in northern South Australia show that the minerals in this very large lode also crystallised from colloidal ferric-hydroxide precursors.

Years later a visit to the Olympic Dam Mine in South Australia on 8th July 2002 revealed that the mine geologists at that mine had also discovered hematite oolites in the large intrusive hematite breccia body that contains the mineable ore. The hematite oolites are exposed in the mine openings and drill cores. Excellent specimens are exhibited as curios in the mine geological office display cabinet. However, the Chief Mine Geologist and most of the academic geologists on this Geological Society visit were disinterested and did not recognise the significance of the occurrence of hematite oolites as an indication of the origin of the ore. Visitors to the core yard in 2002 were invited to photograph the core illustrated in Figure 14.

The advancement of science is totally dependent on logical conclusions from measurement and observation. Research proposals and attainment of higher degrees are focused on what is acceptable to the existing mainstream of professional geoscience practice and this has become the criteria for publication used by editors of scientific journals.

HISTORY OF "PEER REVIEWING" FOR INTERDISCIPLINARY RESEARCH

When the interdisciplinary nature of this industrial research and the long-running systematic investigations that were the basis of many progress reports are understood, reviews of *"The Origin of Rocks and Mineral Deposits – using current physical chemistry of small particle systems"* have been very successful.

However, not all potential publishers have been able to appreciate the interdisciplinary nature of the research on which the new knowledge of the origin of rocks and mineral deposits is based. Thorough scrutiny and competent review of this book was achieved largely as a reaction to breach of an agreement to referee the manuscript properly. That potential publisher was established to promote and advance the science and publish or assist in the publication of scientific knowledge relevant to Australian industry. The manuscript was rejected because at that stage it was yet to be accepted into the mainstream of professional geoscience practice.

How could new innovative industrial research, held confidential for twelve years because its application had demonstrated a 320% increase in exploration cost-effectiveness, have become accepted into the mainstream of professional geoscience practice if it were not published?

Experience has shown that many otherwise competent senior geologists know nothing about synerectic desorption or the formation of critical clusters. Similarly many proficient chemists are unaware that occurrences of granite contain orbicules or incongruous minerals like calcite and hematite. Review by teamwork involving both geologists and chemists or by scientists adequately skilled in both disciplines is essential. Reviewers have to determine whether or not the physical and chemical processes set out in the book provide adequate explanations for the numerous geological observations.

The book contains new knowledge (details of the physico-chemical processes by which rocks and mineral deposits are formed) that is important.

The decision to dishonour the agreed refereeing procedure led to further questioning of the research method and validity of the significant results. AusIndustry (now the Department of Industry, Innovation and Science) wrote on 28th November 2005 commending the results to date but wanted to ensure that these and ongoing research used the scientific method as required to qualify for tax incentive subsidies.

AusIndustry were extraordinarily thorough. They sent a representative to view the progress reports, image library of 4,500 catalogued photographs recording the geological observations, the reports of the colloid chemists providing the physico-chemical processes in diagenesis, the technical library and the stacks of hundreds of photocopies of relevant geological and colloid science papers that had been studied in the course of the work.

More senior officers in the Department challenged the initial enthusiasm of the AusIndustry representatives. Eventually Dr Tom Honeyman was asked to investigate and report directly to the Industrial Research and Development Board. Some three months of questioning and discussion by correspondence, e-mail and telephone provided detailed information. Dr Honeyman recognised that illustrations in the reports and every observation recorded in the image library is a valid experimental test of the central hypothesis. He reported positively to the Industrial Research and Development Board at the end of July 2006. At first the Board was unable to accept that using current physical chemistry of small particle systems had discovered the origin of rocks and mineral deposits. A sub-committee of the Board was selected to further examine Dr Honeyman's report and the detailed information on which it was based. The IR&D Board approved the project and confirmed use of the scientific method on 7th September 2006.

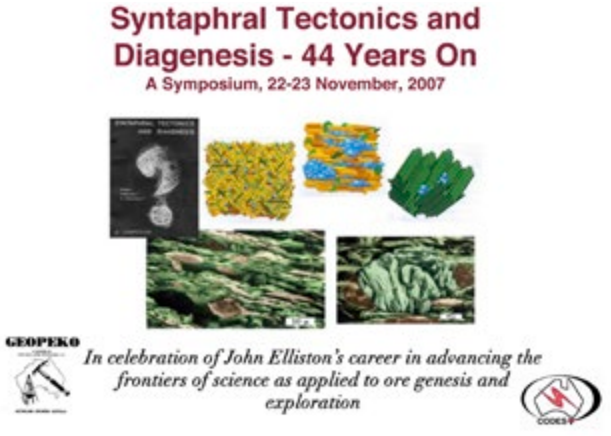
AusIndustry issued a certificate stating that the correct scientific method had been used for this project on 8th September 2006. Ian Bell, AusIndustry Assistant Product manager, gave formal approval to use the AusIndustry "proudly supported by" logo on the *"Origin of Rocks and Mineral Deposits"* and the verification reports on 6th October 2006. This was for an Australian preview edition and any subsequent international hardcopy versions. After thorough review, AusIndustry had recognised the scientific validity and significant industrial value of the research.

There was a very positive reaction to the earlier breach of the agreement to referee the research properly and AusIndustry's competent evaluation. Reviewers whose reports had been disdainfully ignored, principally Professor Ross Large, Director of the Centre of Excellence in Ore Deposits (CODES) at the University of Tasmania and Mr Kim Wright, Manager, Earth Resources Foundation, University of Sydney, organised a symposium to review the whole research program and exploration techniques that had achieved its outstandingly successful application. The Australian preview edition of the *"Origin of Rock and Mineral Deposits – using current physical chemistry of small particle systems"* was printed for this symposium held on 22-23rd November 2007. Fifty-one senior scientists contributed presentations papers and discussion that has resulted in one of the most thoroughly scrutinised and competently reviewed scientific treatises in history.

THE CODES SYMPOSIUM AT THE UNIVERSITY OF TASMANIA 22ND TO 23RD NOVEMBER 2007

This Symposium was held to review the advance in understanding the origin of rocks and mineral deposits that had been achieved since Professor S. W. Carey convened the first international symposium in May 1963. Professor Ross Large, Director of CODES at the time, gave the introductory presentation. His first slide is illustrated as Figure 15.

Professor S.W. Carey, Convenor, introduced and defined the meaning of the term "syntaphral" at the 1963 symposium. For general understanding it would

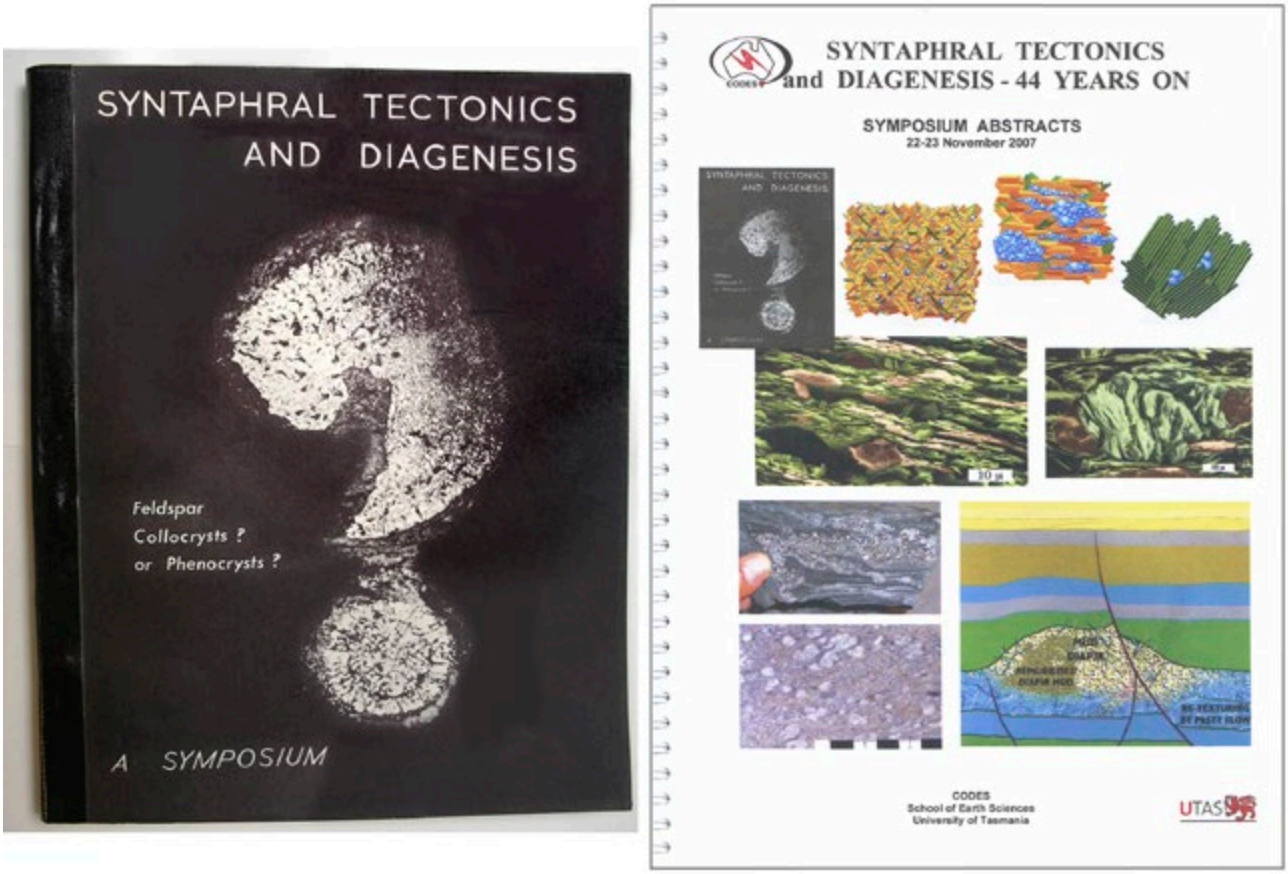


Syntaphral Tectonics and Diagenesis - 44 Years On

A Symposium, 22-23 November, 2007

In celebration of John Elliston's career in advancing the frontiers of science as applied to ore genesis and exploration

Figure 15. The introductory slide for the CODES Symposium at the University of Tasmania in November 2007.



SYNTAPHRAL TECTONICS AND DIAGENESIS

Feldspar
Collocrysts ?
or Phenocrysts ?

A SYMPOSIUM

SYNTAPHRAL TECTONICS and DIAGENESIS - 44 YEARS ON

SYMPOSIUM ABSTRACTS
22-23 November 2007

CODES
School of Earth Sciences
University of Tasmania

Figure 16. Records of the Symposia held at the University of Tasmania to introduce and evaluate the interdisciplinary research programs.

have been much simpler to describe the topic of this symposium as "Structures and re-texturing of fine-grained sediments by mudflows and sliding on submarine slopes". Many geologists are not aware that "syntaphral" means "towards the trough" or "downslope".

Professor Ross Large, Professor R. L. Stanton, Rob Ryan, Bob Richardson, John Elliston, Professor T. W. Healy, Kim Wright, Dima Kamenetsky, Jacob Rebek, Brian Williams, John Davidson, and Dr Ian Gould presented key papers at the 2007 symposium. Records of the 1963 symposium introducing the new concepts and the 2007 symposium evaluating and celebrating its completion are illustrated in Figure 16. Professor Ross Large introducing John Elliston's contribution is illustrated in Figure 17.

The Australian preview edition of *"The Origin of Rocks and Mineral Deposits - using current physical chemistry of small particle systems"* was printed as an e-book and distributed for participants to review the progress of the research since 1963 at this symposium.

Figure 18 is two pictures from Professor T. W. Healy's presentation at CODES Symposium, November

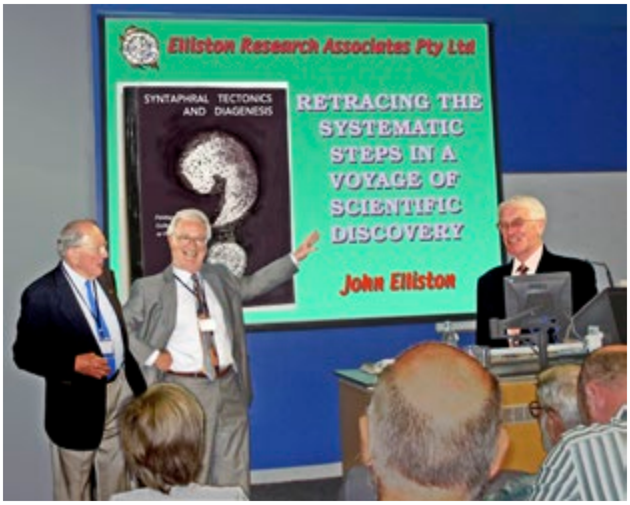
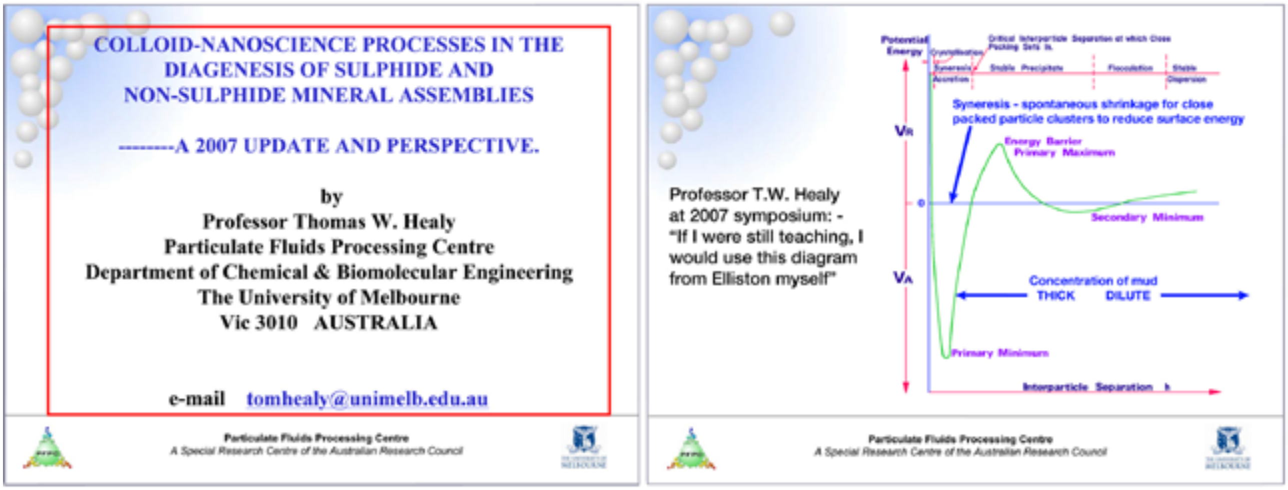


Figure 17. John Elliston (left), Professor Ross Large, Director of CODES, and Professor T. W. Healy, Particulate Fluids Processing Centre, University of Melbourne (right), at the symposium on sediment mobility and ore genesis at CODES in Hobart, November 2007.



COLLOID-NANOSCIENCE PROCESSES IN THE DIAGENESIS OF SULPHIDE AND NON-SULPHIDE MINERAL ASSEMBLIES

--------A 2007 UPDATE AND PERSPECTIVE.

by
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Particulate Fluids Processing Centre
A Special Research Centre of the Australian Research Council

Professor T.W. Healy at 2007 symposium: - "If I were still teaching, I would use this diagram from Elliston myself"

Particulate Fluids Processing Centre
A Special Research Centre of the Australian Research Council

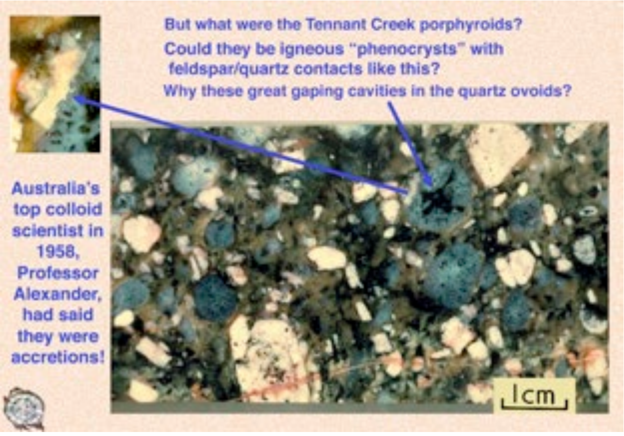
Figure. 18. Pictures from Professor T. W. Healy's presentation at CODES Symposium, University of Tasmania, November 2007.

2007. He explained DLVO theory[9,10,11] and his research that had measured the interparticle forces in relation to distance between particles (concentration of colloidal suspension or paste) that had confirmed it.

Professor T.W. Healy, AO, FRACI, FAA, FTSE, is one of the most highly qualified colloid and surface chemists in the world. His research group adapted an atomic force microscope to measure the interparticle forces in relation to particle separation (concentration) in 1998 as shown in Figure 18. Many geologists remain unaware that DLVO theory[9,10,11] is now confirmed as a natural property of colloidal particle systems such as liquefied mud. In thick mudflows or intrusions therefore plate-shaped clay particles, rod-shaped ferromagnesian hydrates and spherical polymeric silica globules form close-packed clusters that crystallise by exothermic dehydration reactions to result in porphyroid, metamorphic and granitoid textures.

Many examples of clear evidence for gelatinous precursors, polymeric silica and the formation of accretions and concretions were presented and discussed. A selection of these is illustrated in Figures 19 to 23.

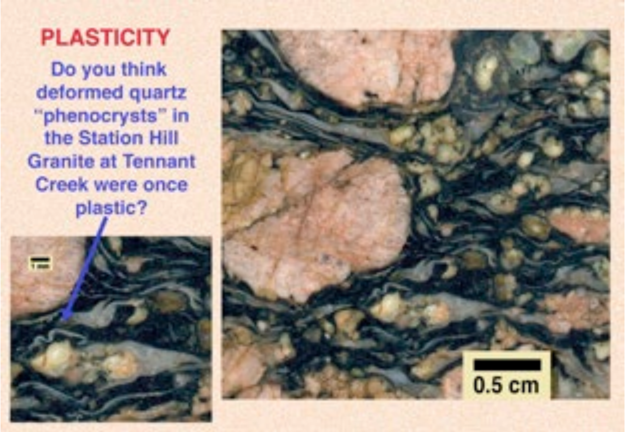
Figure 24 is a group photograph of thirty-eight of the fifty-one participants at the CODES Symposium. It includes a number of the senior scientists who have made significant contributions to the Geopeko/CRA/Elliston Research Associates research.



But what were the Tennant Creek porphyroids?
Could they be igneous "phenocrysts" with feldspar/quartz contacts like this?
Why these great gaping cavities in the quartz ovoids?

Australia's top colloid scientist in 1958, Professor Alexander, had said they were accretions!

Figure 19. This observation is readily explained as the contact between two soft gelatinous substances such as clay and silica gel. The fragmentation of the feldspars and syneresis in the quartz ovoids confirm their accretionary origin.



PLASTICITY

Do you think deformed quartz "phenocrysts" in the Station Hill Granite at Tennant Creek were once plastic?

Figure 20. Most geologists recognise that this wispy crystalline quartz in the Station Hill granite at Tennant Creek, Central Australia, was plastic when the granite was fluid. The former plasticity clearly indicates the quartz crystallised from a polymeric silica precursor.

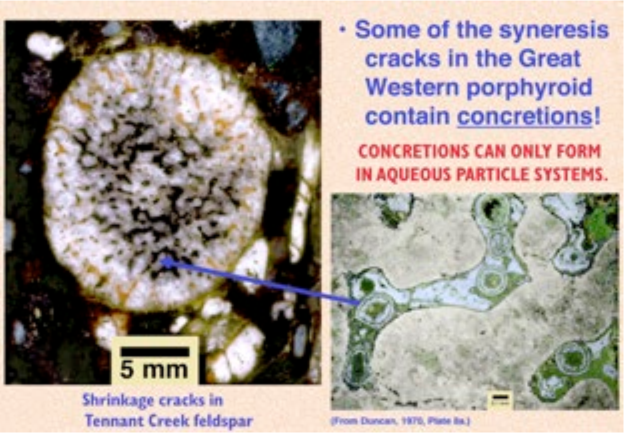


Figure 21. A diffusive gelatinous media is required for the formation of oolites, orbicules and concretions. The occurrence of small poly-rimmed oolites in the shrinkage cracks of ovoidal feldspar from a coarse Tennant Creek porphyroid is positive evidence that the feldspar is a crystallised accretion.

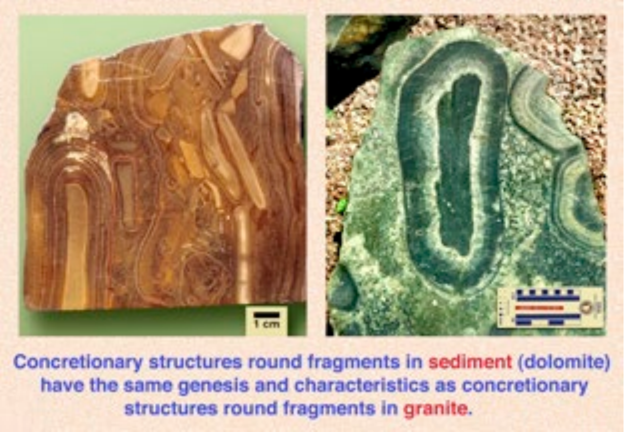


Figure 22. Geologists know that natural sediments like marine mud, lime mud and dolomite are diffusive gelatinous or 'sticky' materials. Orbicules can then form round a synerectic fragment like in this example from Gunpowder Creek in NW Queensland. The formation of an orbicule round a schist fragment in the orbicular granite from Kangasniemi in Finland is clear evidence that the granite crystallised from a diffusive gelatinous precursor.

Figure 23. Quartz oolites in siliceous shale from the Explorer 12 prospect at Tennant Creek and haematite oolites in the granite adjacent to the large Olympic Dam orebody in South Australia is further clear evidence that the granite crystallised from diffusive gelatinous precursors.

THE ESSENTIAL INITIAL CHOICE

Today the theory of the origin of granite is maintained by ignorance of alternatives. The granite controversy has persisted in the geological literature and teaching for years but now our knowledge of the materials from which rocks and the mineral deposits they contain are formed is sufficient to fully explain all the features we see preserved in the rocks.

We have a clear and obvious initial choice. We can remain with traditional teaching and beliefs that are still based on James Hutton's observations and conclusions at Glen Tilt in the Cairngorm Mountains in the Scottish highlands in 1785. Figure 25 is Sir Henry Raeburn's 1776 portrait of James Hutton. At that time James Hutton's studies of the granite contacts with the "alpine schistus" established beyond doubt that the granites had once been fluid in relation to the "schistus" they invaded (Figure 26).

In his "Theory of the Earth", 1788, Vol. 3, he writes:

> *Without seeing the granite actually in a fluid state, we have every demonstration possible of this fact; that is to say, of granite having been forced to flow, in a state of fusion among strata broken by a subterranean force, and distorted in every manner and degree....*

An example of the complex mixing of sediment and granite minerals is illustrated in Figure 27.

However, Hutton's *"Theory of the Earth"*, 1788, Vol. 1 does make it clear that this is a provisional hypothesis. On page 39, he acknowledges that this would not necessarily be true *"if there were any other cause for fluidity besides the operation of` heat"*.

Hutton's molten theory of granite has persisted by default. His *"Theory of the Earth"* recognised uniformitarianism by which the rocks are continually eroded and reformed by compaction of the resultant sediments over extremely long periods of time. His "molten rock" theory for granite displaced the theories of neptunism (granite minerals precipitated directly from sea water) but over the 230 years since Hutton the problem of granite genesis remains for those who can only con-

Figure 24. In this group of Australia's top scientists at the CODES symposium in Hobart on 22nd to 23rd of November 2007 are:
*Jacob Rebek***,** Group Chief Geologist, Rio-Tinto Exploration – remobilisation of ore sulphides and sphalerite with hydrocarbons in the ore beds at Century zinc mine.
Dr David Duncan – discovery of small oolites in shrinkage cracks of the clay precursors of feldspars in the Great Western porphyroid at Tennant Creek.
Dr Wally Fander – found the lobate feldspars in the Tennant Creek porphyroids and small oolites in the intrusive basic rocks from the Ranger open pit.
Bob McNeil – found the porphyroid-like shrinkage patterns in quartz accretions in the formerly fluid mud matrix of the True Blue slip complex.
John Love – found orbicules in the norite at the Empress Mine, orbicules in the amphibolite at Copperfield Creek, the micro-granite marker horizon in British Columbia, and saw Termier's fossil in the granite feldspar at the French Academy of Science in Paris.
Rob Ryan – led the recovery of Geopeko staff and operations following Cyclone Tracy and managed the uranium exploration and development of the Ranger ore deposits.
Kim Wright – found the oolites and colloform textures in the Peko Mine and published magnificent examples of the colloform textures and evidence that minerals from Gecko, Peko, Juno, and Ivanhoe mines had been deposited as a paste and sludge of colloidal precipitates.
Professor Dick Stanton – published his magnificent ground breaking 1989 paper containing the information and data that established the precursor principle for metamorphic and granitic rock crystals.
Professor Tom Healy – formed accretions experimentally and led the research that measured interparticle forces with an adapted atomic force microscope.
Professor Ross Large – found the new mineral 'Proudite' in the Juno Ore.
Bob Richardson – devised the world's first radiometric aerial survey system to use a 256 channel spectrometer.
Brian Williams – found large clay accretions in the lit-par-lit granite at Wilson's Promontory that had crystallised to feldspars.
Andy Browne – detailed the geology of the Ranger ore deposits.

sider the problem within the bounds of current teaching and James Hutton's provisional "molten rock" theory for which this ancient and totally inadequate theory is still the basis.

Rocks are refractory and behave like bricks when they are heated. Hutton's provisional hypothesis that granite fluidity was due to melting of the granite minerals continues to pose unresolved problems that are indeed childishly incongruous in the light of current knowledge. Some of these problematic observations are illustrated in Figures 28 to 32.

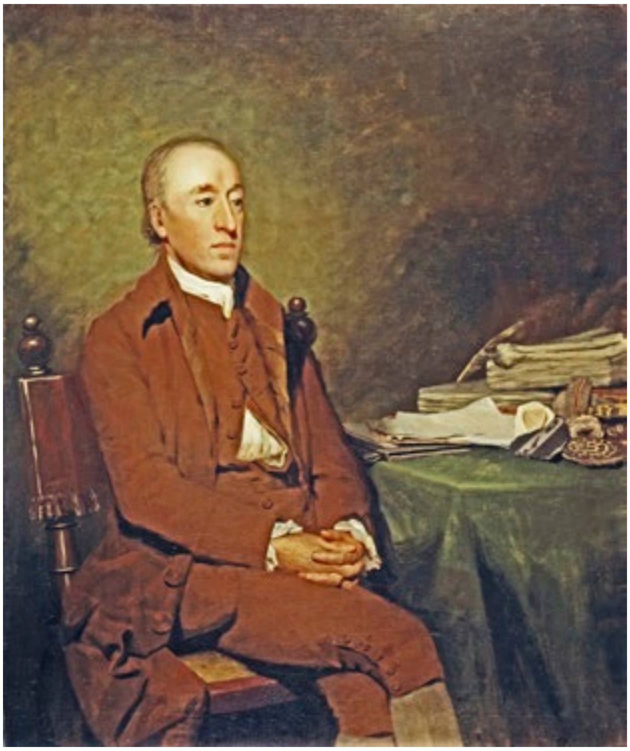


Figure 25. James Hutton 1726 to 1797 (from Wikipedia).

Figure 26. This is the location of Hutton's observations of intrusive granite, Glen Tilt, Scottish Highlands (from Wikipedia).

Figure 27. *"We have every demonstration possible … of the granite having been forced to flow … among strata broken by a subterranean force and distorted in every manner and degree …"* These examples are from West Ava in the Åland Islands, Finland. The thin veins of granite and isolated globular feldspars are inconsistent with high temperature melting

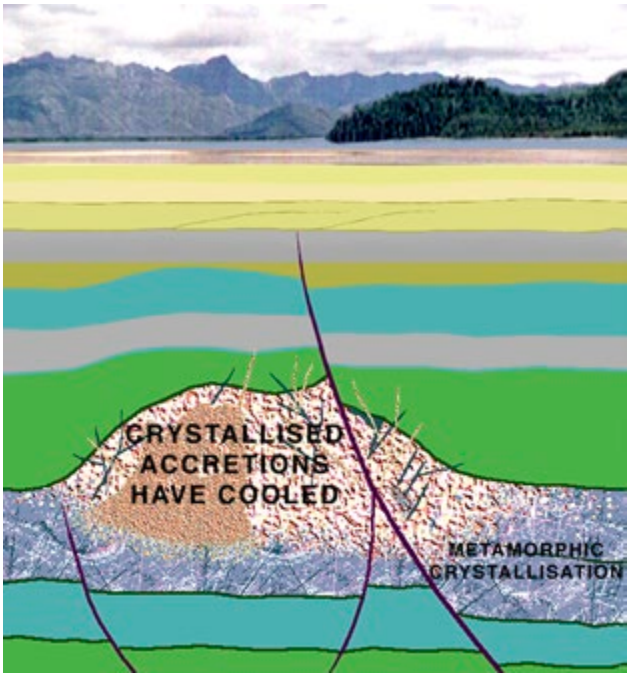


Figure 28. The source of heat including latent heat of fusion that would melt granite plutons remains unknown. Where would the heat come from to selectively melt and re-melt specific large volumes of rock?

Observations relating to granite consistently indicate that this rock was not formed by cooling of a molten rock mass similar to cooling a mass of basalt lava. Palingenesis (repeated fluidity that breaks up previously emplaced dykes), plasticity of granite minerals, 'loopy' irregular (ptygmatic) veins, layers of oriented crystals of biotite and plagioclase (comb layering), re-invasion of previously emplaced plutons without displacement (the room problem), calcite in granite is chemically incompatible, concentrically layered concretions of iron oxide (oolites) in granite are chemically incompatible, chert veins (former colloidal quartz) in granite, and mixing of granite with marginal sediments provide clear evidence of the non-molten origin of granitic rocks.

HUTTON OR MODERN SURFACE CHEMISTRY?

It remains true that rocks and rock minerals cannot assume a fluid condition unless they are melted.

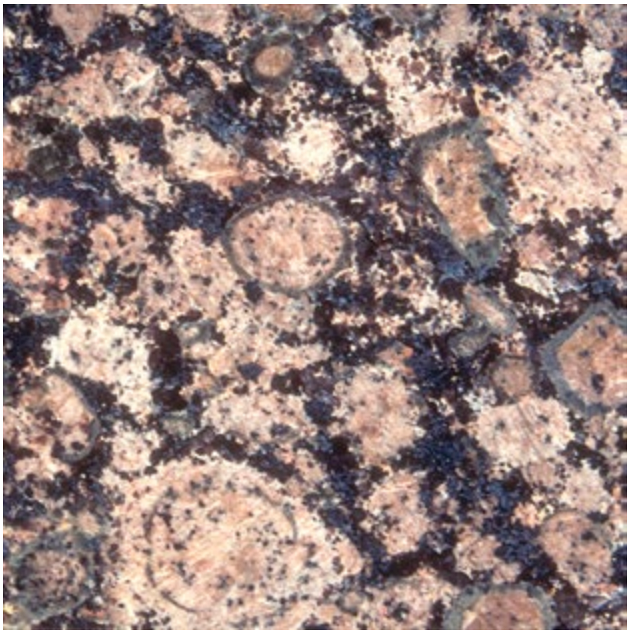


Figure 29. Rapakivi granites are completely inconsistent with melt cooling. They contain large rounded potash feldspars some of which are rimmed or have internal concentric zones of calcic-soda feldspar (plagioclase). Why are the rapakivi feldspars rounded, aggregated and some contain internal or external rims?

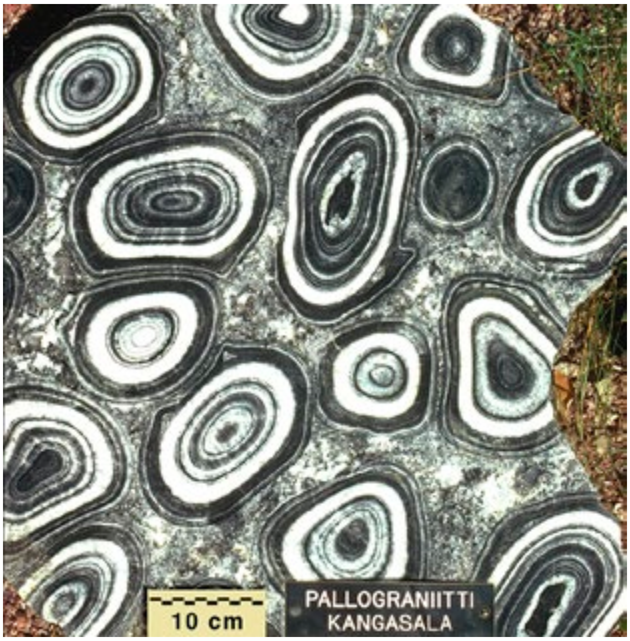


Figure 30. Granites containing orbicules (large concentric spheroids of feldspar and biotite) are simply incompatible with melt cooling. They clearly contradict Hutton's classical molten rock theory. Petrological teaching avoids study or recognition of their existence. Orbicular granites are regarded as a curiosity and the problem of how they are formed is simply not addressed.

Figure 31. Large crystals of quartz and feldspar from the surrounding granite matrix are found embedded in fragments and wall rock. This double-enclosure problem is inconsistent with molten rock theory. The enclosed entities may not have been crystalline at the time of enclosure in the soft fragment or wallrock but general pre-crystalline mobility is clearly indicated.

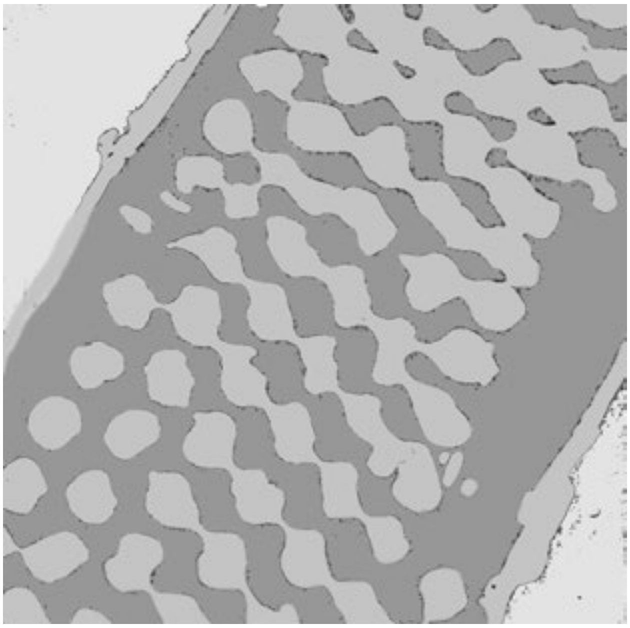


Figure 32. Termier and Termier[4] (1970) found an echinoderm shell within a granite feldspar crystal in the Atlas Mountains in Morocco. It could not have been preserved within any feldspar crystallised from a melt. If the Moroccan granite had been molten when the calcite echinoderm shell was present, it would react to form calcium silicate like the limestone used to flux acidic melts in smelting operations.

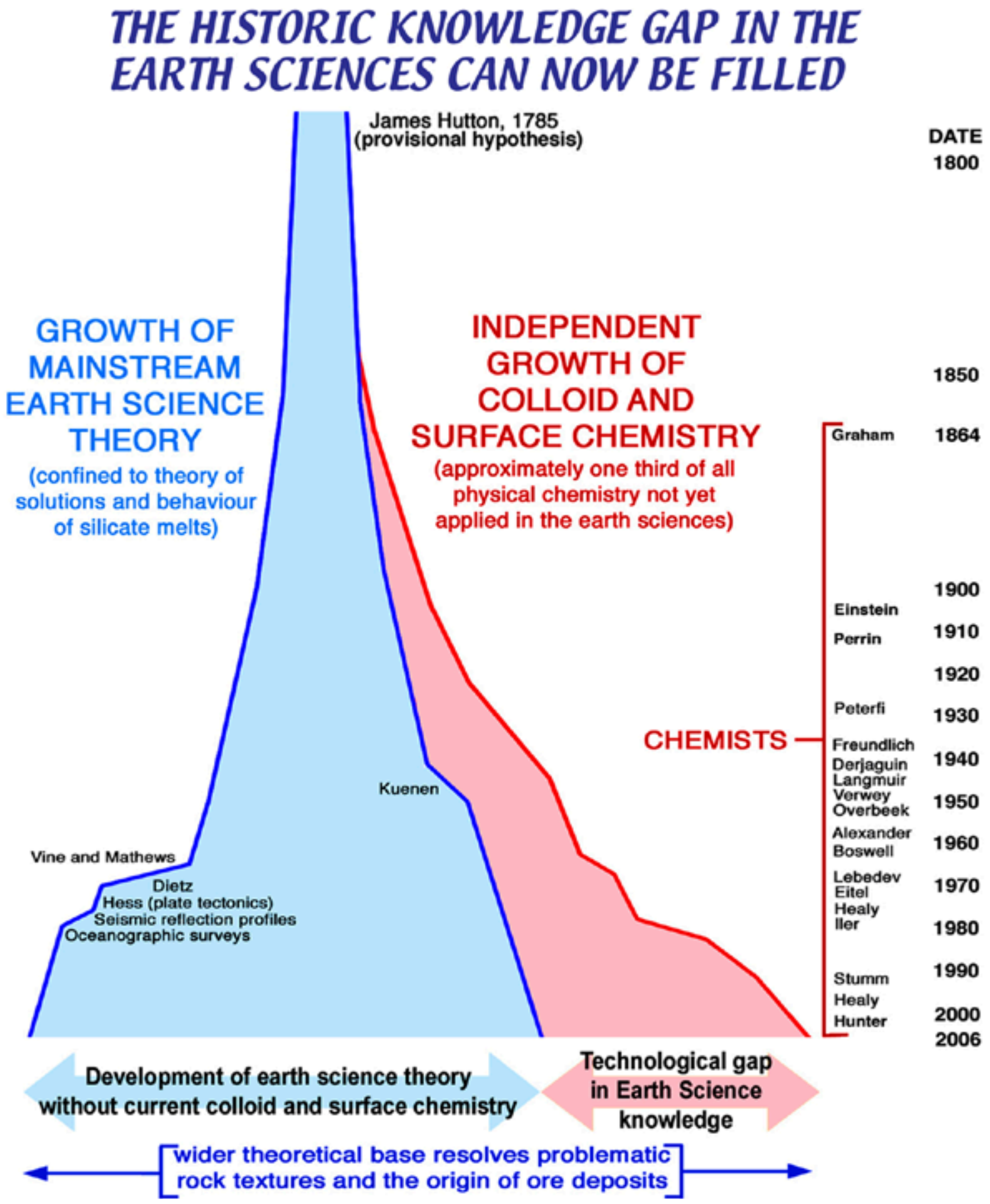


Figure 33. The independent growth of knowledge in the Earth sciences and in colloid science has left a widening gap in our understanding of how rocks and mineral deposits were formed. This can now be filled.

The positive evidence that intrusive granites were not fused rock minerals therefore clearly indicates that at the time of intrusion the common granite minerals, feldspars, biotite, hornblende and quartz must have been some other material that could liquefy, intrude, form rapakivi and orbicular textures, contain fossils, calcite and iron oxide concretions (oolites), chert veins, etc.

Basalts and dolerites have a different composition but the bulk composition of granites corresponds to metamorphic rocks and sediments. For granite batholiths found in the continental rocks of the world then we have to choose between Hutton's 1788 provisional hypothesis or some other means of making the sedimentary materials intrusive (repeatedly in some cases), mobile and able to crystallise to the observed coarse granite ovoids and mineral textures.

Since Hutton we now have the information to demonstrate conclusively that the hydrolysis (chemical reaction with water) of sediment particles, mobility of wet sediments and particle interactions between sediment particles in gelatinous wet sediment pastes can produce all the observed crystalline mineral textures and phenomena. Figure 33 shows the widening gap between the growth of knowledge in the Earth sciences and the developments in the physical chemistry of small particle systems. This additional knowledge can be used to understand the origin of rocks and mineral deposit and observations that have been problematic until now.

WE CAN NOW RELY ON EXISTING KNOWLEDGE FROM OTHER DISCIPLINES

Sediment Mobility

The information on mobile sediments has been available for over 50 years but the physical and chemical properties of wet sediments remained unknown for about 175 years after publication of James Hutton's "Theory of the Earth". Oceanographic surveys and both onshore and marine seismic reflection profiles now show the large-scale sediment liquefactions and intrusions as illustrated in Figures 34 to 39.

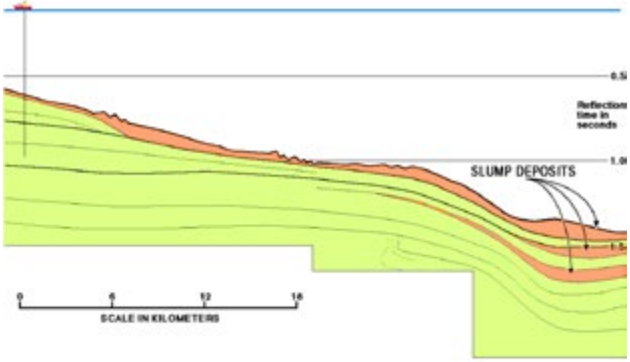


Figure 34. Massive submarine slope failure involves liquefaction of large volumes of sediment. Lehner[12], 1969, fig. 45.

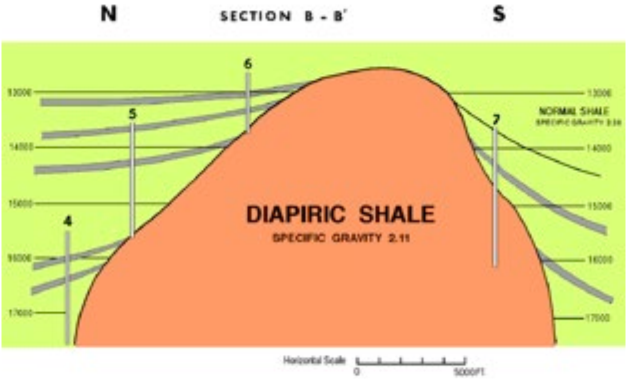


Figure 35. This intrusive shale mass is near Eugene Island, Texas gulf coast. Gilreath[13], 1968, fig. 9.

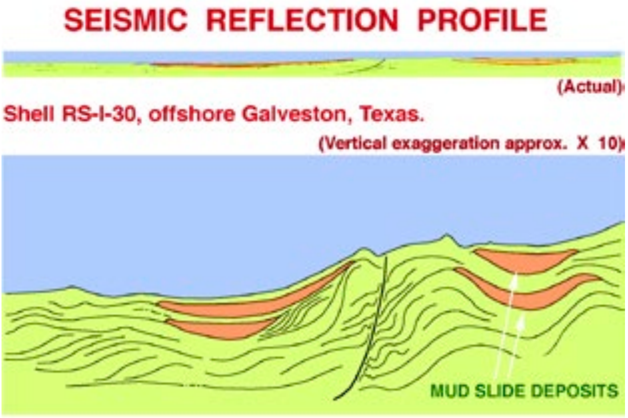
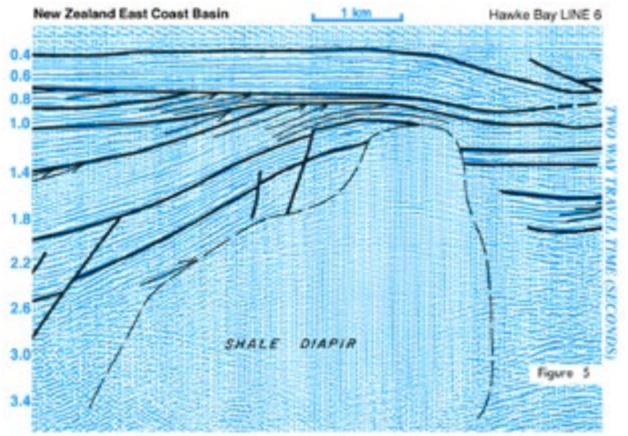


Figure 36. A Shell reflection profile reveals large volume mudslide deposits offshore Galveston, Texas. Wilhelm and Ewing[14], 1972, fig.11.



(From *The Seismic Atlas Australian and New Zealand Sedimentary Basins*, 1984, p.299)

Figure 37. Seismic surveys[15] record a large intrusive shale mass in Hawks Bay, New Zealand.

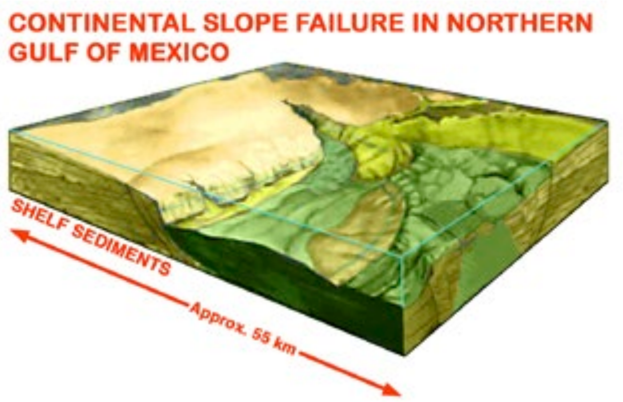


Figure 38. Liquefaction and displacement of large volumes of wet sediment result from submarine slope failure.

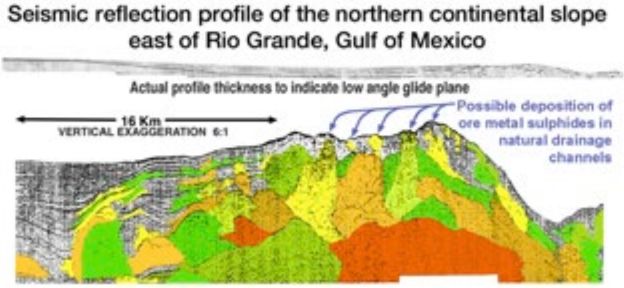


Figure 39. Seismic reflection profiles reveal a thickness of shelf sediments 900 to 1200m thick built up from successive earthquake shocks and downslope sliding. The water-rich and lighter thixotropic buried sediments have then risen as complex of large sediment diapirs through the accumulated slump deposits. (Wilhelm and Ewing[14], 1972, fig. 9.)

PHYSICO-CHEMICAL UPDATE OF SEDIMENT COMPONENTS

Seismic surveys and drilling establish the large and small scale mobility and intrusion of sediments but we have also to consider the chemistry and surface chemistry of the trillions of particles that make up the deep sediment accumulations from which the rocks and mineral deposits are formed.

The physical breakup of the rocks and rock minerals in the cycle of sedimentation is obvious. The immense energy inputs to achieve the physical excavation of the natural valleys as in Figure 40 and the chemical energy to breakdown and change the rocks and rock minerals must be appreciated.

The slow physical and chemical breakdown of the rocks to boulders, scree, cobbles and soil and its transport downstream to finally discharge from the river mouths on to the continental shelf all require physical and chemical energy inputs.

Figure 40. Think of the energy required if cavernous natural valleys were excavated by open cut mining methods (or by ancient quarrying methods before the advent of explosives and mechanical earth moving equipment).

A major chemical change in the environment of natural sediment particles occurs as they enter the sea. Organic matter, soil acids, air-ground water changes, etc. are replaced by very long periods of soakage in slightly alkaline seawater.

The rocks and rock minerals exposed on the land end up as massive accumulations of high-energy particle systems as illustrated in Figure 41. They comprise the continental shelves where further submarine erosion results in the deep marine deposits.

The basic sediment particles are clays, silica and hydrous ferromagnesian minerals but every sediment layer differs in proportion of these components and a variety of organic, carbonate and other lesser components that characterise marine muds. The sediment particles flocculate and precipitate to compact as random aggregates of mixed particles as illustrated in Figures 42 and 43.

HYDRATED SEDIMENT PARTICLES BECOME PRECURSORS OF THE NEXT GENERATION OF ROCKS AND MINERAL DEPOSITS

The essential basis of the cycle of weathering, sedimentation, sediment mobility and compaction to the next generation of rocks and mineral deposits is well understood by everyone. However, an alternative to Hutton's provisional "must have been melted" theory requires the chemistry and behaviour of the high-energy charged particles to be considered.

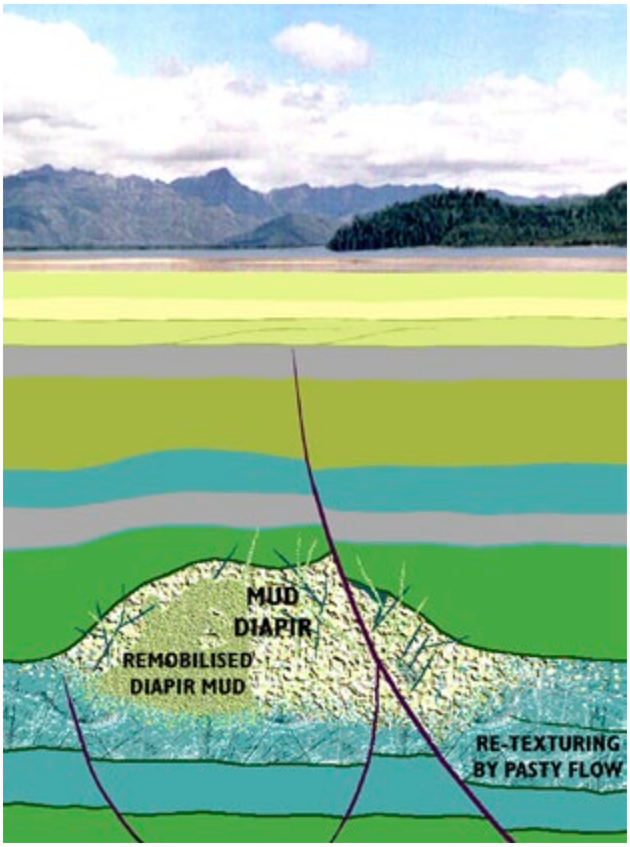


Figure. 41. Accumulated sediments contain re-mobilised sediment lenses and diapirs.

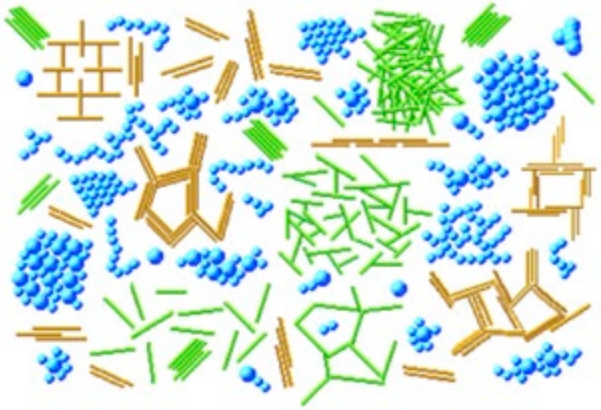


Figure 42. Natural sediment particles are attracted to each other by surface charge to form clusters and particle associations when they first precipitate.

The basic chemical reaction of "weathering" occurs mainly under the sea. The endothermic hydrolysis of the silica and silicate surfaces creates silanol groups (Si-OH) on the surfaces as indicated in Figure 44.

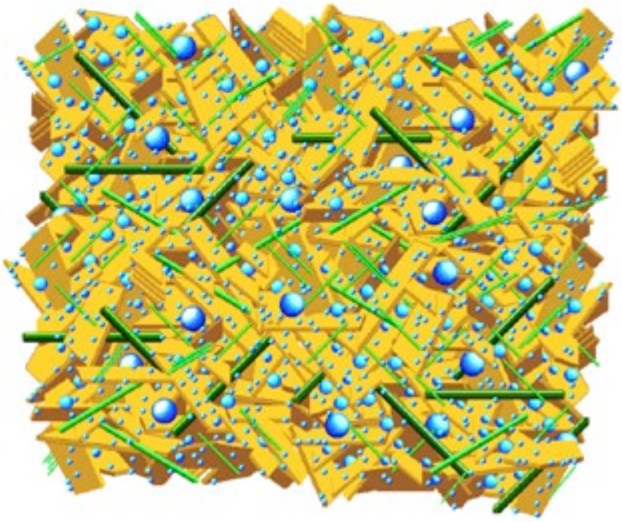


Figure 43. Initially flocculated sediments compact to a relatively random initial aggregate of mixed particles.

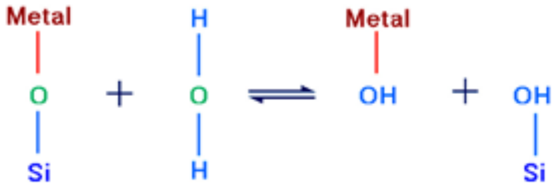


Figure 44. Sediment particles are hydrated metal silicates such as clays. These are mainly potassium or Na-Ca alumino-silicates that hydrolyse further in seawater.

Clays predominate at about 65% of the sedimentary material, silica is usually about 20% and hydrous ferromagnesian and other components make up the rest. Natural sedimentary systems are complex but we have to consider the physical chemistry and fluid properties of small particle systems to understand how all the observed features are simply explained.

Quartz is not the main component of granitic or porphyritic rock (about 20%) but it is the simplest chemical compound and quartz veins are the most common of all mineral deposits.

When 'solubility' is defined as the dispersion of an anion and cation into the solvent, quartz is not soluble in water. Weathering processes, soil acids and stream transport leave the sand grains unchanged chemically but deposition in slightly alkaline sea water hydrolyses silica surfaces as shown in Figure 45.

Silica Hydrolysis

Silica gels therefore disperse in water to form three types of dispersion:

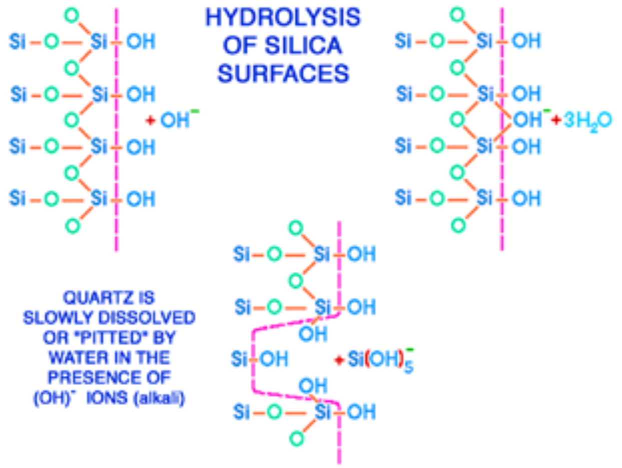


Figure 45. The dispersion of solid silica in water is catalysed by hydroxyl ions such as an alkali or base. Seawater is slightly alkaline and therefore silica (and most silicate) surfaces "dissolve" by these surface reactions. (Redrawn from Iler[8], 1979, fig. 1.11.)

i) simple monomeric complexes such as $Si(OH)_4$ aq.

ii) oligomers or polynuclear complexes such as $Si4O_6(OH)_6^{2-}$ which represent condensed chains of $Si(OH)_4$ tetrahedra.

iii) poly silicic acid where very long chains are produced with cross-linking to yield partly condensed three dimensional networks.

Basic Reaction for Silica Polymerisation

Figure 46. The basic reaction by which hydrated silica polymerises is divestment of water to form siloxane linkages.

HYDRATED SILICA – SI(OH)$_4$ – GROWS TO "LITTLE BALLS"

Monomeric silicic acid is a small non-ionic molecule that is dispersed at low concentration in seawater itself and at higher concentrations within the sea-floor mud. The growth of the polymeric particles depends on pH and salts present. Particles of silica gel form chains and particle structures because the charged particle surfaces interact with each other. The development of silica globules is indicated in Figure 47.

Chains and 'structures' of natural polymeric silicic acid are formed by interaction between the surface charges on the gel globules.

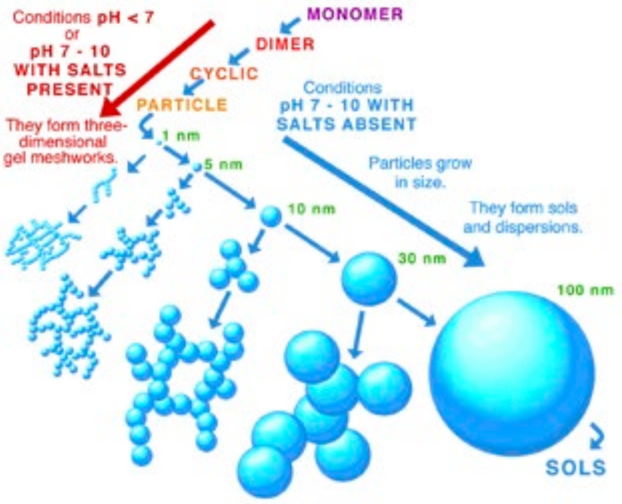


Figure 47. This diagrammatic representation of the growth of natural silica particles is re-drawn from Iler[8], 1979, p. 174.

Clay Hydrolysis

Clay hydrolysis begins in the weathering profile and continues within marine sediment accumulations. Clays are structured macromolecules with a wide variety represented in natural sediment accumulations. The example of simple three-layer clay in Figure 48 indicates the basic hydrolysis reaction. This equilibrium with clay minerals applies generally but if the material is sheared when fully hydrolysed metal hydroxide is released from the interlayers.

Clays, silica gel and hydrous ferromagnesian minerals are the main components of sediments that con-

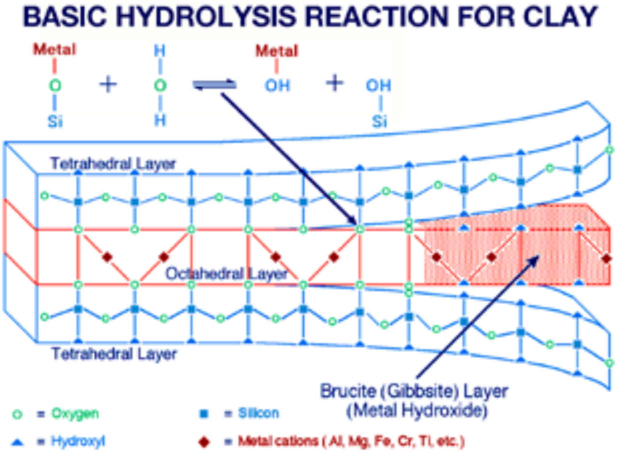


Figure 48. The external surfaces of natural clay platelets are fully hydrated. In the marine environment, further hydrolysis can therefore only progress inwardly from the edges of the platelets (within the octahedral layers).

solidate to rocks. The common hydrous ferromagnesian minerals are chlorite, chamosite and glauconite with lesser amounts of variably hydrated species like antigorite, phlogopite, talc, kaolinite, steatite, allophane, epidote, anthophyllite, greenalite, attapulgite, etc.

Characteristically, the ferromagnesian minerals are highly hydrated. They tend to retain the water of hydration and therefore maintain their mobility as gelatinous slimes and oozes until later in diagenesis and burial. They remain 'oily' during the accumulation of sediments in marine basins.

The 'sticky' gelatinous nature of marine mud is due to its content of clay and polymeric silica gel.

The Precursor Principle

It is a simple fact that mud, a heterogeneous macromolecular mixture of interacting high-energy hydrolysed particles is the material from which rocks and mineral deposits are formed. The properties of these precursor materials provide an understanding of the features and textures observed in the rocks and the way in which the various types of mineral deposits were formed.

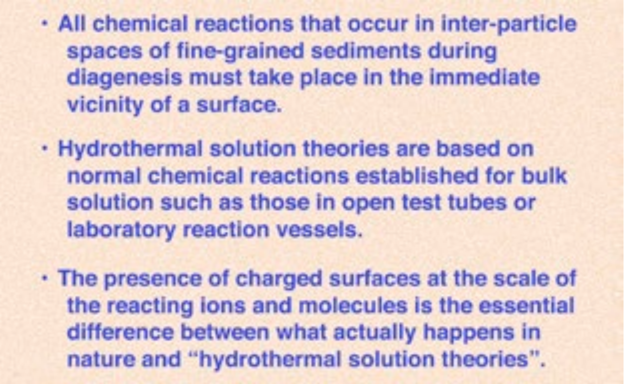
Normally gelatinous and then with various stages of increasing rigidity as chemical dehydration reactions increase and chemical bonds establish between particles, the main properties of sediment accumulations during diagenesis are: -

1) The fluid properties plasticity, liquefaction by shaking and rapid re-setting at low rates of shear (thixotropy and rheopexy). Bulk sediments can deform or become contorted plastically, liquefy by earthquake shock and rheopexy, accelerated re-setting at low rates of shear preserves the form and content of a liquefied sediment mass.
2) Separation of more fluid components (rheological separation) is the important mechanism whereby the content of more mobile components such as liquid silica gel, ferric hydroxide, clay, chlorite, etc. simply run out of disturbed sediments or an accumulated mineral mass. They form veins and intrusive bodies.
3) Diffusion and diffusion gradients. Ions and very small particles dispersed in pore fluids can diffuse in precursor sedimentary material. Precipitation on a nucleus or surface creates a diffusion gradient for more particles to diffuse to the precipitation point.
4) Accretion is the dynamic aggregation of particles of similar shape into a denser close packed cluster at net lower surface energy. Crystallisation of these pre-ordered aggregates subsequently occurs to form a 'porphyroblastic' or granitic textures.
5) Concretion is the slow or step–wise accumulation of material about a central nucleus to produce a banded–textured spherical or elliptical accumulation of higher particle density and compaction than the surrounding medium. The active process of concretion depends on colloidal particles individually diffusing towards the precipitating surface. Precipitation at this surface is a consequence of a marked change in electrolyte concentration that is produced within the denser gel nucleus. Orbicules form in pre-crystalline granite in this way.
6) Synerectic desorption. Within close packed particle aggregates such as accretions and concretions particles are drawn together by van der Waal's strong forces of attraction at very close interparticle separation. Total surface energy is lowered and internal surface and adsorptive capacity are reduced. Species adsorbed on surfaces are desorbed. Polar water molecules, ions, and smaller charged particles are exuded from the clusters into the matrix brines. This results in discharge to the pore fluid brines of exceedingly small metal hydroxide and hydroxy-sulphide particles
7) Critical cluster. As a precipitate begins to form initiation of the solid phase is achieved by chemical reaction between ions or molecules that would lead to the formation of a solid phase. Where the reacting substances are at low concentration or the reaction is controlled by diffusion rates, this leads to the formation of a critical cluster or nucleus that has special properties at the point where a liquid-solid interface is first formed. The extraordinarily high surface energy of such nascent nuclei or critical cluster of molecules is sufficient to dissociate water molecules. Hydrolysed critical clusters can diffuse through the finest openings

STUDY OF PRECURSOR SEDIMENTS NOW RESOLVES THE ORIGIN OF GRANITE AND MINERAL DEPOSITS

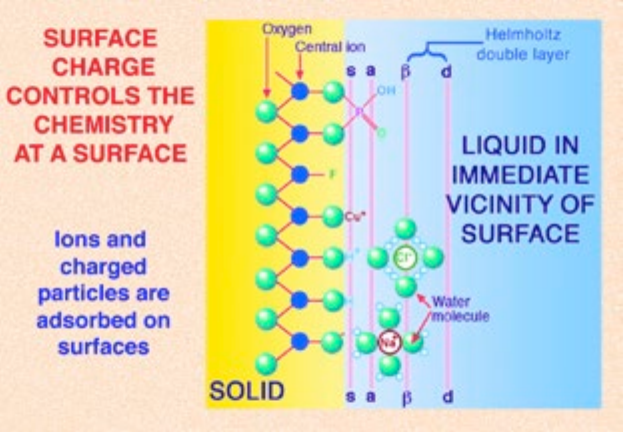
Figures 49 to 61 are selected from presentations at the CODES symposium at the University of Tasmania in 2007. The participants considered the topics under each heading and annotations and explanations draw attention to the photographs and diagrams in each figure. They were recognised as compelling evidence for the formation of accretions in flow-sheared sediment and their subsequent crystallisation to rock minerals.

Over 60,000,000 Square Meters of Surface Area in Every Cubic Meter of Natural Mud



- All chemical reactions that occur in inter-particle spaces of fine-grained sediments during diagenesis must take place in the immediate vicinity of a surface.
- Hydrothermal solution theories are based on normal chemical reactions established for bulk solution such as those in open test tubes or laboratory reaction vessels.
- The presence of charged surfaces at the scale of the reacting ions and molecules is the essential difference between what actually happens in nature and "hydrothermal solution theories".

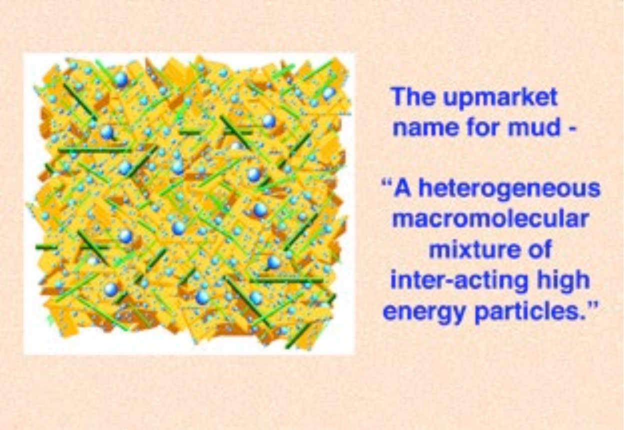
Figure 49. There is an essential difference between what happens in nature and historic geological theory.



SURFACE CHARGE CONTROLS THE CHEMISTRY AT A SURFACE

Ions and charged particles are adsorbed on surfaces

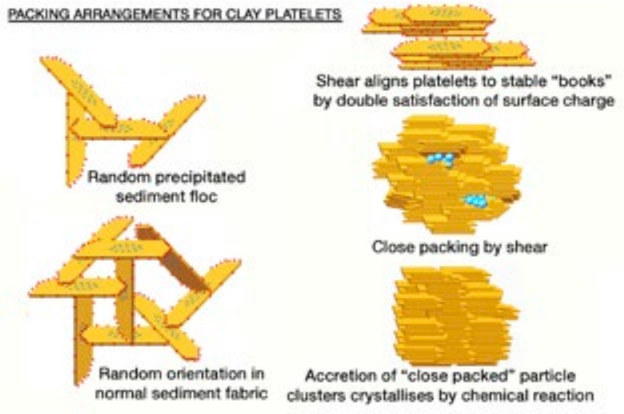
Figure 50.



The upmarket name for mud -

"A heterogeneous macromolecular mixture of inter-acting high energy particles."

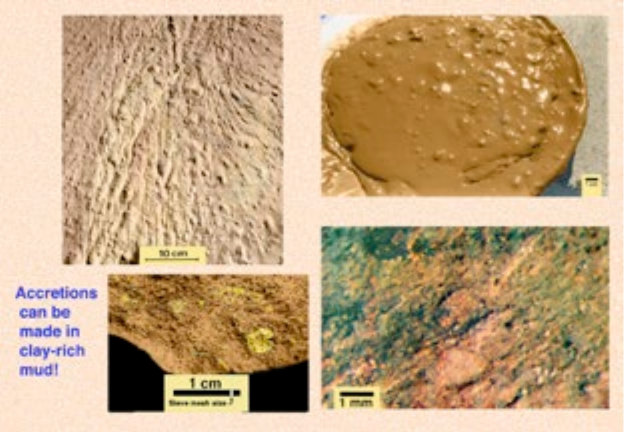
Figure 51.



PACKING ARRANGEMENTS FOR CLAY PLATELETS

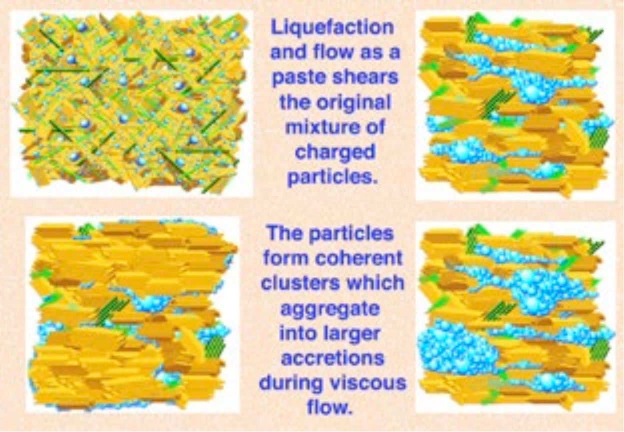
Figure 52.

Experimental Evidence for the Formation of Accretions



Accretions can be made in clay-rich mud!

Figure 53.

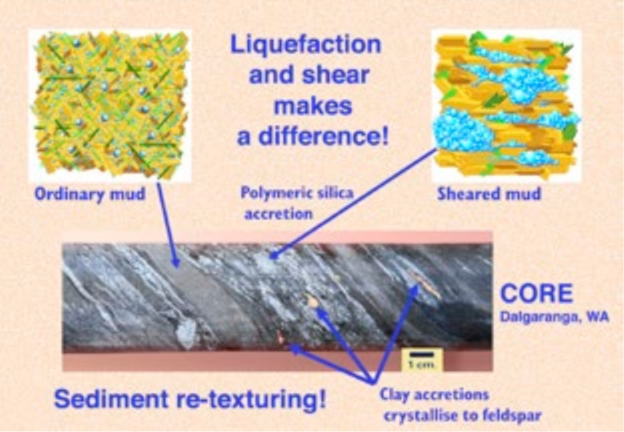


Liquefaction and flow as a paste shears the original mixture of charged particles.

The particles form coherent clusters which aggregate into larger accretions during viscous flow.

Figure 54.

Drill Core and Microscope Evidence for the Formation of Accretions



Liquefaction and shear makes a difference!

Ordinary mud

Polymeric silica accretion

Sheared mud

CORE

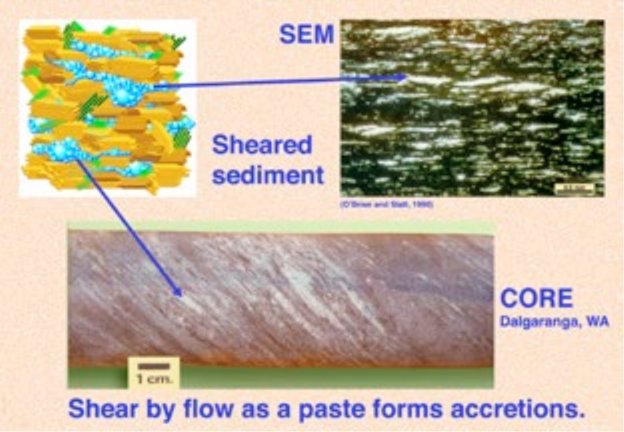
Dalgaranga, WA

1 cm.

Sediment re-texturing!

Clay accretions crystallise to feldspar

Figure 55.



SEM

Sheared sediment

(O'Brien and Slatt, 1990)

CORE

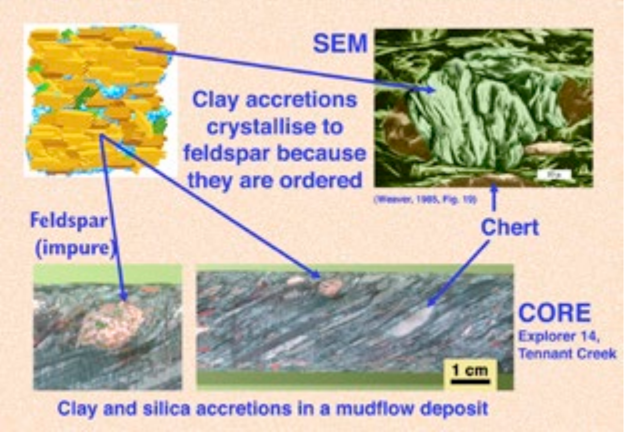
Dalgaranga, WA

1 cm.

Shear by flow as a paste forms accretions.

Figure 56.

The Formation of Accretions Is Clearly Related to Shear and Pasty Flow of Precursors



SEM

Clay accretions crystallise to feldspar because they are ordered

(Weaver, 1985, Fig. 19)

Chert

Feldspar (impure)

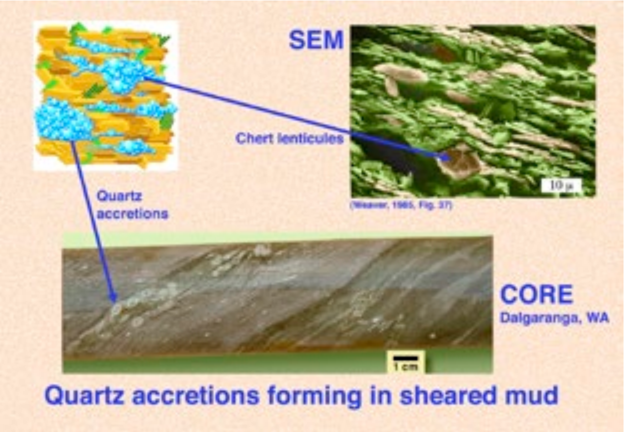
CORE

Explorer 14, Tennant Creek

1 cm

Clay and silica accretions in a mudflow deposit

Figure 57.



SEM

Chert lenticules

10 μ

(Weaver, 1985, Fig. 37)

Quartz accretions

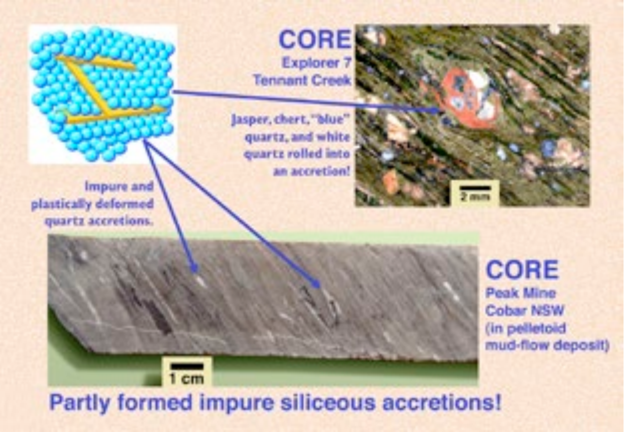
CORE

Dalgaranga, WA

1 cm

Quartz accretions forming in sheared mud

Figure 58.



CORE

Explorer 7

Tennant Creek

Jasper, chert, "blue" quartz, and white quartz rolled into an accretion!

2 mm

Impure and plastically deformed quartz accretions.

CORE

Peak Mine

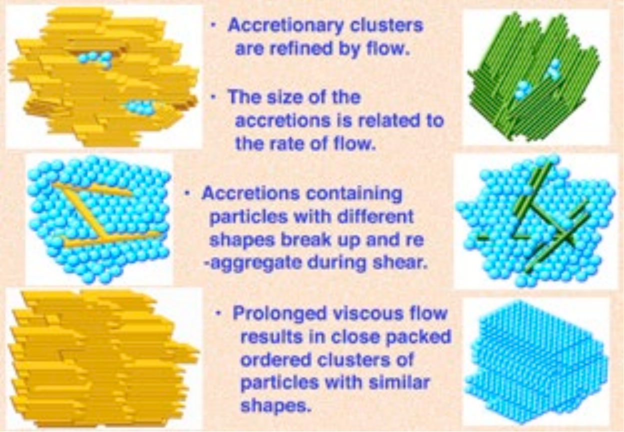
Cobar NSW

(in pelletoid mud-flow deposit)

1 cm

Partly formed impure siliceous accretions!

Figure 59.



- Accretionary clusters are refined by flow.
- The size of the accretions is related to the rate of flow.
- Accretions containing particles with different shapes break up and re-aggregate during shear.
- Prolonged viscous flow results in close packed ordered clusters of particles with similar shapes.

Figure 60.

In Principle the Precursors Crystallise to Porphyroid, Metamorphic and Granite Minerals

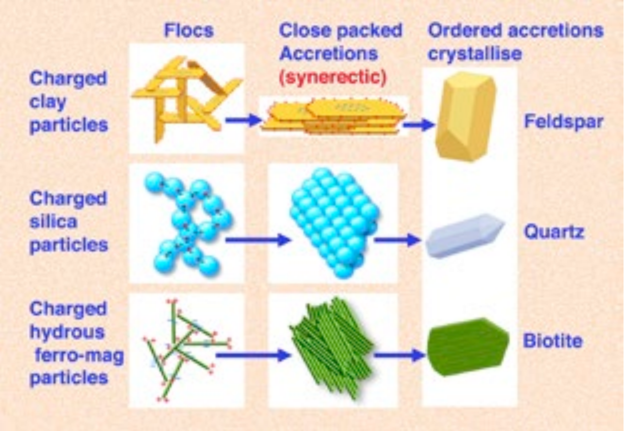


Figure 61.

RECOGNITION OF THE PRECURSOR PRINCIPLE

Wet chemically degraded sediment particles are the materials from which rocks and mineral deposits are formed. Recognition of the precursor principle means recognition of both the bulk behaviour of sediments at various stages of consolidation and details of the surface chemistry and physico-chemical properties of the trillions of particles.

These properties include cohesion and fractural nature, plasticity, liquefaction and re-setting (thixotropy and rheopexy), viscosity varying with the rate of shear (shear thinning), diffusion, adsorption and desorption of ions or charged particles on surfaces, concentric precipitation round a nucleus (concretion), particle aggregation to more ordered clusters (accretion), auto-shrinkage of particle clusters (syneresis), chains and structures of charged particles (long-range ordering), and enhancement of crystal growth.

Small particle systems may seem complex because natural sediment particles range in size from a few nanometres (molecular and macromolecular) to about 1,500 nanometres. Particle sizes vary over four orders of magnitude and although natural sediments are basically clays, polymeric silica and hydrous ferromagnesian minerals, there are many other components. Physical disturbance of accumulated sediments triggers chemical reactions and particle interactions and re-adjustment by diffusion of ions and small particles.

Recognition of the precursor principle now accounts for all the observations. Larger-scale folding, liquefaction and intrusion, rheological separation of the sediment components and details of observed textures such as porphyroids, granites, rapakivi texture, orbicules, concretions, syneresis crack patterns, framboids, myrmekites, oscillatory zoning, oolites, opal, ptygmatic veins, geodes, double enclave, palingenesis, etc. are all explained. Everything does fit neatly into one system.

Energy considerations and observations are explained in the treatise *"The Origin of Rocks and Mineral Deposits - using current physical chemistry of small particle systems."* However, the surface chemistry and particle interactions by which most ore deposits are formed needs some explanation.

Porphyroid Feldspars are Typically Rounded, Impure and contain Syneresis (Shrinkage) Crack Patterns

Figure 62. Recording clear observations resolved the problem of composite, plastically deformed, rimmed, "spongy", bent, broken, joined together again, rounded and apparent shrinkage crack patterns in the feldspars of the Tennant Creek porphyroids. Why do these feldspars have features so very different from their normal angular crystal habit? Why do they contain internal crack patterns? Logical deductions from hundreds of observations has provided answers and defined the origin of these rocks and the mineral deposits associated with them. These feldspars have crystallised from ordered but impure accretions of clay that formed when the sediments were mobilised.

Rounded Impure Quartz Accretions Occur in a Variety of Mobile Sediments

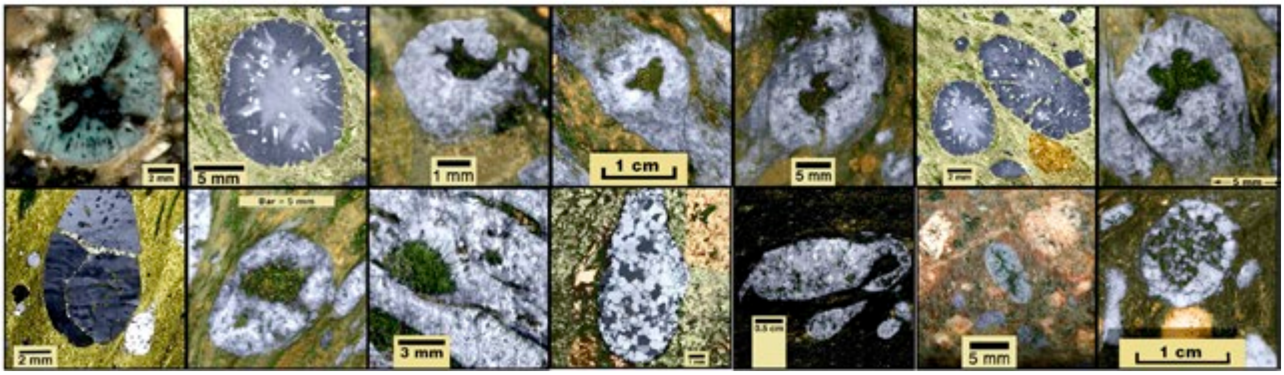
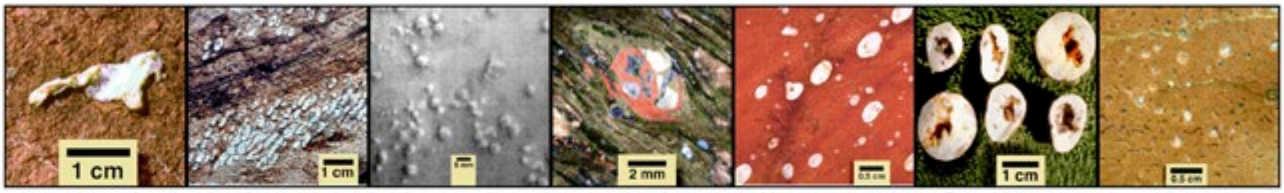
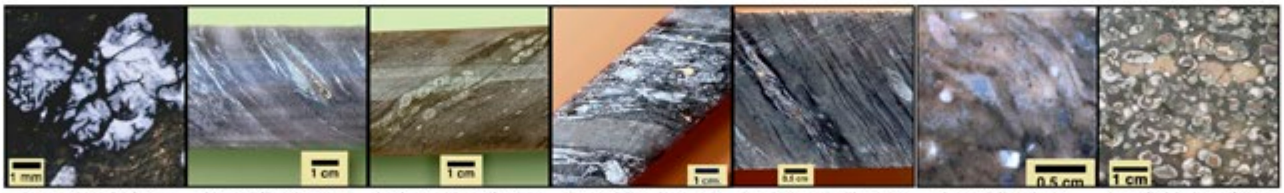


Figure 63. Polymeric silica accretions from Great Western porphyroid, Tennant Creek, have crystallised to quartz.



In sandstone from Westmoreland | In siliceous shale from North Wales | In laboratory silica gel from PFPC research. | In schist from Explorer 7, TC. | In Mammoth intrusive sandstone | From Mammoth intrusive sandstone | In mobile sandstone from Parkes, NSW.



Inporphyroid from Wagga Tank, NSW | In mobile sheared shale, Dalgaranga | Insheared sediment, Dalgaranga, WA. | In mobile sheared zone, Dalgaranga | In sheared siliceous shale, Cobar, NSW | In mobile chert. Explorer 7, TC. | In a fluid chert from Melaney, Qld.

Figure 64. Fourteen examples of silica accretions developed in other locations and contexts are illustrated.

Trace Metals Are Very Sparsely Dispersed in the Soils, Streams and Sediments

The metal ions are transported in stream and ground water systems as ionic species (Figure 65) until they are adsorbed on clays or other sediment substrates (adsorptive surfaces) such as organic materials, metal hydroxides, etc. as in Figure 66. Stream and river waters 'lose' their trace metal ions particularly di- and trivalent heavy metal ions, to the muddy water (particulate species suspended in the stream water).

Mobility and Close Packing Is Required to Release Trace Metals

The systematic search for new orebodies begins with recognition of an ore-forming environment. This was proven successful at Tennant Creek, Parkes, and Kakadu and shown to apply at Cobar, Stuart Shelf, Tanami, Mt. Hope, NW Queensland, and western Tasmania.

Aerial geophysical survey and regional geology can be used to focus on most prospective areas for a portfolio of anomalies to be investigated. The strength and nature of the magnetic, gravity, seismic, radiometric, hydrothermal alteration, and geochemical anomalies give some indication of their possible importance but their relation to the underlying geology and particularly to any indication of synerectic porphyroids is of paramount importance in selecting priorities for drilling.

Favourable source rocks are not necessarily those that have the largest accretions. Trace metal content and nature of the original sediment are important. Repeated mobilisation and re-texturing should not have progressed too far towards completely crystalline granite.

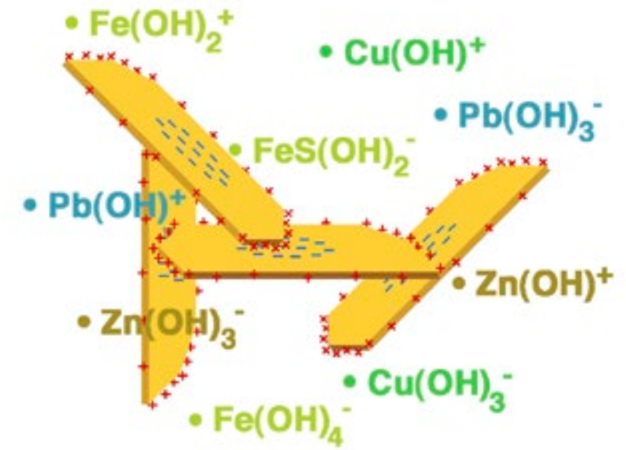


Figure 65. Trace metals are dissolved and leached from soils and rocks by weathering processes. This diagram illustrates a dispersion of hydrolysed metal ions with a simple clay floc but many different particles and surfaces adsorb metal ions from stream water.

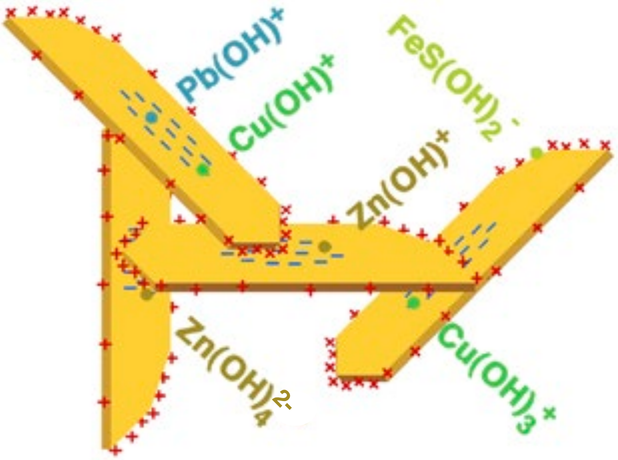
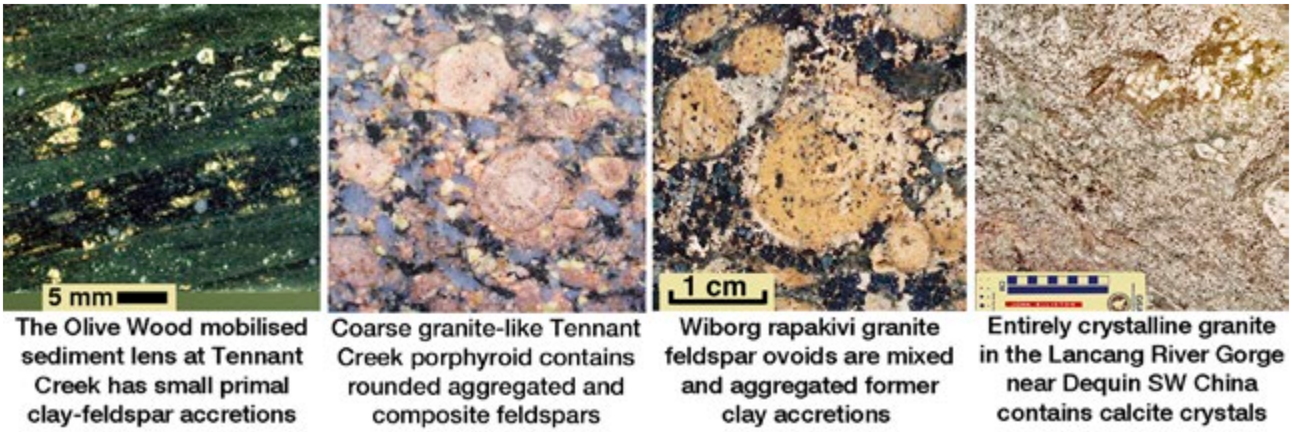


Figure 66. Metal ions hydrolyse or form complexes with water in solution. Charged ions and complexes are removed from solution by adsorption on sediment substrates such as clays, amorphous silica, and organic matter.



The Olive Wood mobilised sediment lens at Tennant Creek has small primal clay-feldspar accretions

Coarse granite-like Tennant Creek porphyroid contains rounded aggregated and composite feldspars

Wiborg rapakivi granite feldspar ovoids are mixed and aggregated former clay accretions

Entirely crystalline granite in the Lancang River Gorge near Dequin SW China contains calcite crystals

Figure 67. Sediments re-textured by former mobility grade from primitive small clay-quartz porphyroids to crystalline granite.

Figure 67 illustrates a gradation of porphyritic textures from primitive clay-feldspar accretions to crystalline granite. Coarse porphyroids are the most prospective source rocks but crystallisation of granite can result in concentrating some rare earths, tin, molybdenum, lithium, beryllium, etc.

Recent detailed seismic and gravity surveys at north Parkes, NSW, have shown that the several large low-grade near vertical copper-gold pipe-like ore bodies being mined were formed in a similar multiple porphyry intrusion environment to that revealed by the Rio Grande survey in the Gulf of Mexico illustrated in Figure 68.

The Cadia deposits near Orange could be similar and the limited data at Wagga Tank near Mt. Hope is also indicative of a similar environment.

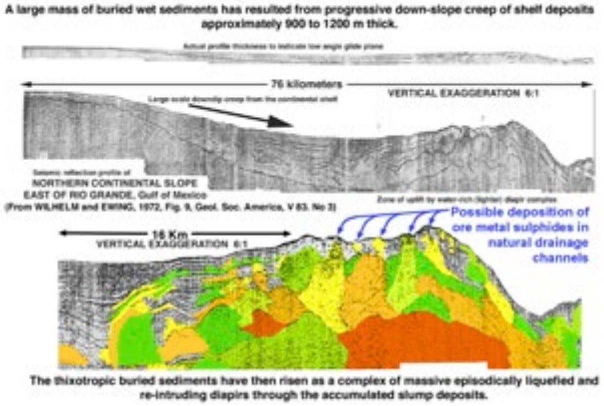


Figure 68. Many rock formations contain porphyroid complexes and granite batholiths formed by a succession of intrusions. Synerectic porphyroids in the rocks are prospective ore source rocks.

Obvious Syneresis Cracks in Feldspars Indicate a Favourable Environment for Ore

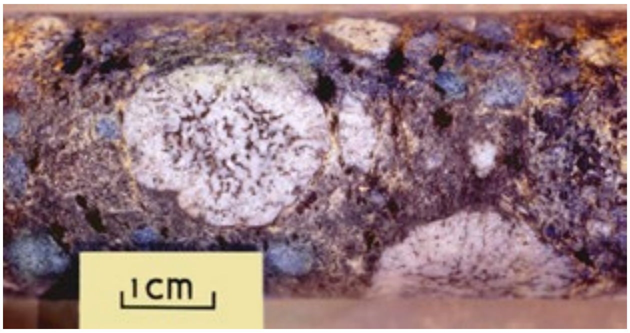


Figure 69. Syneresis shrinkage patterns in Tennant Creek coarse porphyroids have associated orebodies.

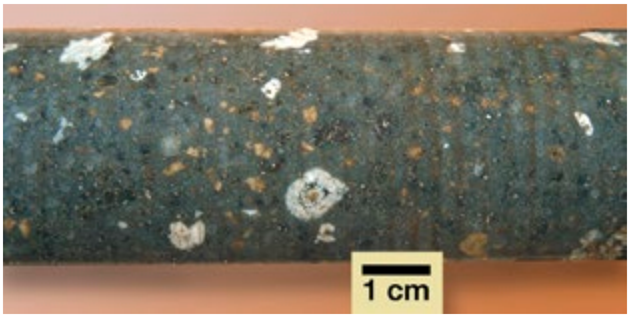


Figure 70. Syneresis shrinkage in coarse porphyroid from Wagga Tank, NSW, may indicate associated ore.

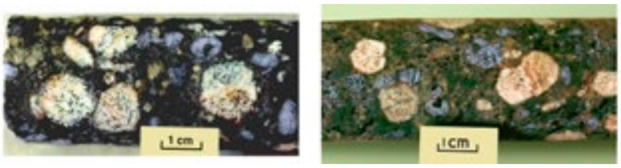


Figure 71. Syneresis shrinkage crack patterns from the precursor clay accretions are preserved in the feldspars of the Great Western porphyroid at Tennant Creek. Figure 69. Syneresis shrinkage patterns in Tennant Creek coarse porphyroids have associated orebodies.

The Physico-Chemical Mechanisms for the Formation of Sulphide Ore

In ordinary basin sediments, the ore-forming base metals and gold are sparsely distributed. Typical ore metals like zinc have a concentration about 110 parts per million, copper is usually dispersed at 60 to 70 ppm, and lead occurs at only some 18 ppm. These divalent ions are spread sparsely at isolated and separate adsorption sites over the very large sediment grain and particle surfaces available to them.

All the surface adsorbed metallic species are exposed to HS^-, which reacts readily with the hydrolysed and adsorbed ions of the heavy metals and iron.

The exposure to sulphidation when diagenetic conditions change to anoxic brings about a great simplification. A wide range of hydrous and surface adsorbed complex metal species are the potential reactants with sulphide ions, but the base metal ions and complexes all form sulphides.

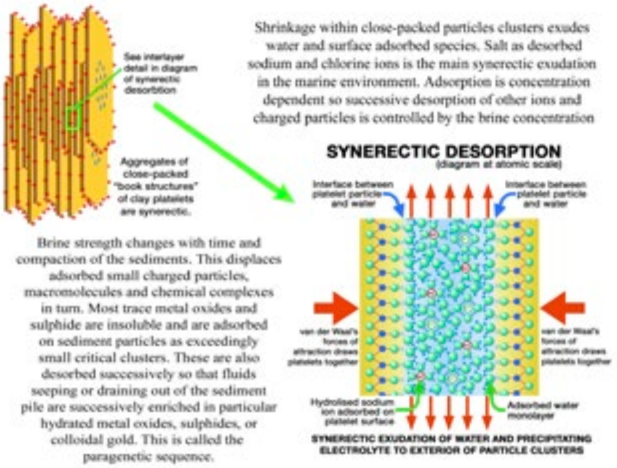
The powerful chemical reaction converts metal ions adsorbed on sediment particles:

$$Me^{2+} + HS^- \rightarrow MeS + H^+$$

This predominates over the many hydrolysing reactions and surface hydration interactions. In the reducing environment, the metal distribution is controlled by this formation of insoluble sulphides. From mobilised sediments containing accretions syneresis and exudation of fluids results in seepage of extremely dilute insoluble metal sulphide molecules dispersed in pore fluid until the insoluble metal sulphide or oxide molecules can coalesce to establish an interface between and liquid and solid to form a particle with sufficiently energy to dissociate water molecules. Precipitation is initiated by:

$$j\ MeS + (2j+2)\ H_2O \rightarrow [(MeS)_j{\bullet}(OH)_2{\bullet}2jH_2O_{ads}]^{2-} + 2\ H^+$$

where j is the unknown number of molecules required to form a critical cluster.



Shrinkage within close-packed particles clusters exudes water and surface adsorbed species. Salt as desorbed sodium and chlorine ions is the main synerectic exudation in the marine environment. Adsorption is concentration dependent so successive desorption of other ions and charged particles is controlled by the brine concentration

Brine strength changes with time and compaction of the sediments. This displaces adsorbed small charged particles, macromolecules and chemical complexes in turn. Most trace metal oxides and sulphide are insoluble and are adsorbed on sediment particles as exceedingly small critical clusters. These are also desorbed successively so that fluids seeping or draining out of the sediment pile are successively enriched in particular hydrated metal oxides, sulphides, or colloidal gold. This is called the paragenetic sequence.

Figure 72. Shrinkage within close-packed clusters of sediment component such as clay accretions exudes water and surface adsorbed minute hydrated sulphide or oxide particles called critical clusters. These are desorbed into the fluid phase and are small enough (8 to 15 Angstroms) to diffuse out through very small sediment pores. Salt is desorbed as sodium and chlorine ions and it is the main component of fluid exudation from marine sediments. Adsorption of other species is controlled by the brine concentration. Adsorption is dependent on concentration and small charged particles cannot compete for adsorption sites at high concentration of Na^+ or Cl^-.

Where volumes of sediment have been re-textured (converted to close-packed accretions) the exudation of insoluble trace metal sulphides and oxides is spontaneous as indicated in Figure 72.

Mobility Followed by Close-Packing of Particles Is Required to Release Trace Metals to the Fluid Phase

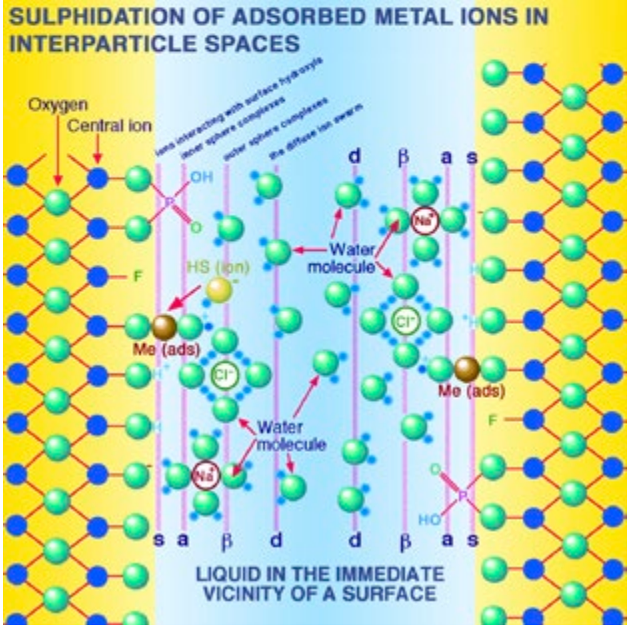


Figure 73. Metal sulphides are formed "molecule by molecule" as soon as buried sediments encounter hydrogen sulphide generated by the bacterial reduction of sulphates. In tidal flats and mangrove swamps reducing conditions (sulphidic) occur a few centimetres below the sediment-water interface but basin sediments generally are anoxic from a few meters below the sea floor.

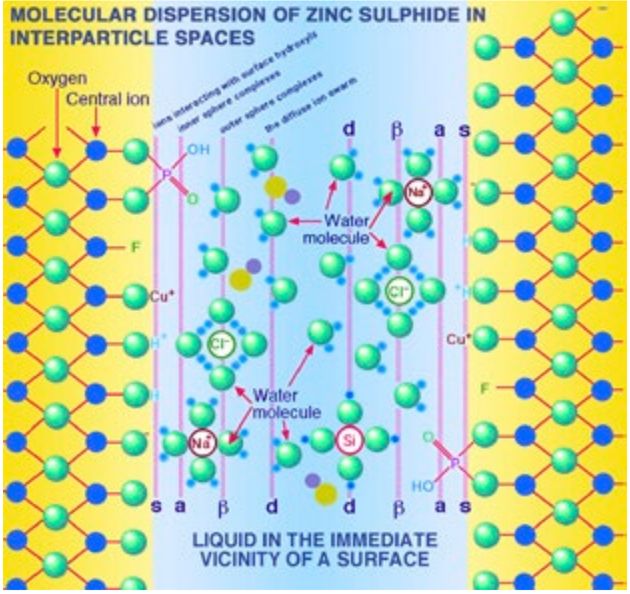


Figure 74. The chemical reaction between hydrogen sulphide ions in pore fluids and trace metal ions adsorbed on sediment particle surfaces "liberates" metal sulphide molecules into the fluid phase. Diffusion controls the rate at which the exceedingly dilute dispersion of molecular zinc sulphide species (represented as tan and blue-grey dots) can begin to nucleate to the solid phase. Nucleation of a critical cluster develops as a particle at maximum surface energy. This dissociates water and combines with it chemically (chemisorbs) to form a hydroxy-sulphide.

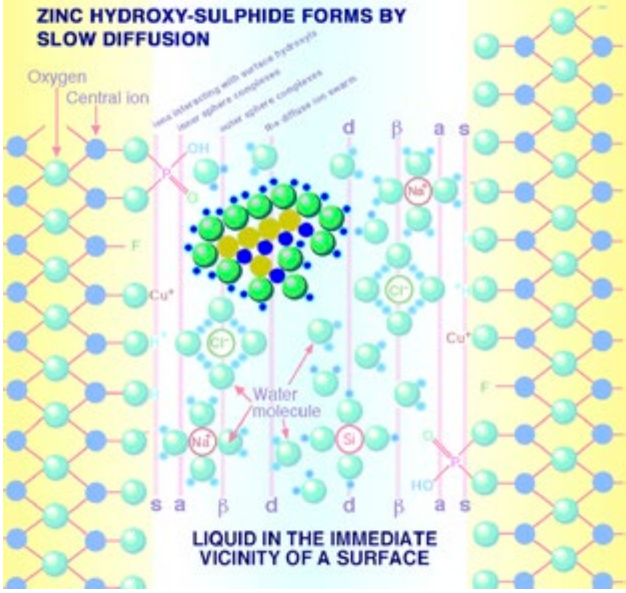


Figure 75. The initial solid phase of zinc sulphide precipitate is too small to be seen by SEM. In this diagram it is depicted as a hydrated nucleus surrounded by adsorbed water molecules. The oxygen atoms in this surface water are two hydrogen atoms short of those required to hydrate the cluster entirely with water molecules. The actual atomic geometry and hydration of a molecular cluster of this nature is quite difficult to determine and it is probably variable. It is quite important that some of the water molecules are dissociated. Hydroxyl groups have reacted with some or all of the high-energy lattice sites.

Stages of Fluid Release Are Related to Pore Fluid, Surface Adsorbed Water and Chemically Combined Water

Stages of fluid release from compacting sediments are related to interparticle water, surface adsorbed water and water resulting from exothermic chemical reactions by which they crystallise.

Without mobilisation and formation of accretions trace metal species are not concentrated.

Where significant volumes of sediment have been liquefied, desorption due to spontaneous synerectic shrinkage releases exceedingly small particles of trace metal sulphides and oxides to form veins and accumulate as mineral deposits.

Repeated mobilisation results in granite formation with higher temperatures from the exothermic chemical reactions by which the high-energy particulate matter (hydrolysed clay, polymeric silica, etc.) crystallises.

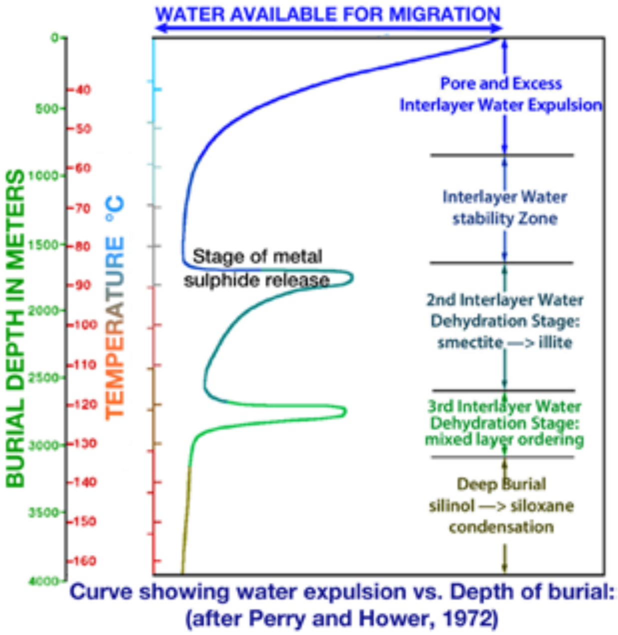


Figure 76: Some 3 tons of water must seep out of sediments for every ton of rock formed by their long slow compaction and crystallisation (Ref. 16).

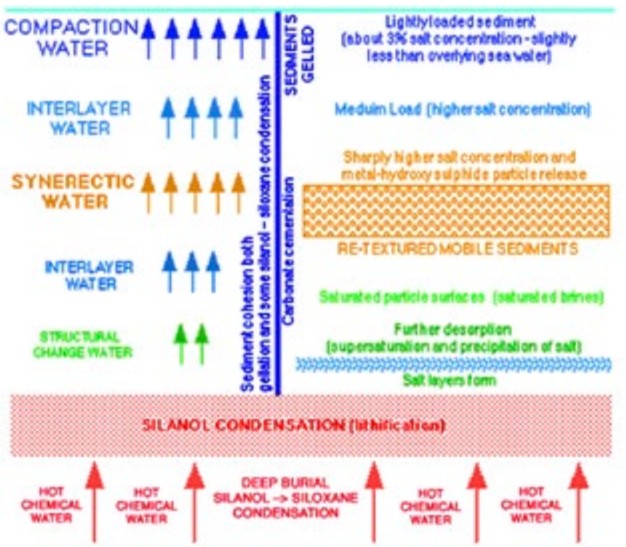


Figure 77. Sediment mobility and porphyroid formation increases adsorbed water release and leads to repeated mobilisation and granite formation.

General Diagram Representing Orebody Formation from Porphyroidal Source Rocks into Overlying Sediment Layers

Figure 78 is a diagram to represent a general sediment "plumbing system" whereby the trace metal hydrated sulphide particles are released from the condensing

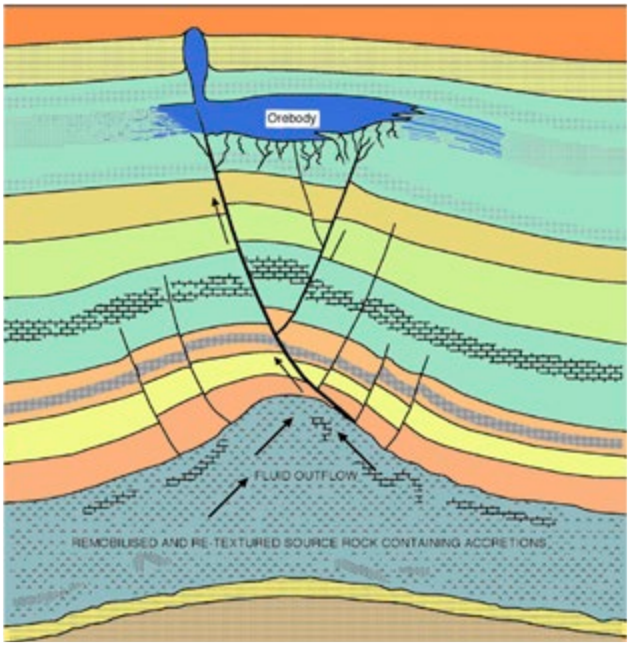


Figure 78. Diagram to indicate possible seepage paths for ore forming fluids from underlying source rocks.

accretions in re-textured source rock to flow out with the warm brines into favourable structures or host horizons.

Exceedingly small critical clusters of trace metal sulphides can pass through the finest openings to “sneak through the cracks” and form the various types of mineral deposits. They are metastable in suspension and the precipitated sulphides attract more particles to surfaces. Colloidal particles dispersed in the pore fluids are coagulated at the interface between fluid dispersion and gelatinous precipitate (particles linked to each other by satisfaction of surface charges). The gelatinous aggregate of successive layers of precipitate (colloform or concretionary texture) becomes synerectic.

Synerectic shrinkage exudes electrolyte from the accumulated layers to the interface. Continued precipitation creates a diffusion gradient by which the successive layers of the ore mineral precursors are built up.

Earlier and more diffuse upward seepage gives rise to stratiform deposits, but bedded, massive, disseminated, vein associated, and re-mobilised ores all have a similar genesis.

ACKNOWLEDGEMENTS

Permission from Connor Court Publications Pty Ltd to publish this summary and to include extracts and figures from the book is gratefully acknowledged. The first eight pages of this paper contain photographs of outstanding scientists and leaders of the successful Geopeko Limited mineral exploration team. Permission from those still living to publish their photographs is also gratefully acknowledged. The author is appreciative and thankful for AusIndustry monitoring of this research since 1984 and for the thorough scrutiny and analysis that certified compliance with the scientific method in 2006.

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REVOLUTIONARY NEW PUBLICATION

This outstanding publication is the result of inspired new fundamental research done in the field and in the laboratory by the author and a world leader in colloid science. Systematic use of the scientific method has established a new and complete understanding of how rocks and mineral deposits are formed.

The application of this understanding resulted in the discovery in Australia of 9 new mines containing 33 orebodies in a 15-year period. An independently commissioned consultants report (McKinsey & Company, Inc New York, 1975) demonstrated this dramatic improvement (+300%) in cost effectiveness of the mineral exploration programs when this revolutionary new understanding of ore forming processes was applied.

Teachers of geology and exploration geologists can now benefit from these new concepts. All involved need to understand the changes so that the principles established by this research can be adopted. This significant development and the new knowledge are paramount to advancing the Earth sciences.

In 1998 a research team at the Particulate Fluid Processing Centre at the University of Melbourne led by Professor T. W. Healy measured the forces between colloidal particles with an adapted atomic force microscope. This has confirmed the new fundamental understanding of the behaviour of surface charged sediment particles. It substantiates the research of John Elliston and his team of exploration geologists and their advisors.

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> ***"We are blinded by what we think we know;***
> ***disbelieve*** (your present convictions) ***if you can."***
>
> **The late Professor Samuel Warren Carey,**
> **1911 - 2002, University of Tasmania.**

BASIS OF THE RESEARCH

There is nothing more fundamental to our understanding of the way that rocks and orebodies were formed than the physical and chemical properties of the materials from which they were derived. This research has assumed that the properties of ancient sediments before lithification had the same properties that have now been confirmed by experiment and observations relating to natural basin sediments as we find them today. This has not been questioned and the conclusion that ancient sediment accumulations did have the same rheological and colloidal properties as the massive high-energy particle systems of today is simple and logical.

Oceanographic surveys, oil drilling, and the data from recent seismic reflection profiles have identified the turbidity current deposits, large-scale continental shelf failures, and massive updoming and diapirs in the shelf deposits and sedimentary basins of today. The geological record shows there were similar mass flow units and updomings in the older sediments that are now rocks.

Ancient sediments must have been hydrolysed and also contained the same extraordinarily large internal surface areas as those of today. Details of the structures and textures preserved in the rocks clearly show that the rheology and behaviour of the charged particles in ancient sedimentary components was in accord with the principles now established in colloid science.

This book illustrates these details. It simply points out that geologists with some knowledge of colloid and surface chemistry can identify inorganic structures and textures preserved in rocks derived directly or by diagenetic processes from ancient sedimentary materials. Geologists with some knowledge of biology are able to identify organic fossils preserved in ancient sediments in the same way. We are now also able to understand the inorganic textures and structures.

Formations and rock types from which dispersed ore minerals were concentrated to form orebodies can now be distinguished from those in which the trace metals remain dispersed. The shape, size, continuity and grade of different mineral deposits is much easier to assess if the ore forming processes are understood.

"If you get the basics right the rest will follow!"

Professor Barry Ninham,
Australian National University

THE RESEARCH ACHIEVEMENT

Geological processes by which mineral deposits are formed have been revealed by a series of industrial research projects based on work confirmed by recent achievements of an Australian Commonwealth Special Research Centre. The research has been applied by geologists to the extent that one of the major mining groups involved recorded one of the most successful periods of mine finding in Australia's history. The work has been extended to establish that the basic principles are relevant to all geological environments and mineral deposits generally. More effective development of mineral resources is of national importance. The confidential aspects of the research no longer apply and the new findings are now published and generally available.

The research introduces an exciting new alternative to traditional thinking in the Earth Sciences. It confirms that natural fine-grained particle systems behave in accordance with principles established in colloid and surface chemistry. This must therefore include diagenetic processes in ancient and modern natural sediment accumulations.

Liquefaction or shear in pasty flow of wet sediment pastes allows colloidal particles in natural sediments to re-arrange themselves into aggregates so that surface energy is reduced. These denser particle clusters are synerectic and subsequently liberate colloidal ore metal sulphide suspensions into brines as they condense. Rock masses are heated by chemical dehydration reactions as the particle aggregates finally crystallise.

This significant development and the new knowledge are paramount to advancing the Earth sciences.

J. N. Elliston, AM

OVERVIEW

T. W. Healy, AO

The scientific method seeks to explain natural phenomena using natural laws, verifiable and reproducible observations and measurements that validate logical conclusions.

Two outstandingly successful Australian research projects based on correct use of the scientific method have resulted in this interdisciplinary research that introduces significant new knowledge. The application of colloid science in this book has embraced the geological sciences in a coherent and compelling way.

In 1998 Professor T. W. Healy led a team of Particulate Fluids Processing Centre researchers at the University of Melbourne. They were successful in adapting an atomic force microscope to measure forces between colloidal particles due to their surface charge.

This substantiates the research of John Elliston's team of exploration geologists and their advisors. From the 1960's they have claimed that natural sediments are immense accumulations of high-energy particles containing colloids (particles 1 to 1,500 nanometers in size). When they are mobilised by earthquake shocks for example, these can achieve a more stable condition by aggregating to close-packed clusters. Heat is generated by chemical reactions when the particle clusters finally crystallise to metamorphic, porphyroidal or granitic rocks.

This fundamental research now resolves many long standing problems in the Earth sciences. The new understanding of the formation of mineral deposits has demonstrated much more efficient and cost effective mineral exploration. Application of these two innovative research achievements will certainly benefit economic development.

Carey, 1996, p.26 recognised this new knowledge, "years of intensive world-wide study of porphyroids, orbicules, and rapakivi granites demonstrated how these developed through colloidal processes". This new geological theory "has the same importance to that subject as Darwin's to biology" (Ninham and Nostro, 2010, p. 72).

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This project is proudly supported by

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Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Research Article

Conservation of Paleontological Finds: the Restoration Materials of the “Problematica Verrucana”

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OPEN ACCESS

Citation: L. Colli, A. Salvini, E. Pecchioni, S. Cencetti (2017) Conservation of Paleontological Finds: the Restoration Materials of the “Problematica Verrucana”. *Substantia* 1(2): 63-73. doi: 10.13128/substantia-27

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The authors declared that no competing interests exist.

Abstract. The materials used in the historical restoration of a fossil collection named “Problematica Verrucana”, have been studied in order to contribute to the creation of a catalogue of restoration materials used in the past. Due to the complexity of the mixtures used with different purposes to restore fossil finds, an extractive technique has been employed in order to separate the compounds soluble in solvents with different polarities. Using this procedure several components, even when found in small amounts, have been identified. The chemical composition of the organic and inorganic compounds used in the restoration material has been determined using extractive procedure, FT-IR and ^{1}H-NMR spectroscopies. A preliminary macroscopic characterisation and mineralogical and petrographical analyses have also been performed on the inorganic filling materials found in several samples. The different compositions of various materials used in the restoration of this fossil collection might be related to the particular conservative and esthetic functions of the product applied on the find.

Keywords. Fossil collection, restoration materials, petrographical analyses, spectroscopic analyses, paleontological museum.

1. INTRODUCTION

Paleontological museums usually preserve recently acquired finds beside ancient and historical collections, where some fossils could have suffered from serious alteration processes due to prolonged storage in depositories and warehouses, while other fossils could have been “restored” during the centuries.[1,7] Furthermore, in order to be conserved into a museum, naturalistic finds need to undergo a specific process, called *preparation*. In the past, the *preparation* and restoration of damaged pieces were generally made by the paleontologists themselves, often in an empirical and artisanal way[3,8] with materials and procedures which have rarely been documented.

The *Natural History Museum* of Florence hosts a fossil collection named *Fucini Collection* or "Problematica Verrucana". This collection is composed of fossil tracks and fossil seaweeds found by Alberto Fucini, geologist and paleontologist of the University of Florence, on the Monti Pisani during the first decades of '900[9]. The peculiar feature of this collection consists in the fact that the majority of finds show signs of historical restoration, probably performed by Fucini himself, perhaps with the aim of facilitating the study of the finds. Unfortunately, no documentation about the products applied during these interventions is conserved at the *Natural History Museum*.

The aim of this research was to identify the materials used for the historical restoration of this collection. With this purpose, several samples recovered from restoration materials were studied by means of chemical and mineralogical analyses.

2. MATERIALS

2.1 The Finds

The *Fucini Collection*, or "Problematica Verrucana", is made up of more than one thousand pieces; the samples for this study were taken from 17 finds, as described in Table 1, with the aim of identifying different kinds of materials.

This collection is composed for the most part of fossil imprints or marks that animals have left in their habitat in the past. The comparison between the *Problematica Verrucana* tracks and those of several tetrapods has not been completed yet[10-13]. Actually the majority of finds have been identified as either impress or reverse marks (the relief of the impress in the specular portion of the sediment) of small dinosaurs. Besides, marks of vegetal rests are also conserved in the Fucini Collection, principally seaweeds like *Sewardiella* e *Gothaniella* (Figure 1).

The term "*Problematica*" refers to the difficult interpretation of the type of traces left behind, while the adjective "*Verrucana*" derives from the term *Monte Verruca* (in the *Monti Pisani* between *Pisa* and *Lucca* - Italy), as does the term *Verrucano*, a geologic period con-

Table 1. Finds and samples.

Find name	IGF[a]	Type of find	Sampling zone	Sample
Gothaniella sphenophylloides Fucinii, forma piumosa	10351	fossil seaweed	junction	Sample 1
Chondrites Fucillatus	10368	print of a prehistoric reptile	junction and back	Sample 2
Thecodontiehnus verrucae	5152	hand-print of a small carnivorous reptile	lateral part	Sample 3
Sewardiella Verrucana	10323	fossil seaweed	lateral, right, part	Sample 4
Sewardiella Verrucana Fucinii, forma multiradiata	10298	fossil seaweed	superior part	Sample 5
Sewardiella Verrucana Fucinii	10301	fossil seaweed	front and lower part	Sample 7
Undefined find	516T	undefined track	back	Sample 8
Undefined find	748T	undefined track	back	Sample 9
Sewardiella Verrucana Fucinii	10302	mold of fossil seaweed	back	Sample 10
Sewardiella Verrucana Fucinii, forma fasciculosa	10315	mold of fossil seaweed	lateral, left, part	Sample 11
Undefined find	692T	undefined track	back	Sample 12
Sewardiella Verrucana Fucinii, forma rotata	10299	mold of fossil seaweed	lateral, left, part	Sample 13
Thecodontiehnus Fucinii v. Huene	5149	hand-print and foot-print of a reptile similar to varan	back, lower part	Sample 17
Undefined find	*not catalogued*	-	back	Sample 18
Rhinocecephalichnus	5195	hand-print and foot-print of a reptile	lower part	Sample19
Sewardiella Verrucana Fucinii, forma lateradiata	10292	fossil seaweed	lower part	Sample 20
Undefined find	348T	undefined track	back	Sample 21

[a]IGF Catalog number of Natural History Museum

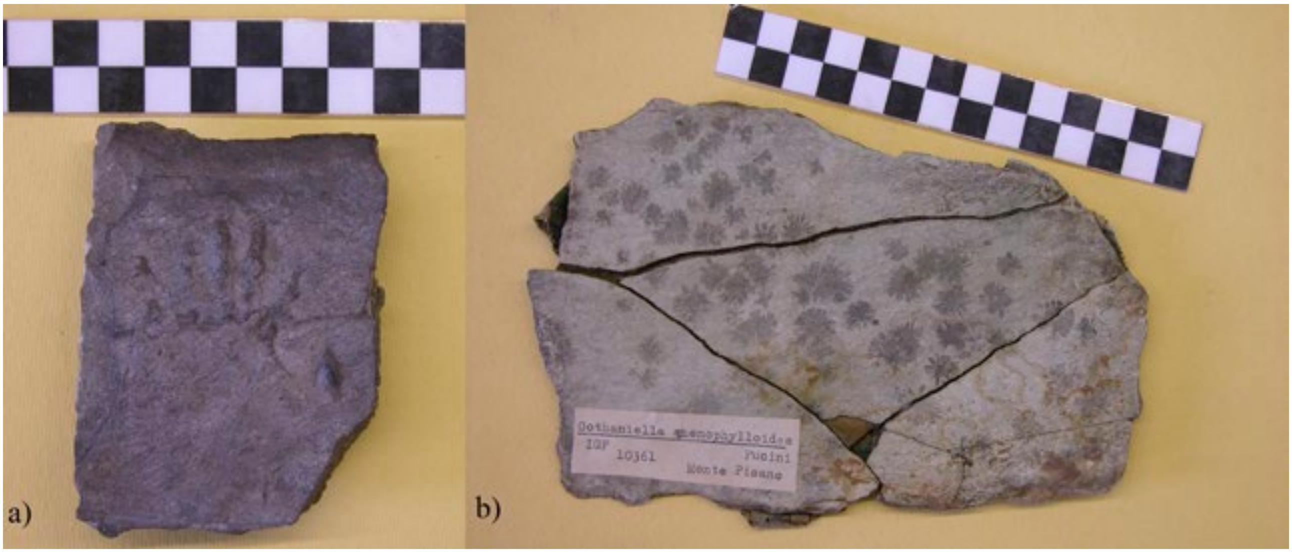


Figure 1. Examples of animal and vegetal finds of Fucini Collection: find IGF 5152, a) hand-print of a small carnivorous reptile: The codontiehnus verrucae; b) IGF 1036, a fossil seaweed: Gothaniella sphenophylloides Fucini.

sidered as a synonym of *Permiano*, which characterises the relevant area.

2.2 Description and Function of Restoration Products

According to their macroscopic aspect and main functionality, the restoration materials used in the Fucini Collection can be divided in four classes, each one containing different kinds of products. Products belonging to the same class may vary in colour or aspect of the aggregate. Sometimes several pieces of the same materials were sampled, for example when a product was apparently used for different functions (Table 2) (Figure 2).

Class A: light-yellow substances with or without aggregate used as adhesive to reconnect separated parts of finds. Materials belonging to this class can be divided in three different categories, all containing an adhesive material, either used alone (Product A), mixed with aggregates having smaller grains (Product B) or larger grains (Product C). Product A is a yellow-orange amber, transparent and hard material. Products B and C are similar to Product A. Product B is used to attach broken parts of medium-dimension finds; it is applied alone or with paper or fabric. Product C is used for pieces of medium and big dimensions. It is rarely used with paper or fabric.

Class B: hard materials used for junctions and for moulds, which appear of two colours (green or gray). The difference between these two products, classified as Product H and Product G, is macroscopically limited to the colour. The two products appear like hard and porous mixtures, of light green or gray colour, and of crumbly aspect. The presence of some drops suggests that the product has been applied in a liquid state. The same product has been sampled in finds in which it worked as adhesive, and in moulds. The gray material has been defined “sulphor” by Fucini [9]. These materials have been used to lend adhesion to broken pieces and to make moulds.

Class C: gummy pastes used for support purposes. These materials appear as rubbery adhesive pastes probably used for integrations (especially Product E) or to create a layer in the back of the finds. Product E appears as a partially hardened rubber. The colour is brown. It was probably used for integrations. Product F appears like a completely hardened rubber. It appears in the form of small, quite flat, cushions. The shape suggests that the product was applied with the pressure of the fingers. It is found only in the back of the finds: it looks as if it was used to create a support base for photographic sessions.

Class D: filling materials of various colours. They are five materials which appear as inorganic products used to assemble broken pieces or to reconstruct lacking parts. Product K is of dark grey colour and it is hard to the touch. Product L and Product M have similar aspects, they are hard and compact, but they have different pigmentations (the first one has a grey colour, the second is brownish-red). Product N is dusty and friable and of brownish-orange colour; it seems hard, but it is not compact, it appears fragile and dusty. Product O

Table 2. Description of the samples: class, product and number of finds.

Sample	Class	Product	Description
Sample 1	Class A	Product A	Light-yellow, hard and poorly compact product, present in 76 finds
Sample 2			
Sample 3		Product B	Light-yellow, hard and quite compact product, present in 169 finds
Sample 4			
Sample 5		Product C	Light-yellow, hard and very compact product, used only for big pieces, present in 8 finds
Sample 9	Class B	Product G	Hard and glassy mixture of grey color, present in 11 finds
Sample 10			
Sample 11			
Sample 12		Product H	Hard and glassy mixture of green color, present in 20 finds
Sample 13			
Sample 7	Class C	Product E	Gummy product of brown color, present in 7 finds
Sample 8		Product F	Gummy product of black color, present in 10 finds
Sample 17	Class D	Product K	Dark-grey filling, present in 2 finds
Sample 18		Product L	Grey filling, present in 22 finds
Sample 19		Product M	Brownish-red filling, present in 23 finds
Sample 20		Product N	Brownish-orange filling, present in 3 finds
Sample 21		Product O	Whitish-grey filling, present in 1 finds

Figure 2. a) Example of Class A materials (Product C); b) Class B (Product H); c) Class C (Product F); d) Class D (Product M).

appears, also at a macroscopic level, considerably different than the others: the binder appears of grey-whitish coloration, the aggregate is poorly sorted (dimensions from the micron to the centimetre).

3. EXPERIMENTAL SECTION

$CDCl_3$ (Aldrich, purity 99,9% in D), D_2O (Aldrich, purity 99.9% in D) and DMSO-d_6 (Aldrich, purity 99.8% in D) were reagent grade and were used without further purification.

^1H NMR spectra of solutions were recorded at 399.92 MHz on a Varian Mercury 400 or at 199.985 MHz on a Varian VXR 200. All spectra were reported in ppm using solvent residual peak as reference.

IR spectra were recorded on a FT-IR Perkin-Elmer Spectrum BX model, using the Spectrum v. 3.02.02 program. The FT-IR spectra of all solid materials were recorded using a mixture of sample (3 mg) and KBr (100 mg). The solutions were analysed using KBr or CaF_2 plates after deposition and solvent evaporation. In the extraction tests, 12 mg of each sample were introduced into a round bottom flask, equipped with a magnetic stirrer, with 0.7 ml of deuterated solvent ($CDCl_3$ or D_2O) and maintained at room temperature under magnetic stirring for 24 hours; then the solid and the solution were separated by filtration. At the end, an extraction with D_2O was also performed at 85°C for 6 hours. The solutions were analysed by ^1H-NMR spectroscopy and then by FT-IR spectroscopy as reported above. The solid residues were washed with the corresponding non deuterated solvent used in the extractive procedure, dried under vacuum and analysed with FT-IR spectroscopy as reported above.

The macroscopic analyses were carried out with a stereomicroscope (Zeiss KL 1500 Electronic). The mineralogical compositions were determined through powder X-ray Diffraction (XRD) using a Philips PW 1050/37 diffractometer, with a Philips X'Pert data acquiring system, operating at 40 kV-20 mA, with a Cu anode, a graphite monochromator and with 2°/min goniometry speed, in interval 2θ between 2°-62°. The petrographic description was performed using a polarised light Microscope ZEISS D7082 OBERKOCHEN (OM) on thin section (30 μm thickness); the microscope photos were taken with a Nikon Coolpix 4500 with a magnification of 10× and 2,5×.

4. RESULTS AND DISCUSSION

The chemical composition of the products used in the historical restoration of the *Problematica Verrucana* was studied by means of FT-IR and ^{1}H-NMR spectroscopies. In order to identify all products, also when found in small amounts, some extractions with solvents of various polarity were carried out on the fragments of samples, as reported in the experimental. A preliminary macroscopic characterisation and mineralogical and petrographical analyses were also performed on the inorganic filling materials found in the products of Class D.

4.1 Characterisation of Class A Products

The chemical composition of the different samples identified as Class A (**Products A**, **B** or **C**) was analysed by FT-IR spectroscopy on the KBr mixture.

The same organic compound, probably used as adhesive, was present in all products of class A as main component (Product A, samples 1 and 2) or as ligand for inorganic fillers (Product B, samples 3 and 4; Product C, sample 5). The FT-IR data [3428 (broad, vs), 2924 (m), 1631 (m), 1423 (m), 1030 (vs) cm^{-1}] suggested the presence of a polysaccharide compound and in particular the fingerprint region of the FT-IR spectrum was similar to the Arabic gum spectrum (Figure 3).

Bands attributable to inorganic fillers could not be found in the spectra of Product A (samples 1 and 2), whereas different inorganic fillers were detected in the FT-IR spectra of the other Class A products. In fact, bands attributable to calcium carbonate [2512 (w), 1799 (m), 1423 (vs), 874 (m), 712 (w) cm^{-1}] and silica [1083 (vs), 794 (m), 778 (m), 694 (w), 517 (w), 467 (s) cm^{-1}] were present in the Product B spectrum (samples 3).

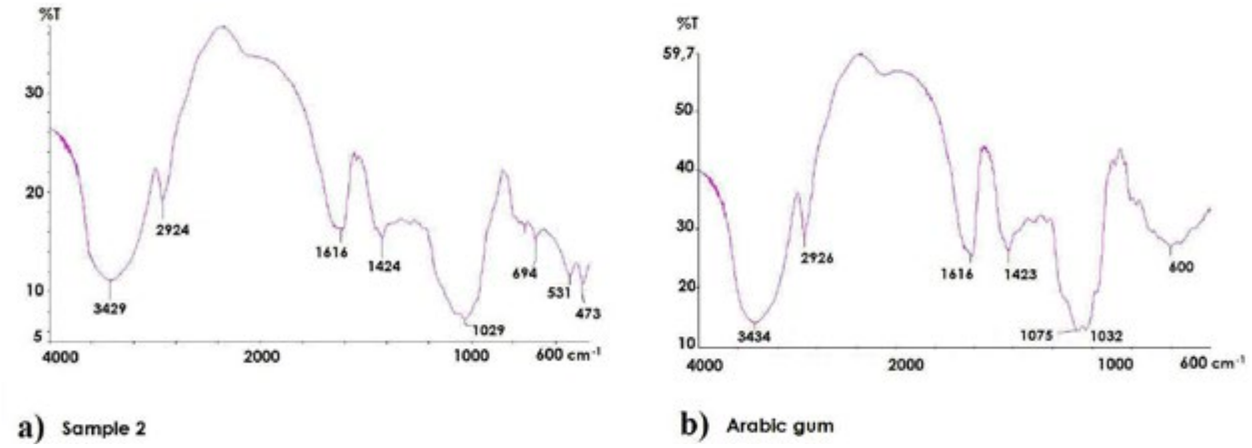
Finally, the presence of some bands of silica [794 (m), 778 (m)] and mica [3628 (m), 1028 (vs), 755 (sp) cm^{-1}] was observed in the Product C spectrum (sample 5), while other bands were not detectable due to their overlap with those of low amounts of polysaccharide.

4.2 Characterisation of Class B Products

A complete absorption of infrared radiations, in the 4000-1000 cm^{-1} range, was observed for **Product G** (samples 9, 10 and 11) and for **Product H** (samples 12 and 13), also with a lower concentration of this sample in the KBr mixture. The presence of specific functional groups could not be detected and only a single band at 464 cm^{-1} was noticed.

After extraction with $CDCl_3$, no organic compounds soluble in this solvent were found. In fact, no signals were present in the ^{1}H-NMR and FT-IR spectra recorded on this fraction. Nevertheless, a yellow solid was recovered in the NMR tube, which suggested the probable presence of sulphur. No changes were observed in the FT-IR spectrum of the solid insoluble in $CDCl_3$.

The behaviour of these samples suggested the presence, as main component, of a grey product, not trans-



a) Sample 2

b) Arabic gum

Figura 3. Product A, sample 2. – a) FT-IR spectrum; b) FT-IR spectrum of arabic gum.

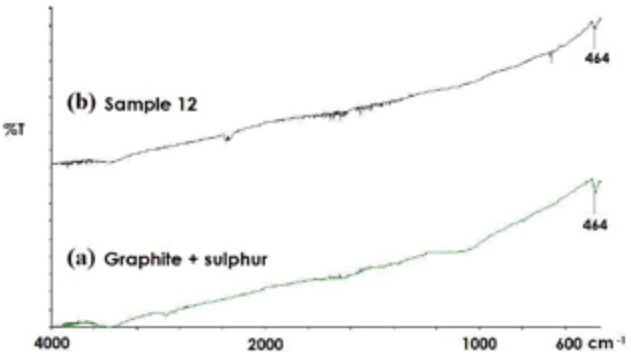


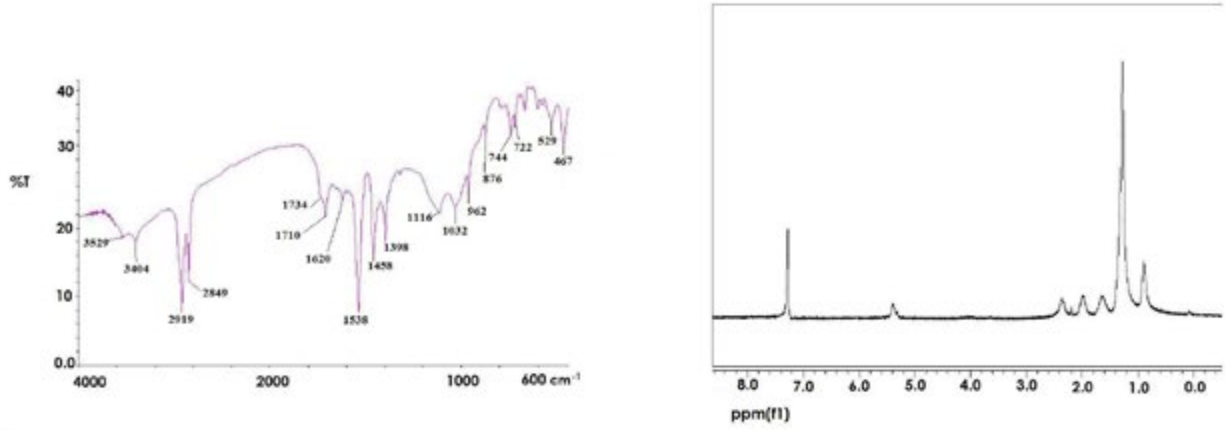
Figure 4. FT-IR spectrum of a graphite/sulphur mixture (a) compared with that of sample12 Product H (b).

parent to the infrared radiation as graphite. Because of the presence of this compound, it was not possible to observe other characteristic absorption bands. In order to confirm the hypothesis identifying graphite as the grey part of the solid and sulphur as the yellow part, a mixture containing graphite and sulphur was prepared and analysed by FT-IR spectroscopy. The FT-IR spectrum recorded on this mixture was identical to that recorded on sample 12 (Figure 4). Moreover, the colour appeared analogous with the sample material one.

4.3 Characterisation of Class C Products

The FT-IR spectrum of **Product E** (Sample 7) showed several bands attributable to the presence of a mixture of different organic products [2919 (vs), 2849 (s), 1734 (vw), 1710 (w), 1538 (vs), 1458 (m), 1398 (m), 1032 (w) cm^{-1}], probably waxes (1734 cm^{-1}), terpenoids (1734, 1710 and 1398 cm^{-1}) and salts of saturated and monounsaturated fatty acids (1538 cm^{-1}). Furthermore, gypsum ($CaSO_4{\cdot}2H_2O$) [3529 (w), 3404 (w), 1116 (w) cm^{-1}] was identified in lower amounts as inorganic material. The ^{1}H-NMR and FT-IR spectra of the $CDCl_3$ solution (Figure 5), obtained by extraction from the solid material at room temperature, suggested the presence as main components of salts of saturated and monounsaturated fatty acids [band at 1538 (vs) cm^{-1} in the FT-IR and signals at 0.89 (m, CH_3), 1.27 (m, CH_3-$\underline{CH_2}$), 1.65 (m, CH_2-$\underline{CH_2}$- CH_2-COO), 2.00 (m, $\underline{CH_2}$- CH=CH -), 2.38 (m, $\underline{CH_2}$-COO), 5.41 (m, -$\underline{CH}$=$\underline{CH}$-) in the ^{1}H-NMR]. Low amounts of free fatty acids or terpenoid acids and esters can also be found (band at 1731 (w), 1710 (m) cm^{-1}), whilst glycerol, linoleic and linolenic acids, free or esterified in triglycerides, were not detected in the ^{1}H-NMR spectrum. The solid residue contains gypsum [3535 (m), 3405 (m), 1623 (w), 1116 (vs) e 670 (w), cm^{-1}] together with mica [3613 (w), 1030 (vs), 750 (w) cm^{-1}], while the contemporary presence of silica can be identified for the weak bands at 797 (w), 777 (w), 531 e 472 cm^{-1}. The bands at 2925 (w) and 2851 (w) cm^{-1} were attributable to the presence of an organic compound insoluble in $CDCl_3$.

Several bands were found in the FT-IR spectrum of **Product F** (sample 8), attributable to a mixture of several organic and inorganic compounds [3445 (m), 2917 (vs), 2849 (vs), 1736 (s), 1709 (m), 1496 (m), 1465 (s), 1244 (w), 1173 (w), 873 (w), 854 (w), 718 (w), cm^{-1}]. The presence of waxes [1736 cm^{-1} in the FT-IR and signals at 0.89 (m, CH_3), 1.27 (m, CH_3-$\underline{CH_2}$), 1.65 (m, CH_2- $\underline{CH_2}$- CH_2-COO), 2.38 (m, $\underline{CH_2}$-COO), 4.06 (m, O-$\underline{CH_2}$-) in the ^{1}H-NMR] as main component, probably along with terpenoids (1736 and 1706 cm^{-1}), was identified in the fraction soluble in $CDCl_3$. In the spectrum of the solid resi-



a)

b)

Figure 5. Product E, sample 7 - a) FT-IR spectrum; b) Soluble fraction in $CDCl_3$, ^{1}H-NMR ($CDCl_3$) spectrum.

due, insoluble in chloroform, bands [3434 (m), 2918 (s), 2849 (m) cm^{-1}, 1496 (vs), 873 (w), 712 (w) cm^{-1}] attributable to a mixture of an organic compound and calcium carbonate were found. In particular, the organic compounds could be diterpenes (sandarac, rosin) polymerised due to ageing, according to their low solubility in chlorinated solvents.

4.4 Characterisation of Class D Products

The inorganic filling present in the products of class D was characterised using mineralogical and petrographical analyses.

Under stereomicroscope observation, **Product K** (sample 17) appears shiny on the surface. It is possible to observe that it is constituted by a binder and the aggregate. The binder is of grey colour and compact. In the aggregate three different typologies of grains are distinguished: the first one presents crystals of fine dimension, white colour, scaly fracture, and greasy surface. The second is constituted by a black and fine particulate of rounded shape. Finally, it is possible to observe traces of red particles of fine dimensions. The presence of hemihydrate gypsum as main component with low amounts of bi-hydrate gypsum was detected by FT-IR spectrum [3608 (m), 3564 (m), 3400 (m), 1623 (m), 1152 (vs), 659 (s), 601 (s) cm^{-1}]. Low amounts of a protein (1650 and 1549 cm^{-1}) used as binding material were also identified. No compounds soluble in $CDCl_3$ or D_2O at room temperature were detected. It is possible to hypothesise that Product K has a binder which is probably constituted by gypsum and protein, while the aggregate might be constituted by dolomite. In fact, the mineralogical analyses (XRD) of sample 17 reveal the presence of bassanite ($CaSO_4 \cdot 1/2H_2O$) and dolomite ($CaMg(CO_3)_2$). However, petrographical analyses were not carried out due to the small dimension of the sample and it was not possible to carry out a complete characterisation.

Product L (sample 18) was sampled from a piece of large dimensions (not catalogued). It was removed from the back of the find. Under stereomicroscope observation, it is possible to distinguish a binder and the aggregate. The binder is of white-yellowish colour and it appears compact. The aggregate is constituted by two different typologies of grains: crystals of white colour with a scaly fracture and greasy surface and a fine particulate of black colour and rounded shape. Hemihydrate gypsum as main component and lower amounts of gypsum were identified in the FT-IR spectrum [3611 (s), 3549 (s), 3404 (m), 1622 (m), 1150 (vs), 659 (s), 601 (s) cm^{-1}], together with a protein in small amounts (1650 and 1549 cm^{-1}). The mineralogical analysis (XRD) of sample 18 reveals the presence of bassanite ($CaSO_4 \cdot 1/2H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and traces of quartz (SiO_2). The observation under the polarised light microscope in thin section shows a binder of grey colour, which is mainly composed of gypsum. The porosity is medium and of irregular shape. The aggregate shows crystals of sub-euhedral shape and fine dimensions (prevalence of 50 µm and rare of 100 µm); the composition is mainly constituted by little needles of gypsum and traces of quartz and calcite. Iron oxides with opaque and globular appearance, probably Magnetite (Fe_3O_4), are present. The binder/aggregate ratio is 1/2 (Figure 6). Therefore, Product L is constituted by gypsum and protein substances as binder, along with an aggregate main-

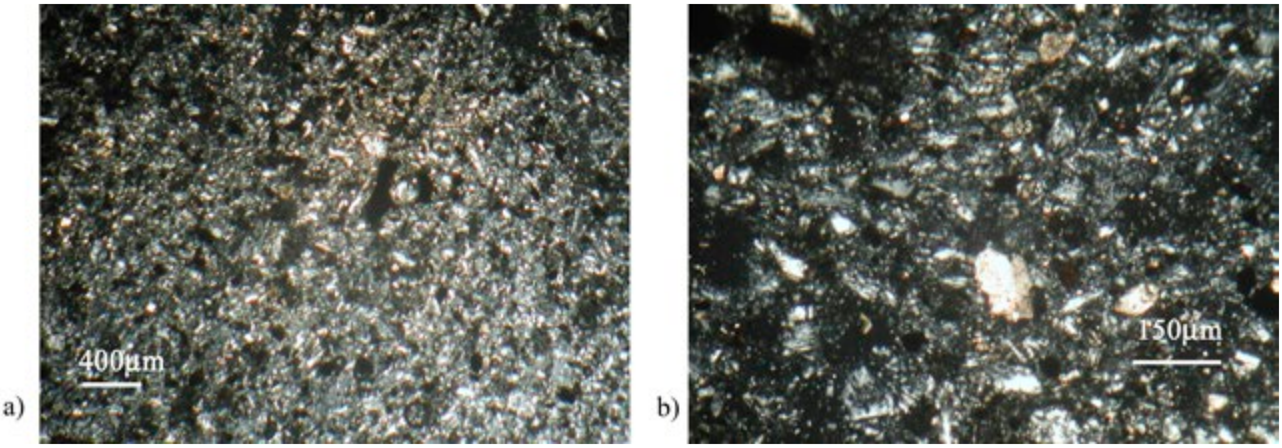


Figura 6. Product L, sample 18 – a) Cross nicols image: general view of the plaster with gypsum in the binder and in the aggregate; b) Cross nicols image: particular of the binder of dark colour, constituted by gypsum; it is visible aggregate, with prevalence of gypsum and trace of quartz and calcite (in colour brown in the top of image).

ly composed of gypsum, iron oxides (probably responsible for the darker pigmentation) and subordinate quartz and calcite.

Under stereomicroscope observation, **Product M** (sample 19) appears shiny on the surface. It is possible to recognise a binder and the aggregate. The binder is of brick-red colour and compact. The aggregate is constituted by three different typologies of grains: the first one presents crystals of fine dimensions, white colour, scaly fracture and greasy surface. The second is constituted by a black and fine particulate of rounded shape. Furthermore, it is possible to observe traces of particles of fine dimensions and of red colour. Bands attributable to the presence of hemihydrate gypsum as main component with lower amounts of gypsum were present in the FT-IR spectrum [3610 (m), 3546 (m), 3404 (w), 1622 (m), 658 (s), 601 (s) cm^{-1}]. A protein as organic binder was present in small amounts (1546 cm^{-1}) and the presence of an iron oxide (hematite, 537 cm^{-1}) was also observed. The mineralogical analysis (XRD) reveals the presence of bassanite ($CaSO_4 \cdot 1/2H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and traces of quartz (SiO_2). The observation under polarised light microscope in thin section, shows a binder of brownish-red colour, with anisotropic appearance and mainly constituted by gypsum. The porosity is medium, with irregular shape. The aggregate presents dimensions between 50-100 µm in prevalence and rarely 200 µm, of sub-angular shape. It is constituted by gypsum, quartz and traces of calcite and mica. Iron oxides are present. The binder/aggregate ratio is 1/3 (Figure 7). Therefore, Product M is constituted by gypsum and protein substances as binder, along with an aggregate composed mainly of gypsum, iron oxides (probably responsible for the brownish-red pigmentation) and subordinate quartz, calcite and mica.

The stereomicroscope observation of **Product N** (sample 20) shows a binder and the aggregate. The binder is of yellow colour and compact. The aggregate is constituted by three different typologies of grains: the first one shows crystals of fine dimensions, white colour, scaly fracture and greasy surface. The second is constituted by a black and fine particulate of rounded shape. Moreover, it is possible to observe traces of particles of fine dimensions and of red colour. Gypsum hemihydrate as main component and lower amounts of gypsum were identified in the FT-IR spectrum [3610 (m), 3549 (m), 3400 (w), 1622 (m), 1151 (vs), 659 (s), 601 (s) cm^{-1}]. The presence of calcium carbonate and traces of a protein were also observed. The mineralogical analysis (XRD) of sample 20 reveals the presence of bassanite ($CaSO_4 \cdot 1/2H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$) and calcite ($CaCO_3$). The presence of quartz (SiO_2) is also probable. The observation under polarised light microscope in thin section shows a binder of brownish-orange colour, with anisotropic appearance and constituted mainly by calcite and minor amounts of gypsum. The porosity is low and of irregular shape. The aggregate, of variable grain size from 50-300 µm, is constituted by gypsum, calcite and iron oxides. The binder/aggregate ratio is 1/3 (Figure 8). Therefore, Product N is constituted predominantly by calcite, low amounts of gypsum and protein substances as binder, with an aggregate composed mainly of gypsum, iron oxides (responsible for the brownish-orange pigmentation) and subordinate calcite.

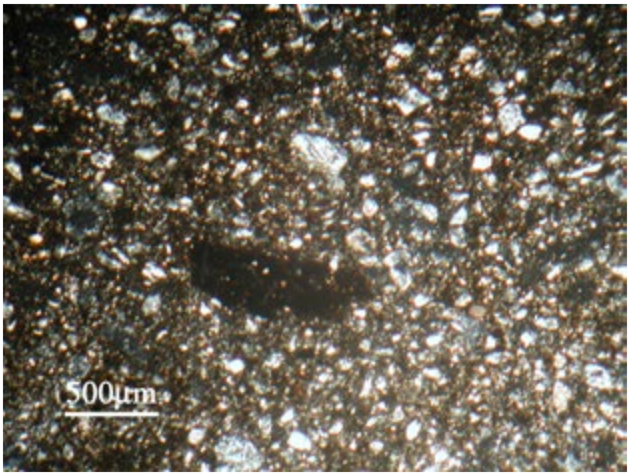


Figura 7. Product M, sample 19 - Cross Nicols image: particular of the gypsum binder with brownish red colour for the presence of iron oxides. Gypsum and quartz, constituting the aggregate, are visible.

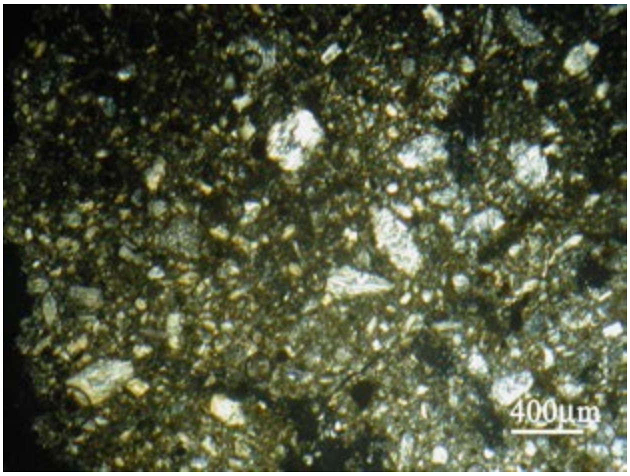


Figura 8. Product N, sample 20 - Cross Nicols image: particular of the binder of brown colour constituted by lime and gypsum; gypsum, calcite and iron oxides are visible in the aggregate of bigger dimensions.

Product O is only applied on the catalogued piece IGF 348T (indefinite trace). It was removed (sample 21) from the back of the find. Under stereomicroscope observation sample 21 shows a binder and the aggregate. The binder is of whitish-grey colour and compact. The aggregate is composed by grains of extremely variegated shape, typology and dimension. The FT-IR spectrum suggested the presence of calcium carbonate [2514 (w), 1432 (vs), 875 (s) and 712 (m) cm^{-1}] and of polysaccharide [3441 (m), 1028 (m), 469 (w) cm^{-1}] as binder. No organic products soluble in $CDCl_3$ were detected. The mineralogical analysis (XRD) of sample 21 shows the presence of calcite ($CaCO_3$), quartz (SiO_2), plagioclase-albite ($NaSi_3AlO_8$) and traces of fillosilicates. The presence of larnite (Ca_2SiO_4) is probable. The petrographical analyses were not carried out due to the small dimension of the sample. Therefore, one can hypothesise that Product O has a binder which is probably constituted by a hydraulic lime (for the presence of larnite) and polysaccharide; the aggregate might be constituted by quartz, plagioclase and fillosilicates, but it is not possible to carry out a correct characterisation without a petrographical analysis.

4.5 Conservation Properties of Products

Class A products are composed of a polysaccharide either used alone as adhesive (Product A) or thickened with different inorganic materials as aggregate (calcium carbonate and silica for Product B and silica and mica for Product C). Each different composition of the three products of Class A corresponds to a different use of the materials. In fact, rubber is used alone when it is applied as an adhesive, whereas it is mixed with an inorganic aggregate when the product is used to fill internal or external gaps and to reconnect big and irregular pieces (plaster).

The presence of calcium carbonate in Product B may also be attributable to carbonation of lime; in fact, lime could have been added to polysaccharides to improve mechanical properties. This formulation was probably chosen with the purpose of giving a mimetic effect and finishing touch in spite of a mechanical support and was used for finds of small and medium dimensions. On the contrary, Product C which contains an aggregate with larger grains and has a composition with quartz and without calcium carbonate, is preferred to Product B, as the dimensions of the find increase.

Class B materials (Products G and H) are compounds used for the fabrication of moulds and junctions. As confirmed by the analysis of a standard mixture, their composition reveals the presence of sulphur and an amorphous carbon product as graphite. These products are also used as plasters; in this case the adhesive properties are conferred to the composite by the presence of graphite.

Class C materials (Product E and F) are mixtures of organic and inorganic compounds. Product E is composed of terpenes, waxes, salts of fatty acids, and gypsum. Product F is composed of terpenes, waxes, and calcium carbonate. Gypsum and calcium carbonate could have also been used as aggregate, especially in Product F, where no further aggregate is present to fulfill this function. In Product F the presence of carbonate could also be ascribable to lime carbonation. Lime could have been added to the mixture to enforce the grip or the hardness of the product [14, 15].

From the comparison of chemical, mineralogical and petrographical results for **Class D** materials, one can infer that Product K, Product L and Product M have gypsum and protein substances as binding materials with gypsum, iron oxides (Product L and Product M) and quartz, calcite and mica (mica only for Product M) as aggregates. For Product K, a correct identification of the aggregate cannot be performed due to the absence of petrographical analyses; it is only possible to hypothesise (by XRD analyses) a dolomitic composition. The composition of Products K, L and M is in agreement with a standard glue-gypsum plaster. In particular, in Product K the presence of protein is more copious than expected and it is in agreement with a major hardness of the material.

Product N differs from the former products of Class D; in fact, it can be defined as a plaster with a binder constituted by lime and gypsum; the aggregate (gypsum, calcite and iron oxides) has higher granulometry. Probably the presence of lime along with gypsum, the abundance of aggregate and the higher granulometry allowed the development of a tougher structure (in fact the plaster has been used to repair a long fracture in the find) [16-21]. Product O is probably an hydraulic mortar (for the presence of larnite), perhaps cementitious[22] and with a polysaccharide as additional binder. Furthermore its function is different: Product O was applied to create a firm base to maintain the finds in vertical position during the photographic sessions of Fucini, therefore the use of a mortar with higher resistance is to be deemed correct for this purpose.

Therefore, the products of Class D (except for Product O with only a particular function of support) were realised by Fucini as plasters with a prevalent presence of aggregates with a variable granulometry and the addition of glue to improve the hardness of the material. Furthermore, Fucini took into account other factors than the compositional characteristics, mainly the colour of the filling, giving importance to the similarity of the pigmentation between restoration products and the finds.

Products A, K, L, M, N can be compared with similar ancient recipes mentioned in literature. Product A is mainly a polysaccharide material, according to the recipe of Cecchini[23], which contains Acacia gum (the Cecchini recipe specifies "Acacia gum, sugar and honey"). Product K is a standard glue and gypsum plaster as, for example, the recipe mentioned in Arcolao[14]. Products L and M are glue and gypsum plasters with iron oxide for the pigmentation and sand for the aggregate, in agreement with the traditional recipe of Cecchini [23]. Product N is a plaster realised with lime, gypsum and glue, sand for the aggregate and iron oxides for the pigmentation, and similar products are described in the literature ("lime, glue, gypsum, sand, pigments, alum") [25].

5. CONCLUSIONS

Important pieces of information were obtained analysing the products used for the fossil restoration of the *Fucini Collection*. The results show an example of application of traditional recipes in a yet unexplored field. Moreover, even among the wide variety of organic and inorganic materials, this study adds new information regarding some combinations of products; for example in the case of plaster of polysaccharide rubber with inorganic aggregate[24,25].

The possibility to identify materials used in old restorations represents a starting point for the study of conservation of paleontological finds of ancient collections. Further insights on these products and especially the extension of this research towards other classes of compounds will allow to obtain a more complete picture on the restoration techniques used on fossils in the past.

Moreover, some products (especially Class D materials and Product A) seem to fulfill exceptionally well, even one hundred years later, their conservative and esthetic functions. A dedicated study would also permit to evaluate their applicability to current restorations of paleontological finds. Knowing products and techniques, evaluated according to the present status of conservation, will allow to develop operative protocols for the conservation of paleontological material.

ACKNOWLEDGEMENTS

The authors thank the Museum of Natural History of the University of Florence for the supply of samples.

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Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Citation: J.(H.) Lyklema (2017) Interfacial Potentials: Measuring the Immeasurable? *Substantia* 1(2): 75-93. doi: 10.13128/substantia-28

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declared that no competing interests exist.

Feature Article

Interfacial Potentials: Measuring the Immeasurable?

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Abstract. The scientific background of measuring and interpreting potentials at interfaces is discussed in a historical setting. Various types of potentials have to be distinguished. Some are measurable, others not. Static and dynamic aspects will be covered and, as applications, the interaction between electric double layers and the slip process in electrokinetics will be considered. In several cases it is expedient to interpret results in terms of charges rather than in terms of potentials.

Keywords. Interfacial potential, surface potential, zeta potential, colloid interaction, electrokinetic slip.

1. INTRODUCTION

> – *Zum Unterschied von $\Delta\psi$, das wenigstens prinzipiell immer messbar ist, sind Absolutwerte von $\Delta\varphi$ bis heute noch nicht zugänglich*[1]
> – *... the value of the potential of a single electrode is not amenable to direct experimental determination*[2]
> – *We measured the electrosurface potential electrophoretically*[3]
> – *The keyword "surface potential" occurred in a recent paper on modern AFM – like techniques*[4]
> – *Surface potentials can be evaluated by second harmonic generation and similar non-linear optical techniques*[5]

These five statements all relate to the measuring of surface potentials, but that seems to be the sole binding element between them. For the rest these quotes differ in many respects, even regarding the definitions and even with respect to the basic tenet whether or not these potentials are experimentally accessible at all. It sounds as a cacophony. Do all quotes refer to the same quantity? It is noted that between the oldest and the more recent of these quotes almost a century elapsed. One would wonder if over such a long time span the improvement of the experimental techniques and the development of better defined systems would have contributed so much to our physical insight that quantities that could not be measured long ago are now within reach of our technical achievements. Or, are there certain generic laws of principle precluding that?

The present paper intends to help solving this basic question and considers how our understanding developed historically.

Prior to that it is necessary to agree on the meanings of basic concepts, their terminology and definitions. In trying that, it is realized that in certain scientific circles group-specific nomenclature is used, that does not necessarily match with that of other teams. Some people state that they have studied potentials whereas it appears that they are dealing with something else. One typical illustration is the notion of *pair potential,* routinely encountered in simulation science. This dubbing is a generally adopted habit, which everybody involved in this field appears to understand. Nevertheless, it is basically incorrect because the quantity under discussion is an energy and not a potential. Routinely, interaction potentials are expressed in units of kT or eV, that is in units of *energy* whereas potentials ought to be expressed in *Volts.* Another illustration is that of measuring so-called electrokinetic or zeta potentials (ζ), a daily routine for every colloid scientist. The procedure is straightforward: one measures, say the electrophoretic mobility, of a colloidal particle and interprets it in terms of, say the Helmholtz-Smoluchovski law, which immediately produces ζ in Volts. This looks like a direct potential measurement. However, in reality this is not what happened; an applied electric field can lead to the displacement of free *charges*, not to the displacement of *potentials.* So, in the derivation of the Helmholtz-Smoluchovski equation some conversion of a charge into a potential must have taken place. Not everybody is conscious of that. We shall come back to this in sec. 6.

In the present paper we shall reserve the notion of "potential" to the *electric potential*, expressing it in Volts.

With this in mind, it is realized that, before dealing with the issue of measuring interfacial electric potentials, it is mandatory to agree on terms and definitions. To that end we shall heed the recommendations made over the past decennia by the International Union of Pure and Applied Chemistry (IUPAC). This organization is appreciated for its attempts to recommend internationally accepted rules for definitions of standards and nomenclature. The obvious reason is to "decacaphone" the literature from incorrect statements. Some of its recommendations refer directly to the measurement and interpretation of interfacial potentials.[2,6-10] and below we have heeded them maximally. In this way it is hoped that at least the text is understandable for a wide readership. This might be particularly useful when addressing the older literature, stemming from before the time that such recommendations were available.

2. EARLY 20TH CENTURY

There are good reasons for starting the historical considerations with the first part of the 20th century. The centuries before that saw the development of rigorous theories for electric fields, some of these resulting in field vector equations like Gauss' and Stokes' theorems and general phenomenological laws derived from these, such as Poisson's law for the relation between charges and potentials and Smoluchovski's laws for electrophoretic mobilities and streaming potentials. These theories did not address the basic question what the origin is of the spontaneous charging of colloidally dispersed particles; it was just accepted that (surface) charges were apparently present and that hence the particles would be the seats of an accompanying (surface) potential. The advent of understanding these origins, together with the development of options for their measurements take us to the beginning of the 20th century, and to the central theme of the present study. What was the state of understanding electrified interfaces around ca. 1920?

In that year theory of diffuse double layers was already available, thanks to the pioneering work of Gouy[11] and Chapman.[12] Their model is based on the Poisson-Boltzmann (PB) distribution for the countercharge. Underlying the PB theory are two assumptions. In the first place, ions are considered point charges, *i.e.* as volume-less charges. As a result, the theory is *generic*: dependent on the valences of the ions but not on their sizes. The second, mostly tacit, assumption is that the potential occurring in the Poisson equation is the same as that in the Boltzmann equation. This is not necessarily correct: the former is an average potential whereas the latter is a potential of the mean force. This distinction is rather esoteric, and considered in the domain of statistical thermodynamics. If needed we shall return to this issue later; but let it for the moment be accepted that the difference between the two types of potential are negligible when the potentials are low and when the potentials are very high.[13] Notwithstanding these quantitative limitations, the Gouy-Chapman (GC) theory was an important leap forward because it was one of the first relevant attempts to quantify some surface potential. However, with respect to our main question about the origin and measurability of the interfacial potential, GC theory does not help. The reason was that this theory was developed as an attempt to interpret electrocapillary curves, in the measurement of which the surface potential across a mercury–water interface is simply applied externally. This leaves unanswered why isolate colloidal particles can also carry a charge, let alone what their surface potentials are.

Apart from this central issue in the present context, let us recall another piece of wisdom of the GC model. It predicted the screening of charges to scale with the square root of the electrolyte concentration, a law observed often thereafter, but which was difficult to understand otherwise.

Still another feature of diffuse double layer theory was the prediction of expulsion of electrolyte by a charged diffuse double layer, a phenomenon that was independently measured and called the Donnan effect.[14] The basic phenomenon is the electrostatic expulsion of co-ions, which is a purely electrostatic phenomenon. However, phenomenologically it is observed as the expulsion of *electroneutral* electrolyte by charged surfaces, colloids and polyelectrolytes. The insight that this phenomenon found its basic origin in diffuse double layer theory grew only several decades later.

What was *not* yet known around 1920 included (what is now known as) Stern theory for non-diffuse layers[15] and the Debye-Hückel theory[16] for the activity of strong electrolytes. Nowadays it is common practice to consider as a first approximation the aqueous side of double layers as consisting of two parts, an inner part, or Stern layer and an outer diffuse part, or Gouy layer. The inner part is the seat of ion specificity, meaning that the sizes and non-electric binding Gibbs energies are different between different ionic species. The impact of Stern theory is in recognizing that ions can also adsorb without electric attraction and hence spontaneously create or reduce an electric potential difference. The idea itself of a molecular condensor was familiar around 1920 though, thanks to the work of Helmholtz in the 19th century. Such layers were mostly called Helmholtz double layers and considered as an alternative for diffuse double layers, rather than as an addendum to them. However, around 1920 this essential step in the spontaneous creation of interfacial potentials by specific adsorption in the Stern, or Helmholtz *part* of a double layer was not yet so clear.

3. FREUNDLICH

With this in mind it is historically interesting to read the pertinent literature from that period. A very rich source for obtaining this information is found in the standard books by Herbert Freundlich (1890-1941), one of the most versatile and all-round colloid scientists of that era. He wrote a sequel of books under the main (German) title *Kapillarchemie*, where the subtitle *Eine Darstellung der Chemie der Kolloide und verwandter Gebiete* explained what he understood by the title and subtitle. Nowadays one would call it “Colloid and related science”. Later, also English translations appeared under the name Capillary Chemistry. For the present purpose we shall now consider the second print of 1922.[17]

The problem that Freundlich was facing was matching the interfacial electrochemistry of large flat surfaces and colloidally dispersed systems. Are there common principles in the creation of electric potentials at the surfaces of dispersed particles and macroscopic amounts of surface? It is particularly interesting to read how Freundlich interprets disparate measurements, some even for ill-defined systems. In chapter 6 of that book he starts with comparing measurements on Nernst-type potentials for macroscopic surfaces with those obtained electrokinetically for colloids.[17] At that time it was by no means clear to which extent measured potentials would be identical under identical ambient conditions. Translated into modern symbols, his question was by how much ψ^o (the electric potential at the phase boundary) and the electrokinetic potential ζ differ. At that time for colloids no other independent experimental evidence (like titrations) was available. It was even not yet clear whether there was a difference of principle between transversal and tangential potentials jumps. Of course, potentials being scalars, their absolute values are only determined by the position in the double layer, hence this question can be translated into that of the spatial variation of ψ and ζ along a surface.

Given the scarcity of experimental evidence, Freundlich approached this problem by investigating how the addition of certain substances affected ψ^o and ζ. Of the many reported facts involved he states that, following Nernst, oxide and carbon electrodes may be considered as hydrogen or oxygen electrodes. With a bit of surprise he also refers to glass electrodes in the sense that their ”potential jumps” with respect to electrolyte solutions behave as if the glass were a swollen gel layer containing a fixed concentration of H^+ and/or OH^- ions. He reports that the ζ potential for this system, in agreement with earlier measurements, is very sensitive to the presence of low concentrations of additives. For example, H^+ ions can reduce ζ without changing its negative sign, whereas $AlCl_3$ and crystal violet do invert the sign of ζ already at concentrations as low as 1-2 and 50 μM, respectively, without having any substantial influence on the Nernst potential, ψ^o. The only effect $AlCl_3$ had on ψ^o was changing the spontaneous acidity of the solution, because it is a weak electrolyte. If this effect was suppressed by carrying out the experiment in an (acetate) buffer, the influence on ψ^o disappeared completely. Freundlich had to conclude that ψ^o and ζ are different quantities. Supposed that ζ would be measurable that would not yet mean that ψ^o would be measurable as well.

His qualitative explanation for this difference is essentially the same as our present idea, namely the existence of a slip plane, or a thin slip range. His argument was that upon tangential shear of the water the forces involved are not strong enough to move the water by shearing it at the solid-liquid border. Rather a thin adhering layer remains *stagnant*. Freundlich also realized that the very fact that electrokinetic phenomena could be observed at all must mean that the double layer must have a certain thickness, supporting the existence of a diffuse part. He quoted Smoluchovski who already in 1914, two years before the publication of Gouy theory, arrived at the same conclusion.[18] Figure 1 sketches these ideas.

Qualitatively, the shapes of the two curves do not differ that much from our present insights. Curve 1 applies to simple double layers, curve 2 for systems with overcharging (as it is nowadays called). The most striking difference with (good) recent pictures is the absence of anything quantitative. There are no ideas about the potential inside the solid, it is not clear why there is a bending point in curve 1 and whether the position of that point coincides with the minimum in curve 2. That minimum ($x = d$) is apparently the distance from the surface where specific adsorption takes place. However, Freundlich identifies the potentials at that distance as ζ-potentials and this suggests that the plane of specific counterion adsorption is assumed to coincide with the boundary between tangentially moving and tangentially stagnant water, nowadays called the slip plane. No argument for this is given; at any rate the identity between the two is not obvious: the distance from the solid surface where bound counterions are situated is determined by short range forces and water structure, whereas the position of the slip plane is determined by the tangential motion of many water molecules. There is no *a priori* reason for their identity. We shall return to that in sec. 6.

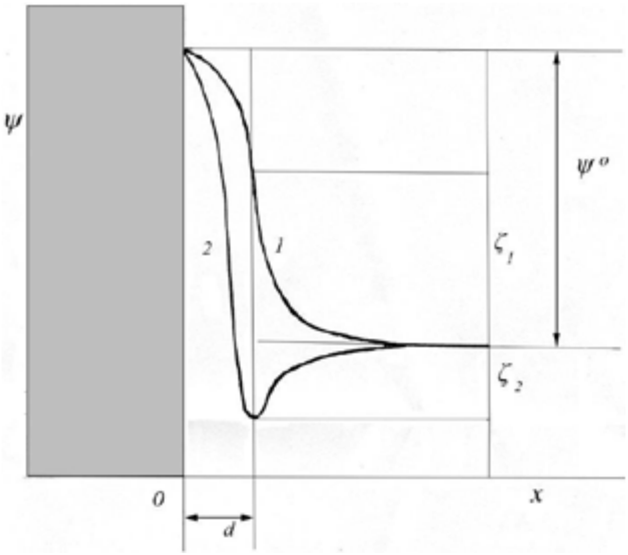


Figure 1. Sketch of the potential distribution $\psi(x)$ in a flat double layer after Smoluchovski (1914) and Freundlich (1922). The border between the solid (hatched) and the liquid is situated at $x = 0$. Discussion in the text.

3.1 Application of Gauss's Law

One feature underlying the sketches of figure 1 that Freundlich did not further elaborate, although its basic physics were perfectly well known to him, was the inference on the various surface charges that can be drawn, using Gauss's vector theorem (also known as Ostrogadski's or Green's theorem). It is a general theorem for a vector field $\boldsymbol{E}$ in a volume V, bound by a closed area A of arbitrary shape. The space (triple) integral over the divergence of $\boldsymbol{E}$ equals the surface (double) integral over the inner product $\boldsymbol{E}\cdot\boldsymbol{n}$ where $\boldsymbol{n}$ is the unit vector normal to the surface and directed outward. The mathematics becomes easy if applied to a flat interface, say for a charged sphere with radius $r\to\infty$ Then $\boldsymbol{E}\cdot\boldsymbol{n}$ simply becomes the field strength $E = -\mathrm{d}\psi/\mathrm{d}x$ normal to the surface. E corresponds to the slope of the curves drawn in Figure 1, integrated over the entire surface A. The triple integral over div·$\boldsymbol{E}$ can be written as div·(gradψ), mostly written as $\nabla^2\psi$ which, according to Poisson's law equals $-\rho/(\varepsilon\varepsilon_0)$ where ρ is the local space charge density, ε is the local relative dielectric permittivity and ε_0 is the dielectric permittivity of free space. This triple integral leads to the total charge in the volume V. In our specific case with no space charges in the solid interior, this charge is the surface charge σ multiplied by the area A. Combining all of this leads for one-dimensional situations to the simple expression

$$\frac{d\psi}{dx} = -\frac{\sigma}{\varepsilon_0\varepsilon} \tag{1}$$

Eq. (1) is generally valid: at any position in the double layer can we make a cross-section where the part on the left and the part on the right have equal, but opposite charges, given by this equation. For instance, just to the right of the $x = 0$ plane the slope for curve 2 is steeper than that for curve 1, which means that in the second case the surface charge is higher. Phenomenologically this trend is correct: stronger screening leads to higher surface charge at given surface potential. However, curve 2 cannot be correct, because it predicts a maximum in the countercharge around the slip plane, which is physically unrealistic. Moreover, it would also predict a zero charge coinciding with the slip plane for which also no physical reason can be given. Far from the surface all charges are zero, which is obviously correct.

Although all of this must have been known around 1920, little of such argumentation is encountered in Freundlich's book. In his attempts to get hold of the charging principles he collected many data on the electrokinetic properties of a great variety of systems. Regrettably, in that respect he was not very successful, mainly because he did not have sufficiently well-defined systems at his disposal.

4. LANGE AND KOENIG

About ten years after Freundlich, Lange and Koenig wrote a completely different approach, in which they considered electrical potentials thermodynamically.[1] Not surprisingly, this approach also involved the question of the measurability of surface potentials. The paper is "deutschgründlich" written, with the excuse that they could not present it in even more detail because of lack of space. The Lange–Koenig paper helped the understanding of interfacial potentials in at least two respects: distinguishing between measurable and immeasurable potentials and the introduction of the notion "potential-determining ions".

Their most significant contribution is the insight that there is *in principle* no way for measuring the (electric) potential difference between two adjacent, chemically different phases. Let us by way of paradigm consider the potential of a solid (particle or electrode) with respect to the solution in which it is imbedded. Measuring electric potential differences, say between locations A (the solution) and B (the solid), requires bringing a unit charge from A to B and determining the electric work per unit charge involved. However, when points A and B are located in chemically different condensed phases, the transport of the charge carrier also involves chemical work. For colloids the charge carriers are ions, which have finite sizes and hence they also interact non-electrostatically with their surroundings. The Gibbs energy of that interaction is non-zero even if the phases are uncharged. This chemical contribution cannot unambiguously be separated from the electrical one. Hence, absolute values for the potentials in condensed phases are in principle immeasurable.

It is historically interesting that, in the first quote of the present paper Lange and Koenig take a less absolute stance; they just state that separation is *as yet* not possible, apparently they believed in technological solutions for all scientific problems. Nowadays the insight is that the impossibility of measuring absolute potentials in condensed phases is intrinsically coupled to the impossibility of measuring thermodynamic potentials of single ionic species. In no way can the energy and entropy of, say a mole of protons be determined because no process can be envisaged to prepare and transport that mole without simultaneously also transporting the same amount of anions. Otherwise stated, potential differences between different condensed phases are *inoperable.* Lange and Koenig realized that.

Given this impossibility, the problem was, and is, how to cope with that in practice. Generally, for such issues two ways are open: avoiding it or subjecting it to penetrating theoretical analyses, two options that are not very handy in daily practice. Lange and Koenig came with two suggestions, the introduction of the notion of *potential-determining* (*pd*) *ions* and distinguishing various types of potentials, some measurable, others immeasurable.

4.1 Charge-Determining Ions

As to the former, although absolute potential differences between adjacent condensed phases of different compositions are inoperable, *changes* therein are often accessible, in particular when the material under study can function as an electrode in a Galvanic cell. The simplest example is a cell containing the electrode under study in an electrolyte solution and a reference electrode. The cell potential E_{cell} is in principle measurable and consists of the sum of the sought electrode-solution potential difference $\Delta\psi$ and the reference electrode-solution potential jump $\Delta\psi_{\text{ref}}$. With such a cell one can measure changes in the cell potential as a function of changes in the composition of the solution, like changes of the electrolyte concentration or changes in pH. If the reference electrode is insensitive to those changes, as is the case for a suitable calomel electrode, the change in cell potential comes only on the account of $\Delta\psi$. So, although $\Delta\psi$ is inoperable, $\mathrm{d}\Delta\psi$ is relatively well accessible. It was already known to Freundlich that in many systems $\mathrm{d}\Delta\psi$ shows Nernst behavior, according to which $\mathrm{d}\Delta\psi$ is proportional to the log of certain electrolyte concentrations to the amount of 58 mV per decade of the concentration of that ion. In many cases that electrolyte contains the proton, H^+ and this rule is the basis for applying glass electrodes for the pH measurements. The thermodynamic background of Nernst's law led to the introduction of the notion of potential determining ions by Lange and Koenig.

According to Lange and Koenig, potential-determining ions are thought as being present in both of the adjacent phases in sufficient amount as to be thermodynamically significant. Then, an electrochemical potential can be assigned to the activity of the proton in the solution and the solid and their equalization leads to the establishment of the $d\Delta\psi(\text{dpH})$ relation. Mathematically, electrochemical potentials consist of three terms, for pd ion i generally written as $\mu^o{}_i + z_i\,F\psi + RT\ \ln\ a_i$.We are interested in the variation upon changes in a_i. In the solution this leads to $z_iFd\psi(\text{solution}) + RT\text{dln}\ a_i$ and in the solid to $z_iFd\psi(\text{solid})$. Equating these two changes in chemical potentials, writing ψ^o for $\psi(\text{solid}) - \psi(\text{solution})$, leads to

$$z_iFd\psi^0 = RTdlna_i \tag{2}$$

which predicts $d\psi^o/(RT\ \text{dln}a_i)$ to be constant and equal to $RT/(zF)$ per decade of the activity of z-valent pd ions. At room temperature this amounts to 58 mV/z per factor 10 in the activity of i, i.e. the observed Nernst behavior.

The above derivation gives some insight into the assumptions that had to be made in order to arrive at Nernst's law. The observed applicability of this law for a given solid-liquid interface is a justification *in retrospect* for the applicability of the model assumptions for that particular system. As to the measurement it has to be added that measuring relative activity changes of single ionic species ($\text{dln}a_i$) is not possible; only activity changes of neutral electrolytes or electrolyte mixtures are measurable. To overcome this problem in practice, the procedure is working in swamping electrolyte that has the anion in common with the acid that produces the protons to be measured. For example, if the activity of protons must be measured in HCl, the measurement is carried out in swamping KCl, of which the concentration is fixed so that in $\text{dln}a(H^+) + \text{dln}a(Cl^-)$ the second term vanishes. Calibration is necessary to ensure that this situation is attained. If it is not sufficiently controlled the trend is that lower than 58 mV is found for the Nernst slope. It may be added that "swamping" means "large as compared to the concentration of i", implying that not necessarily high salt concentrations are needed.

The notion of potential-determining ions has been generally accepted and used for several decades. Nowadays these ions are rather dubbed "*charge-determining* (cd) *ions*", just because of the reason that the absolute value of the potential in a chemically different phase cannot be determined, whereas charges can be very well measured. Below we shall adhere to the term "charge-determining".

The conclusion of this part is intuitively sound: Nernst behavior means that upon transport of one ion from one condensed phase to the adjacent requires an energy of kT per unit charge z_ie and as energy = charge x potential its quotient is a unit potential $kT/(z_ie) = 58/z$ mV. Ions for which this is in practice measurable are charge-determining ions.

4.2 The χ-potential

As to the fundamental impossibility of determining absolute values of the potential difference Lange and Koenig proposed to distinguish between different types of potentials, each with its own symbol: the Galvani (φ), Volta (ψ), real (α) and χ-potentials. Ref. 1 is replete with relationships between these potentials, and with the thermodynamic and electrochemical potentials in solutions. Galvani potentials are the (immeasurable) inner potentials, in our example the potentials in the heart of a colloid particle or electrode with respect to the bulk of the solution. Volta potentials are measured in the solution so close to the outside of the condensed phase that the effect of the nature of that phase is not felt, but close enough to pick up any longer range effect of the electric charge on the phase. By this definition Volta potentials are in principle measurable, but the information they carry is much less interesting than that of Galvani potentials. Real potentials refer to a specific ionic species, say i, and they are combinations of μ_i and the Volta potential. We shall not use this quantity but note that it is identical to the electronic work function for extracting an electron from a metal (or ion from a non-metal) and take it to infinity. Lange and Koenig distinguished between Galvani and Volta potentials through the different symbols φ and ψ, respectively. Hence the distinction between $d\varphi$ and $d\psi$ in the first quote of this paper.[1] We shall not use this distinction and only use ψ for the electric potential. Where needed, we shall provide enough information on the way in which the non-electric contributions are sequestered.

The last suggestion by Lange and Koenig, was the introduction of the notion of *χ-potential,* also recommended by IUPAC. We shall call it the *interfacial potential jump*. The potential jump in going from A to B we shall denote as χ^{AB}. In the Lange-Koenig nomenclature $\chi = \varphi - \psi$. The quantity χ is immeasurable but has a clear physical meaning: it accounts for the potential jump at the interface between two phases caused by the local polarization of the molecules at the interface, orientation of water dipoles at the interface, polarization of the surface layer of the solid; in short, all contributions to the potential difference between uncharged adjacent phases, that is: at the point of zero charge. The reason why the introduction of χ is so handy, even though it is immeasurable, is that all contributions grouped into it are short-range, a few molecular diameters at most, whereas electric double layers have thicknesses of the order of κ^{-1} which can be orders of magnitude larger. For colloids an additional argument is that surfaces are rarely perfectly flat. Roughness of the order of a few molecular layers can rarely be avoided. An additional consideration for using χ is that the properties of diffuse double layers that are relevant for the daily practice of colloid science (say for the interpretation of colloid stability and electrokinetics) can to a large extent be understood by considering the diffuse part only. However, assuming that the surface charge σ^o has been measured, the very relevant and interesting issue is which fraction of the countercharge ($-\sigma^o$) finds itself in the region very close to the surface, that is: in the Stern layer, and which fraction remains for the diffuse part. This is one of the most recurrent question of double layer science anyway, because the Stern layer coincides with the layer determining χ.

One typical illustration of employing this insight is in establishing the point of zero *charge* (p.z.c.) for amphoteric colloids, that is the point where the total amount of positive charge on the surface is the same as that for negative charge. This is a measurable quantity. For oxides it is a specific value of the pH, to be indicated as pH^o. Tables of pH^o values can be found in the literature.[19] The point is that these points are not identical to the corresponding points of zero *potential.* The difference between the two zero points is just χ, the elusive unknown.

"Elusive" is a disputable notion. Nowadays χ is a popular topic of investigation because many modern techniques do shed some light on it, if not in the literary sense of optical measurements but also by molecular simulation, statistical mechanics, colloid chemical, and even thermodynamic tools. As to the last one, thermodynamics are phenomenological, hence cannot tell something about molecular organization but do teach us how to obtain surface excess entropies, which in themselves are challenging quantities. For example, for the surface of pure water the surface excess entropy, (that is: the entropy of the layer that is responsible for the χ-potential) has been obtained from the temperature dependence of the surface tension.[19] In this way the difference between the surface energy and the surface tension could be quantified. On the other hand, Guggenheim refused to discuss χ at all because of its immeasurability.[20,21] However, if one is not from the very onset at war with model assumptions or approximating experiments, some information about the χ potential of water (χ^w) can, and has been, obtained. It stems from different sides, like making assumptions for single ionic activities for some untypical electrolytes, comparisons between different electrolytes or of ionic Gibbs energies in different media and simulations, jokingly called "experiments". All these "partial" or approximate analyses led to roughly the same order of magnitude of a few tens of mV positive.[19] The positive sign means that water is positive with respect to water vapor: the negative sides of the superficial water molecules (the oxygens) are on the average pointing outward. Recent studies of the present author seem to indicate that that is also the case for water in contact with condensed apolar media like mercury or silver iodide. The conclusion is that the immeasurability of potential jumps between condensed phases is basically upheld, but that there are interesting attempts of measuring the immeasurable. See also briefly sec. 8.2.

Figure 2 illustrates how Lange and Koenig visualized the χ-potential at the boundary between a condensed phase (left) and an aqueous solution (right). The picture is extremely simplified. As to χ^w the authors are thinking of a monolayer of oriented parallel water dipoles, This is a very unrealistic model because forcing all those molecules into parallel positions is entropically very improbable. In fact, the numbers for χ and ψ^o that the authors substitute by way of illustration are about a factor of 10 higher than we now know and the peak at $x = d$ cannot be that sharp. The figure also contains a diffuse double layer part that in their text is not discussed; apparently they envisage that the creation of a double layer by adsorption of charge-determining ions simply comes additively, a view that is mostly adhered to till today.

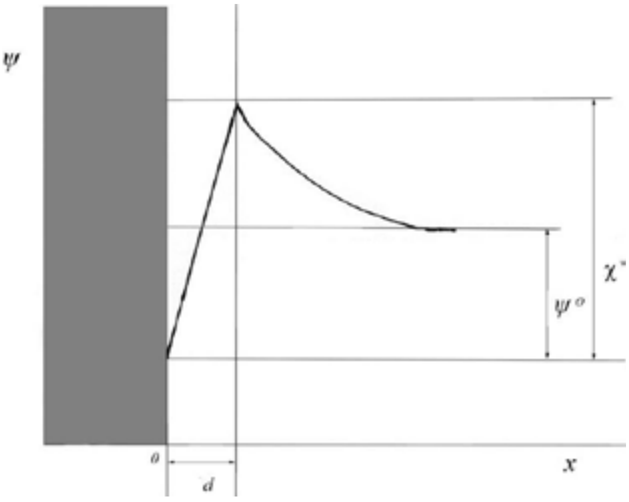


Figure 2. Sketch of the potential jump at a solid-liquid phase boundary as caused by the χ-potential. Modified after ref. 1, their figure 1. Discussion in the text.

In the last pages of their longish (190 pages) paper Lange and Koenig discuss electrokinetic phenomena, emphasizing the complicated influences on the ζ-potential by various electrolytes. In their figure 75 they place the slip plane at the boundary between the Stern layer and the diffuse part, subsuming the χ-potential in the potential of the solid, which is not further discussed, leaving a variety of issues about double layer potentials and charges for their successors., as we shall do in sec.6).

The conclusion of this section is that essentially the impossibility of measuring the absolute value of the potential difference between adjacent condensed phases of different chemical composition is translated into the problem of evaluating the corresponding χ-potential. For many purposes working with charges rather than with potentials is preferable.

5. SILVER IODIDE, THE LUCKY STRIKE OF THE DUTCH SCHOOL

In the years before World War II one of the major challenges in the domain of interfacial potentials and charges was finding systems for which potentials and/or charges could be assessed, if not measured, *both* for macroscopic surfaces and for colloids. For macroscopic surfaces, in electrochemical cells double layer capacitances could at that time be measured with great precision for mercury electrodes, using Wheatstone bridge techniques. For colloids, stability against coagulation and electrokinetic potentials could be measured for several systems with reasonable confidence. However, from mercury it is virtually impossible to make colloidal sols and for colloids it was impossible to determine the surface potential or surface charge. Otherwise stated, systems for which surface potentials/charges and electrokinetic potentials/charges were both measurable did not (yet) exist. It appeared that silver iodide was an excellent candidate to fill that gap.

Colloidal studies with the AgI system have been carried out over more than a century with a major contribution of the Dutch School of Kruyt, Overbeek and offspring. As a model substance for both interfacial electrochemistry and colloidal studies, AgI has many attractive features. The material is chemically nearly inert, its solubility in water is very low (solubility product about 10^{-16} at room temperature), stable sols (many years without perceptible coagulation) can be made of it and the material is very hydrophobic (contact angles for water droplets around 120°). AgI sols are really hydrophobic sols; their stability is exclusively determined by the interaction of overlapping electric double layers. Changes in the surface charge of dispersed AgI can be measured by titration with KI or $AgNO_3$: changes in $\psi°$ obey Nernst's law, with silver and iodide ions charge-determining, *i.e.* changes in the surface charge $\sigma°$ can be measured as a function of changes in pAg or pI. This last fact means that d$\sigma°$ as a function of d$\psi°$ is measurable, so that the differential capacitance $C = d\sigma°/d\psi°$ can be established. For mercury, the primary measurable is also the differential capacitance, hence properties of very disparate materials in different states (macroscopic surfaces versus finely dispersed) can be compared with each other, a most rewarding exercise! Studying all of that does not require information on the absolute values of $\psi°$. Hence, they can be carried out without being thwarted by its principally immeasurability. Given the fact that the point of zero potential cannot be established, one usually refers the point of zero charge for which good experimental methods are available (the common intersection point in Figure 5, see below).

The development of all that insight took several decades and in the following sections some typical achievements in line with the present theme will be considered. For historical reasons it be noted that Kruyt et al. were not the only investigators of the AgI system. For example, older, but more primitive titrations have been carried out by Lange and Berger[22] and for AgBr by Lottermoser and Petersen.[23] One of the first, but still rather primitive, titration of AgI with different Ag salts was conducted by De Bruyn.[24]

5.1 Interaction at Constant Potential or at Constant Charge?

During the Second World War colloid science got a tremendous boost by the publication of the DLVO theory for the stability of hydrophobic colloids.[25,26] The abbreviation stands for Deryagin, Landau, Verwey and Overbeek. The history is well known: the Russians wrote their paper in 1941 in a Russian journal,[25] which because of the war conditions did not make it to the West, whereas the Dutch couple elaborated the theory during the War and then wrote an extensive monography on the matter.[26] It was only after the War that it became clear that the two theories were identical as to the main principles stability is determined by a balance of van der Waals attraction and double layer repulsion. The qualitative insight that the stability of hydrophobic colloids had its origin in the interaction between electric double layers was more or less generally accepted in 1940 but the quantifications, some of them by respectable scientists like Levine and Langmuir, were not successful: after all, it is not so obvious to prove that interaction between two double layers that as a whole are electroneutral are repulsive at any distance between the surfaces. In addition, it must be realized that, say around 1935, the role of attractive van de Waals forces was not yet quantitatively established, so that some investigators even considered electric double layers, that, although electroneutral as a whole, could nevertheless be electrically repulsive over some part of the interaction, but attractive over another range. Now we know that attractive van der Waals forces are quantitatively comparable to electrostatic double layer repulsion forces. However, this part of the story, interesting for its own sake, does not belong to the present theme. Let us state that at the start of the Second World War the main problem was to develop a quantitative theory for the electric double layer repulsion that was strong enough to protect the particles against coagulation by van der Waals attraction. Needless to state that this repulsion is sensitive to the potential - and charge distribution during overlap, which brings us back to the theme of this paper.

A crucial proof of the pudding was to explain the observed extreme sensitivity of the stability of hydrophobic sols to the valence of the counterion (the so-called Schulze-Hardy rule). Both DL and VO were able to do so quantitatively and the two couples arrived at the same law. As to the way of presentation, in particular the motivation of some decisions, the VO book is far more useful than the DL paper: the former gives a careful consideration of all the decisions taken, whereas in DL theory sometimes hand-waving arguments are used. For example, when V and O make a conscientious distinction between double layers at high potential and those at high charge, DL only speak of "strong double layers". In connection with the present theme, we are now dealing with double layers resulting from free ionic charges, which may reside in the diffuse or Stern part; the fact that there exists something like a χ-potential does not (yet) play a role, but may show up later.

As to the elaboration of the electric interaction, DL and VO have in common that both compute the charge and potential distribution between two approaching particles at any distance d using a charging process. In this way, not the energy but the Gibbs energy of interaction is obtained, which also contains the entropic contribution. The interaction Gibbs energy is then found as the isothermal-reversible work to adjust the charge and potential distribution upon increasing the overlap between the two surfaces. In passing, it is a pity that this procedure seems to be forgotten when interaction between more complicated colloids has to be considered, for example upon the interaction of oppositely charged polyelectrolytes, as in the formation of complex coacervates.

Overlap of (diffuse) double layers implies that the two original $\psi(d)$ curves will change. The sum of the two contributions at given distance d is not necessarily additive. For the elaboration of the differential equations describing the potential and charge distributions it is mandatory to know the boundary conditions. Will ψ° remain constant or will it increase? And what will happen with the concomitant charge σ°? Pondering this question, it becomes clear that the problem exceeds that of something purely mathematical: basic physical processes are involved. This becomes immediately clear when eq. (1) is considered. See Figure 3B. Keeping the potential fixed upon the approach of a second double layer of the same charge sign can only be realized by reducing the charge, that is: by desorption of charge-determining ions. This is a *chemical* process. When the double layers are far apart the double layer forms spontaneously; its Gibbs energy of formation is negative. Thus, the origin of the stability has a chemical nature. Case A is the other extreme. Then no ion desorption takes place; upon approach the potential must shoot up and now *electric* work must be done to let the surfaces approach. In reality always repulsion is observed, at any d, but the mechanism can be different. Otherwise stated, equal double layers always repel but not necessarily for

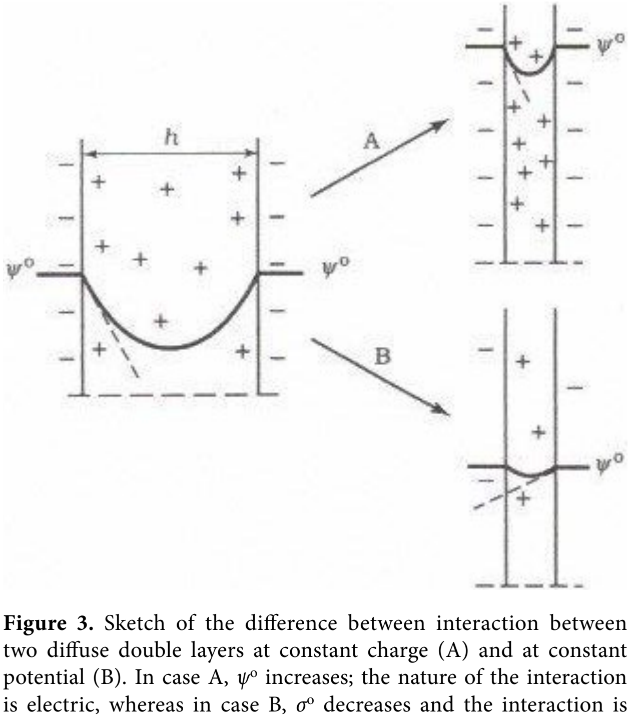


Figure 3. Sketch of the difference between interaction between two diffuse double layers at constant charge (A) and at constant potential (B). In case A, ψ^{o} increases; the nature of the interaction is electric, whereas in case B, σ^{o} decreases and the interaction is of a chemical nature. Dashed lines: the slopes, proportional to the charges because of eq. (1). Reprinted from J. Lyklema, *Fundamentals of Interface and Colloid Science*. Chapter 3: Pair Interactions. **2005**. Elsevier, Amsterdam. Copyright © 2005 Elsevier

electrostatic reasons. Case B could well apply to the AgI system, and most of the oxides. Adsorbed Ag^+ ions have to desorb upon approach. Case A is representative for clay minerals for which the charge is more or less fixed because σ^o is determined by isomorphous substitution of ions inside the solid.

On closer inspection, the distinction between constant potential and constant charge has a dynamic origin. The critical question is whether or not the adsorbed charge-determining ions have enough time to desorb during particle encounter. Supposed we would be able to shoot the particles very rapidly onto each other, so fast that the adsorbed ions would not have enough time to escape, repulsion would still prevail, but the nature of the repulsion would be different.

Returning to Verwey and Overbeek, they realized all of this but for practical reasons had to make a choice which system to elaborate in detail. Not surprisingly, they had the AgI system in mind. Their decision was to treat purely diffuse double layers interacting at constant potential. Theory for such double layers at large separation was available.[11,12] Going for diffuse double layers implied ignoring ion specificity and was motivated by the fact that the challenge of explaining the very dramatic ion valence effect on sol stability was generic (as diffuse layers are) whereas the less pronounced ion specific effect (typically in the Stern layer) depends on the nature of the colloidal material. (In passing, Ref. 26 also contains a section on Stern layers). As a consequence, the DLVO model is that of a diffuse double layer with surface potential ψ^o and surface charge σ^o. The choice for interaction at constant potential was also made with the AgI system in mind: because of the Nernst behavior: ψ^o is determined by pAg and as the latter remains constant upon particle interaction, so does the former. Nowadays dynamic arguments support this choice: the time for particle interaction is large compared to the relaxation time of a diffuse double layer. In summary, the theory considers interaction between two (flat) double layers at fixed ψ^o. In fact, the Russians arrived at the same model, although they did not justify their arguments in so much detail.

In order to apply the theory quantitatively a measure for the stability had to be developed. Nowadays that would go in terms of turbidities, but V and O did not yet have such data at their disposal. The alternative of that time were critical coagulation concentrations (c_c), that are the salt concentrations above which the sol is unstable. At that time, by trial and error a procedure was developed to determine such data with a surprisingly good reproducibility. The procedure involved making series of test tubes containing the sol to which increasing amounts of the electrolytes were added. Using a smart empirical mixture of what is now called perikinetic and orthokinetic coagulation, sharp boundaries between fully coagulated and fully stable sols could be created. The virtue of this time-consuming method was that the relatively complex phenomenon of aggregation could be translated into only one single number, the critical coagulation concentration c_c, a parameter wanting theoretical interpretation.

5.2 DLVO Stability and the Schulze-Hardy Rule

The DLVO relation between the critical coagulation concentration c_c, and the valence of the (z-z) electrolyte can for the present purpose be written as

$$c_c = const \cdot \frac{\left(tanh zy^0\right)^4}{A^2 z^6} \tag{3}$$

where the *constant* contains known quantities (like natural constants, temperature, dielectric constants, etc.) and A is the Hamaker constant, a measure of the van der Waals attraction between the particles, not surprisingly in the denominator. The most crucial parameter is the surface potential, for which the dimensionless abbreviation

$$y = \frac{F\psi}{RT},\ y^0 = \frac{F\psi^0}{RT},\ etc. \tag{4}$$

is used. For the interpretation of the role of the surface potential the dependency of tanh$y$ on y is critical. At sufficiently high potentials the hyperbolic tangent is independent of y and equal to unity. Verwey and Overbeek pondered the issue. They wondered whether they should substitute y^o or the dimensionless electrokinetic potential $y^{ek} = F\zeta/RT$. One argument for the latter was that for hydrophobic sols often a good correlation between zeta potentials and stability was found. However, the desired data available at that time were not yet sufficiently reproducible and it was not clear where the slip plane was located. Hence they fell back on the well-known surface potential, which at the pAg where the stability measurements had been carried out was several hundreds of mV negative, that is, well into the domain where the tanh function equals unity. In that case the critical coagulation concentration is independent of the surface potential and inversely proportional to the 6th power of the (counter)ion valency. In passing, as the Russians considered "strong" double layers, they also arrived at the z^{-6} power.

Establishing this law was the beautiful vindication and quantification of the qualitative Schulze-Hardy rule and it became the justification of DLVO theory, even to the extent that the 6th power was sometimes identified as *the* Schulze–Hardy rule. Verwey and Overbeek tested the inverse 6th power law for critical coagulation concentrations of AgI and other hydrophobic sols. They confirmed the quantitative applicability of the law for the difference between z =1 and z = 2, with as a trend a lower power for the difference between z = 2 and z = 3. This solved one of the main problems of colloid stability at that time. However, it was a pity that for the present issue the result is not useful because the potential does not play a role when it is high enough.

5.3. Hofmeister Series and Stern Layers

Superimposed on the 6th power law of DLVO there is a less dramatic, but certainly quite interesting and not negligible ionic specificity effect. At that time, series of data for different ions of the same valency were called *lyotropic* series. Nowadays, the term *Hofmeister* series is more common. For the critical coagulation concentrations of AgI sols these data were well known. Verwey and Overbeek were familiar with the data by Kruyt and Klompé,[27] which were also obtained during the war time. (Marga Klompé was a PhD student of Kruyt; later she became the first female Dutch Minister of education). In the table her results are given for monovalent nitrates.

Table 1. Coagulation concentrations of some (1-1) electrolytes for AgI sols. Data by Kruyt and Klompé (1942).

$LiNO_3$	165 mM
$NaNO_3$	140 mM
KNO_3	136 mM
$RbNO_3$	126 mM

For alkali ions, the differences in the ion specificities are relatively large, about 30% between Li^+ and Rb^+ as the counterion. Other investigators of AgI find somewhat different concentrations but always the same sequence. As a digression, it depends on the nature of the colloid whether the sequence is in the direction of increasing or decreasing ion radius. Otherwise stated, the Hofmeister *sequence* depends on the surface properties of the colloid. In fact, recent studies have confirmed the fact that generally such series are not properties of isolated ions but of pairs. In passing, it is an idiosyncrasy of the AgI system that for HNO_3 c_c = 137 mM, similar to that for the cations mentioned in the table: the proton behaves as an ordinary counterion, in contradistinction to most other systems. For oxides protons are even charge-determining.

Not knowing how to deal with ion specificity, Verwey and Overbeek just took the average value, 142 mM for the monovalent alkali ions. By the same token, for seven bivalent cations they obtained the average of 2.43 mM. The ratio 142/2.43 = 58.4, is close to 2^6 = 64. They also tested other colloidal systems, like As_2S_3 and Au sols, and positive sols, like Fe_2O_3 and Al_2O_3 which gave rise to Hofmeister series of anions, and grossly confirmed the z^{-6} dependence. So, the interpretation of stability by overlap of the diffuse layers is almost quantitatively explained. This result is still considered as the most important quantitative success of DLVO theory.

Around 1955, when I started my PhD work with Overbeek I focused on the, then still open Hofmeister trend, trying to exploit the other characteristic propensity of the AgI system, namely that it is possible to measure double layer charges by titration. Do the titration charges also depend on the nature of the (counter) ion? In figure 4 results are presented for three of the four alkali nitrates considered in the table.

The p.z.c. is located at pAg = 5.6. To the left of it the surface is positively charged; there the nitrate is the (common) counterion so that no cationic specificity is observable; to the right, at sufficiently negative charge, Hofmeister effects do show up upon increase of the surface charge in the direction $Li^+ < K^+ < Rb^+$. It was a satisfying result of this research that the ion specificity found in the stability recurred in that of the double layer. At

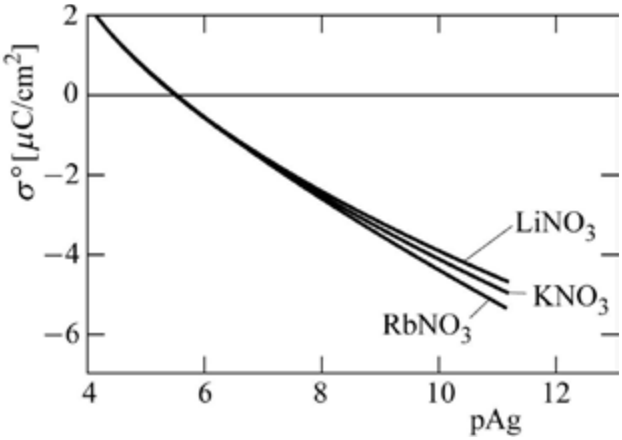


Figure 4. The surface charge on AgI as a function of the pAg in decimolar solutions of the indicated electrolyte, that is the order of magnitude of the c_c. Reproduced from B.H. Bijsterbosch, J. Lyklema, *Adv. Coll. Interface Sci.* **1978**, *9*, 147, Copyright 1978, with permission from Elsevier.

the same time it posed a problem in that the direction was unexpected: along the lines of DLVO one would not expect that sols for which the surface charge at given pAg is higher would correspond to less stable sols.

On mercury the same sequence was found in the surface charge but the alkali ion specificity was lower by about a factor of 10.[28] In fact, had the specificity been so low on AgI, it would have been impossible to measure it at all. Had it been possible to measure the stability of mercury sols, the result as to the Hofmeister effect for alkali ions, would be very dull. This comparison indicates that not only the sequence but also the extent of the specificity depend on the nature of the adsorbent.

Returning to the AgI case, the seemingly contrasting Hofmeister sequences between c_c and σ° proves that one is dealing with the non-diffuse part of the double layer, that is: with Stern layers. For AgI the non-electrostatic affinity increases in the sequence $Li^+ < K^+ < Rb^+$. Rb^+ ions screen the negative potentials near the surface better than Li^+ ions do, apparently because they adsorb stronger. Consequently, at given ψ°, σ° will become more negative but at the same time more of the countercharge is compensated in the Stern layer so that less charge is left for the diffuse part, which controls interaction, hence the lower c_c values.

The combined action of electric and specific interactions in determining double layer properties is also very well reflected in by overall σ°(pAg) curves, given in figure 5. The 10^{-1} curve corresponds to the KNO_3 curve of figure 4. On the r.h.s the surface becomes more negative with increasing salt concentration because of screening of the surface charge by electrolyte. The counterion plays the more important role. A large part has an electrical origin, where, typically for PB theory, the vertical distances between the curves scale as √c. The chemical contributions become visible at higher charges and higher salt concentrations, see also Figure 4. On the left hand side of the point of zero charge the surface is positively charged, this charge becomes even more positive by the addition of electrolyte for the same reason as what happens at the negative side. Only at the point of zero charge there is no charge to screen, hence there is no effect of electrolyte, unless one of the ions adsorbs specifically. In fact, this is the common way of establishing the (pristine) *p.z.c.*, that is the *p.z.c.* in the absence of specific adsorption. For AgI the common intersection point is located at pAg = 5.6 till concentrations of 1 M, where the surface is no longer pristine: a slight shift to the right is observed, indicating specific adsorption of the anion, NO_3^- in this case.

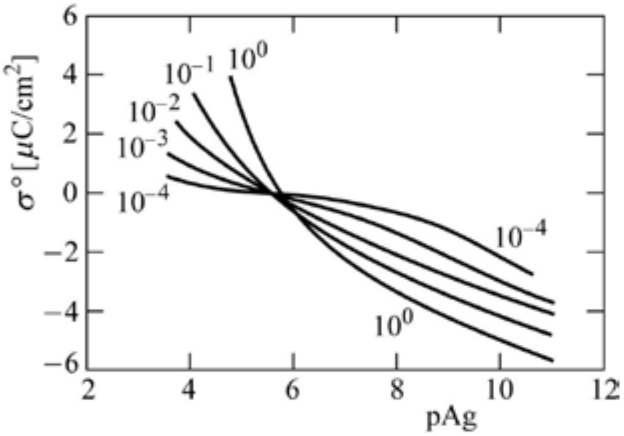


Figure 5. Surface charge as a function of pAg for silver iodide. T = 25°. Electrolyte, KNO_3. The pAg axis may also be read as a ψ° axis with 58 mV per unit of pAg.

So, the double layer properties of colloidal AgI are well understood, without the need of measuring ψ°. It be repeated that the point of zero *charge* is not identical to the point of zero *potential*, which remains immeasurable.

The difference between the pAg of zero potential and that at zero charge is just the χ-potential at the AgI-water interface. When comparing with mercury, the model surface for the electrochemist, it appears that the AgI did become a grown-up counterpart model for which the lesser reproducibility and precision is outweighed by the propensities that double layer charges can be measured because the areas are so large and because the charge-determining ions have been identified.

At this place it is interesting to note that curves like those of figures 4 and 5 have also been measured by the "mercury" method, that is by direct measurement of the differential capacitance of AgI electrodes. The trick is that the adsorption of charge-determining ions is suppressed by working at very high frequencies. The results are very close to those obtained by titration.[19,29]

This does not yet exhaust the analysis. It is obvious from the above that the DLVO idea of a purely diffuse double layer is untenable. At least a Stern layer has to be added, to account for the fact that even the closest counterions cannot approach the layer where the surface ions are located because of their non-zero volume. That gives rise to a thin charge-free layer close to the surface, the so-called zeroth order Stern layer. It has a (differential) capacitance C_i that is in series with the capacitance C_d of the outer, diffuse part of the double layer. The sum capacitance C is given by

$$\frac{1}{C}=\frac{1}{C_i}+\frac{1}{C_d} \tag{5}$$

The total capacitance is dominated by the lower one of the two. When, in addition to the ion size exclusion, also specific ion adsorption has to be considered, eq. (5) has to be modified The point is that Figure 5 shows that the double layer is completely diffuse only over a narrow range of very low potentials. The differential capacitance of a purely diffuse double layer depends on ψ° according to a cosh function, which has a minimum at the p.z.c. For AgI these capacitances are, except for a constant, the slopes of the curves in this figure. Obviously such a minimum is clearly visible only in very dilute solutions around the *p.z.c.* This conclusion is at variance with the popular statement that one has worked with a "diffuse double layer with Stern corrections". Nevertheless, as long as no specific adsorption is detectable, the relation between charge and potential for diffuse layers remains valid, except that the diffuse part does not start at the surface but at a short distance from it, corresponding to the thickness of the Stern layer.

Figure 6 illustrates how we look nowadays at the structure of double layers. The distinct subdivision between a diffuse and a non-diffuse part is well-motivated and has many practical advantages, even if we neither know exactly how thick the Stern layers are, nor how much charge they contain. All short-range effects are subsumed in it, so that beyond this layer the layer is purely diffuse, where Gouy-Chapman theory does apply with impunity. Depending on conditions the diffuse part may contain all or only a minor part of the countercharge but even if this is only a low fraction, it nevertheless plays a dominant role in colloid stability and rheology.

Figure 6a is the most simple double layer with a charge-free Stern layer. In this case the diffuse charge σ^{d} equals minus the surface charge, which is measurable. For a flat double layer (in practice, for $\kappa a >> 1$) Gouy theory has derived the following useful equation,[19] relating the surface charge to the diffuse potential ψ^{d} ($y^{d} = F\psi^{d}/(RT)$):

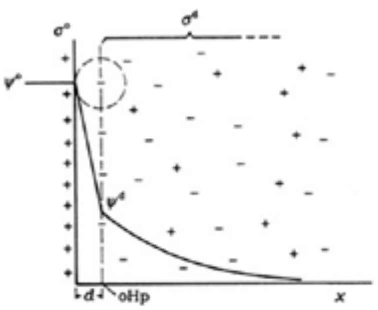
$$\sigma^{d} = -\sqrt{8\varepsilon\varepsilon_{0}RT}\, sinh\ \frac{zy^{d}}{2} \tag{6}$$

In the inverse situation, when the charge has been measured, the potential follows from its inverse:

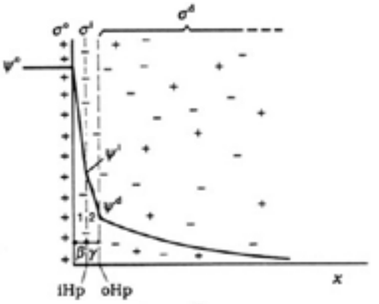
$$y^{d} = \frac{2}{z} sinh^{-1}\ -\frac{\sigma^{d}}{\sqrt{8\varepsilon\varepsilon_{0}RT}} \tag{7}$$

This equation is often used in electrokinetics, where the charges on moving particles are measured but where these charges are by force of habit converted into ζ-potentials, (sec. 6).

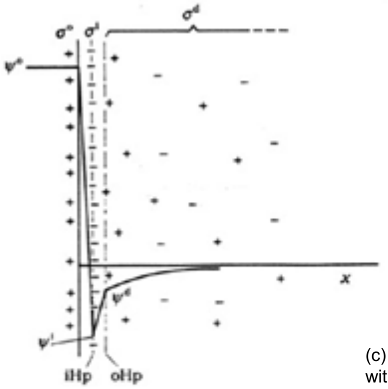
Figure 6b is characteristic for situations where ion specificity is observed, as in the AgI case of figure 4. The specifically adsorbed charge is called σ^{i} and the potential at their locus of adsorption is denoted ψ^{i}. Sometimes the planes where the specifically adsorbed ions reside and the plane from whereon the layer is diffuse are called the "inner and outer Helmholtz layer" (iHp and oHp, respectively). As to our present theme, ψ^{i} is immeasurable. Eq. (6) remains valid, of course, but only for the diffuse part. Beyond that, its application becomes problematic because from the charge balance $\sigma^{\circ} + \sigma^{i} + \sigma^{d} = 0$ the diffuse charge σ^{d} cannot be computed (unless additional data are available, see sec 5.4). In this connection, eq. (6) is often used under conditions where it is not



(a) Gouy-Stern double layer without specific adsorption. Finite counterion size.



(b) Gouy-Stern double layer with specific adsorption.



(c) Gouy-Stern double layer with superequivalent adsorption.

Figure 6. Actual view of Gouy-Stern double layers. Taken from Ref. 19 with permission. Copyright © 1995 Academic Press. Published by Elsevier. Discussion in the text.

allowed. Perpetrators are psychologically lured by the scientific magic and apparent rigor, and by the suggestion that unknown potentials can seemingly, but erroneously be identified. With three unknown potentials and two unknown charges there are six ways of going wrong and only one of them is correct.

Turning to Figure 6c, this is a sketch of the potential distribution in cases where the double layer contains more countercharge in the Stern layer than needed to compensate the surface charge. This phenomenon is commonly called overcharging. Several theories have been proposed to explain it. For the AgI case, and probably much more generally, overcharging occurs for counterions of higher valency if they hydrolyse in the adsorbed state. The hydrolyzed complexes have a strong chemical affinity to the surface. That this is the right mechanism can be proven by systematically investigating the pH dependence of the charge inversion.[30] So, it is a chemical, rather than electrical phenomenon.

5.4 DLVO Theory Revisited

It is obvious from the previous sections that the premises of DLVO theory, notwithstanding its successes, have to be reconsidered. The main correction is that only part of the counterlayer is diffuse and that the potential of the diffuse layer is not ψ° but ψ^d. The latter potential is quite a bit lower than the former and depends on the nature of the counterion. Let us consider these points systematically.

Is ψ^d measurable? There is no argument against measurability of the nature as we invoked when explaining why ψ° is immeasurable, because the location of the potential ψ^d is in the same solution as the reference. On the other hand, ψ^d is a model parameter; it is based on a number of assumptions. The most relevant is that of having replaced some gradual functions by step distributions, say the extent to which the dielectric permittivity changes with distance. So, in practice quantification is rather a matter of doing independent experiments that give information on the charge of the diffuse part of the double layer only and then subtracting that from the total (titration) charge to find how much is left for the inner layer. Electrophoresis is one of these (a double layer with only a Stern layer as the counterlayer will not move in an electric field), to which we shall come back in sec. 6. Electrokinetic potentials are difficult to measure for systems on the verge of instability, but the order of magnitude is at least a factor of ten lower than the ca. 400 mV assumed for ψ° in DLVO theory. This means that in (3) it is no longer allowed to replace the hyperbolic tangent by its high potential limit (unity), rather tanh*y* must rather be replaced by the first term of its series expansion, tanhy ≈ y. Consequently for the coagulation concentration we obtain instead of (3),

$$c_c = const' \frac{\left(\psi^d\right)^4}{A^2 z^2} \tag{8}$$

So, for low diffuse double layer potentials ψ^d can be obtained from stability measurements. The inference is that the interpretation of the Schulze-Hardy rule is more complicated than expected by DLVO. An exact z^{-6} power would require ψ^d to scale as z^{-4}. More pertinent to the present theme is the finding that ψ^d depends on the nature of the counterion in the Stern layer, hence the Hofmeister effect is automatically incorporated. It is a small step to consider again charges instead of potentials, by moving further and use (6) to compute σ^d, subtract that from σ° (from titration) to find the Stern charge σ^i. In many situations the charge in the diffuse part is only a minor fraction of the total. In those cases one does not have to estimate σ^d very accurately but still find for σ^i an acceptably correct value. Applying the Frumkin-Fowler-Guggenheim adsorption isotherm equation (a modified Langmuir isotherm) it is even possible to estimate the specific ionic Gibbs energy of adsorption of the alkali cations on silver iodide.[31] The ranges are 2.3 - 3.6 *kT*, 2.5 - 4 *kT* and 2.9 - 4.2 *kT* for Li^+, K^+ and Rb^+, respectively. (The uncertainty margins are mainly caused by the uncertainties in the assessment of ψ^i). That is about as a far as we can get with classical means for a well-studied model system. Similar exercises have also been carried out for other systems, like oxides.

The general message is that for a proper handling of interfacial potentials measuring absolute values for the surface potentials are not needed and that there are advantages in considering charges instead.

Introduction of a Stern layer has also an important advantage when considering the interaction dynamics. Recall that, according to DLVO theory, interaction at constant (surface) potential required discharging of the particles upon encounter. For negatively charged AgI sols that would mean desorption of adsorbed I^- ions and transporting them through the narrowing gap between the approaching surfaces toward the open space further away. This does not look like a simple and fast process. On the other hand, if there are two Stern layers between the surfaces, discharging can be rapidly realized by the formation of ion pairs between surface charges and the close-by counterions.

This, somewhat extended, review of the AgI work illustrates how far one can get nowadays with the simple Gouy-Stern picture without worrying about the immeasurability of ψ°. It is questionable whether more advanced models would work better because of the inherent imperfections of solids such as the reproducibility of the interface, and the homogeneity of the surface charge distribution.

6. ELECTROKINETIC POTENTIALS.

Having dealt in some detail with the (im)measurability of various static potentials it is appropriate to also consider the domain of electrokinetic, or zeta (ζ) potentials. The main reason for that decision is their outstanding practical relevance for colloid stability and hence for much industrial process control. As over the years the instrumentation has become quite sophisticated, measuring them is nowadays more or less routine, but instead now the interpretation is the issue. In particular the question is how electrokinetic potentials match into the static pictures of figure 6? Anticipating the discussion, we shall show that in many practical cases identifying the slip plane with the (oHp) plane where the diffuse part of the double layer starts appears to be a very acceptable approximation. This identification has no scientific background, but it adds to the accessibility of ψ^{d}.

Electrokinetic potentials are very different from static potentials. They do not relate to equilibrium situations but to stationary state processes, involving tangential shear parallel to the surface. It leads to slip between a thin liquid layer, close to the surface, that remains stagnant and a mobile layer in which charge transport takes place. The shearing motion creates a potential difference between the tangentially mobile and the tangentially stagnant parts of the liquid. Phenomenologically it looks as if the fluidity of the liquid decreases rapidly with distance from the (solid) surface, but for lack of simple theory about this, the fluidity profile is usually replaced by a step function with a slip plane, where the fluidity increases jump wise from zero to its bulk value. The double layer potential at the slip plane is identified as ζ.

Of the many electrokinetic phenomena we shall emphasize electrophoresis, perhaps the most familiar illustration, and indeed suitable to discuss how ζ-potentials fit into the picture. For a more extended review see Ref. 32. Many equations have been derived for converting electrophoretic mobilities into ζ-potentials, depending on the nature, size and shapes of the particles and their conductivities. Here, we shall consider two limiting cases: spherical, non-conducting particles for high and low κa. The equation for converting the electrophoretic mobility u into a zeta potential depends on κa where κ is the reciprocal Debye length and a the radius of the (spherical) particle. For the κa >> 1 limit the Helmholtz-Smoluchovski relation is

$$u = \frac{\varepsilon_0 \varepsilon \zeta}{\eta} \qquad (\kappa a \gg 1) \qquad (9)$$

whereas for κa << 1 the Hückel-Onsager equation applies, which reads

$$u = \frac{2\varepsilon_0 \varepsilon \zeta}{3\eta} \qquad (\kappa a \ll 1) \qquad (10)$$

Equation (9) is characteristic for dilute sols of small particles whereas (10) rather represents macroscopically flat surfaces, where the flow takes mainly place parallel to the surface. Equations also exist for intermediate κa cases. We shall not worry here about these and neither about surface roughness problems, although these are very relevant for daily practice.

Equations (9) and (10) are straightforward: a mobility is measured and the ζ-potential follows directly, by force of habit. This procedure looks as a direct measurement of a potential. However, as stated in sec. 1, things are not as they like. Rather a charge is measured, which is converted into a potential. For example, in the derivation of (10) this step involves the writing of the total charge Q as $4\pi a \varepsilon_o \varepsilon \zeta$. This is a decent equation of electrostatics where ζ stands for the potential at the surface of a charged sphere with radius a. However, electrostatics does not consider something like a slip plane or stagnant layer; hence the border between the moving particle and the stationary fluid is taken to be identical to the borderline between the solid and liquid, demanding that ζ and ψ° coincide. A colloid scientist would therefore rather say that a is the particle radius, inclusive the stagnant layer. A similar argument can be presented for the derivation of (9). In this case the Poisson equation is used, which relates the space charge density to the second derivative of the potential, similar as in the derivation of (1).

For all electrokinetic phenomena the question is what determines the existence of a slip plane. By what factors is it determined? It is imaginable that some of the fluid molecules, in close or immediate contact with the surface could remain somewhat adhered to that surface, and it could also be imagined that upon increasing distance from the surface the fluidity would gradually increase with increasing distance. As stated, the basic electrokinetic assumption is that for practical purposes the gradual transition from stagnant to mobile may be replaced by a step function. Such a step function was also assumed for the double layer potential to introduce ψ^d. Given the very different origins for assuming a step function in the potential and in the fluidity there is no *a priori* reason for assuming the outer Helmholtz plane and the slip plane to be identical. Or, for that matter, assuming ψ^d and ζ to be identical. Nevertheless, experience has shown that often the two are so close that they are experimentally indistinguishable.

Perhaps the most cogent argument for identifying the oHp and the slip plane is in the very meaning of the slip plane: it separates the electrokinetically active charges from those inactive. The former category coincides with the diffuse parts of the double layer, the latter with the Stern part, just as is the case for the oHp. Ions in the Stern layer are not electrokinetically active (a particle with a Stern layer around it will not move in an electric field), although the ions there are not immobile (they do contribute to the surface conductivity). So, the oHp and the slip plane have in common that for both the outer side is the diffuse part of the double layer. Hence, for both can we apply equations (6) and (7) to relate charge and potential of the diffuse part.

In order to better understand the slip process, in Figure 7 for some amphoteric model systems the electrokinetic and surface charge are plotted. These are all experimental data, the only difference with more classical measurements is that charges are plotted instead of potentials. This makes the role of the position of the slip plane better visible.

The skewed straight line ($\sigma^{ek} = \sigma^o$) would apply if the thickness of the stagnant layer would be zero (slip plane coincides with solid-liquid boundary), or if the diffuse layer is so extended that no measurable amounts of charge are detectable between the surface and the slip plane. This limit is always reached for very low surface charge, say about 1 μC cm^{-2}. But when the surface charge becomes a bit higher, the electrokinetic charge always falls far below that of the surface charge, meaning that a relatively large fraction of the countercharge resides within the stagnant layer. Electrokinetic charges are not very high. About 2.5 μC cm^{-2} appears the maximum that can be reached, independent of the nature of the surface. This charge can be compared with the surface charge which can become 10 times as high, especially for oxide surfaces. So, only a minor fraction of the counterlayer is electrokinetically active. The same may be stated about the fraction of the countercharge that is accounted for by the diffuse parts of the double layer. Also in this respect there is a definite analogy between the diffuse part and the electrokinetically active double layer part.

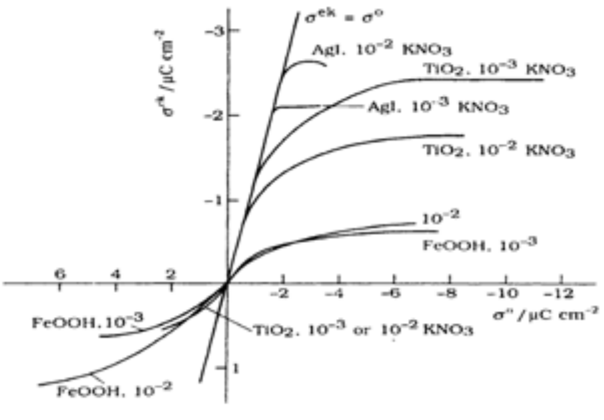


Figure 7. Comparison between electrokinetic (σ^d) and surface charges (σ^o) for a number of amphoteric model colloids. Taken from Ref. 32 with permission. Copyright © 1995 Academic Press. Published by Elsevier.

A second striking point is that the influence of indifferent electrolyte is not as strong as when the data would have been presented in terms of potentials. For iron oxide the 10^{-2} and 10^{-3} curves even coincide. It would be interesting if more data of this kind would become available to generalize this observation.

Given the present query about the nature of the slip process this figure contains some interesting pieces of information. Consider first the situation with the iron oxide (FeOOH), which is typical in that it is rather symmetrical with respect to the point of zero charge. This important observation means that the stagnant layer is the same to the right (surface negative) as to the left (surface positive) of the point of zero charge; it does not depend on the *sign* of the charge. Stagnant layers must also be present around the zero point of charge, even though there we cannot electrokinetically measure them. We conclude that the formation of macroscopically stagnant layers is a *hydrodynamic* phenomenon; it does not have an electrical origin and the double layer is there only to measure and quantify its existence. For rutile (TiO$_2$) the situation is less symmetrical but here the presence of a stagnant layer on the uncharged surface is beyond discussion.

Stagnant layers are not very different between hydrophilic and hydrophobic surfaces: compare the hydrophobic AgI with the hydrophilic oxides. This observation means that attraction between water in the first adjacent rows and the surface does not lead to thicker stagnant layers. Neither is there a thin empty layer between the AgI surface and the first adjacent bulk water along which the liquid could slide away (of course, sliding might occur if the interfacial layer would contain microscopic air bubbles).

The collected inference on the slip process is that stagnancy results from the mutual *repulsion* between adjacent fluid molecules. This repulsion gives rise to a layer-like ordering in the fluid: the density distribution exhibits a few maxima and minima, petering out rapidly with distance. As this mutual stacking of the water molecules holds for all liquids in contact with solid surfaces the phenomenon is general. One must therefore expect that also for non-aqueous systems such a process with slip occurs.

The general conclusion is that the observations made are sufficiently relevant to look for additional information on well-defined systems

7. POTENTIAL DANGER?

In May 2014 a conference on electrokinetic phenomena took place in Gent (Belgium). At that occasion a problem surfaced with the measurement of electrokinetic potentials. As this issue has its ramifications it deserves paying attention. The problem had to do with the sophistication of instrumentation that went so far that the very truth was huddled in uncertainties about the software.

At the beginning of electrokinetic investigations, say about a century ago, measuring electrophoretic mobilities was very laborious. Stable sols had to be made, thin homogeneous glass tubes blown, arrangements made to view the motion of individual particles ultramicroscopically, and exhausting velocity measurements carried out on different levels inside the capillary. Inconvenient as such measurements were, they had at least the advantage that the individual behaviour of the particles could be directly observed. With time novel techniques were developed and marketed; in the first place those based on laser-Doppler techniques. More recently very powerful instrumentation was developed on the basis of modern techniques that could, hand-waivingly summarized as electroacoustics.[32] Very sophisticated instruments based on these principles are now commercially available. They allow fast electrokinetic and rheological studies of concentrated systems in a variety of media. Industrial labs are willing to pay prices of the order of 10^5 € apiece. The challenge is that the road from primary data to the desired end product is long and replete with problems. The ways in which these problems are solved depend on the different providers and is so deeply hidden in the software that the average user will not notice them.

During the conference mentioned above, a discussion developed when measurements of the electrolyte concentration dependency of silica sols in alcohol, measured by two electroacoustic apparatus of differing provenance, did give different results for the zeta potentials.[33] (The difference was smaller if electrokinetic charges were considered instead of potentials). The roots of this difference must be attributed to differences in the software and in the assumptions made in developing it. At the time of the meeting representatives of both industries were present but they were not available to explain how their software worked on grounds of propriety arguments.

Although the dispute did not assume Faustian dimensions it is mandatory to remain alert on the possibility that such issues may develop more easily than with less sophisticated apparatus. Anticipating and dealing with them involves also an ethical aspect.

8. STILL OTHER POTENTIALS

Or should we say "still other ways to measure (interfacial) potentials"? More recently, increasingly sophisticated techniques have been developed for "measuring" surface potentials and more will become available. Do these attribute really new insights or do they just reflect a repetition of techniques already considered? We shall briefly discuss two of those developments, anticipated in two of the quotes with which we started this discussion.[4,5]

8.1 Surface Potentials from AFM and Related Techniques

To this category belong the several techniques by which properties of a surface are measured by probing it with a probe, measuring the force of interaction as a function of distance and position. When the force that the probe experiences as a function of distance obeys classical laws of colloid interaction (say, an exponential decay with distance) extrapolation to zero distance yields a "surface potential". However, this is not our (immeasurable) ψ^{o} but ψ^{d} because the exponential decay only applies to the interaction of diffuse double layers. So, the immeasurability is not affected although measuring ψ^{d} has its virtues.

8.2 Surface Potentials from Non-Linear Optics

This is a new development with a physical basis, which offers promised additional information on measuring interfacial potentials. The techniques involve modern developments of surface spectroscopy and go under acronyms like SHG (second harmonic generation), and

SFG (sum frequency generation).[34-36] For our present purpose the challenging new element is that molecules can be studied that are located under non-centrosymmetry conditions, implying that in a two-phase system molecules at the interface are selectively measurable, in fact through their molecular susceptibilities. Charges at the interface lead to an additional dipole contribution, which is measurable and can be analyzed to produce an interfacial potential. Which potential?

It is obvious that, as far as our present theme concerns, the added value refers to the Stern part of the double layer, not to the diffuse part. This is immediately seen in figure 6, where the high field strengths (slopes of the curves) are almost exclusively in the Stern part. In fact, the habit of dividing the counterlayer in a diffuse and a non-diffuse part tacitly presumed ideality, and hence centrosymmetry, of all ions in the diffuse part. More arguments can be given, such as the fact that the charges in the Stern part (figure 7) are too low for dielectric saturation. All of that is a happy coincidence because the Stern part is much less understood than the, relatively dull, diffuse part.

In practice, so far only very few elaborations have been given leading to values of a potential, be it ψ^{o} or ψ^{i} or still something else. These elaborations are somewhat suspicious because they contain hyperbolic functions, typical for the diffuse part only. The conclusion is that here is a field awaiting systematic elaboration from a team containing physicists and colloid scientists.

9. CONCLUSIONS

The issue of surface potential measurement is considered in a historical context. The absolute value of the potential difference between two condensed phases is and remains principally immeasurable. Changes in it as a function of the composition of one of the phases are sometimes accessible, with Nernst's law as a typical illustration. Immeasurability does not mean that no theories can be made for them. Many of these attempts belong to the domain of model approaches to assess interfacial potential jumps χ. Avoiding these immeasurabilities, a variety of other interfacial potentials have been introduced. These are discussed with a critical evaluation of the steps and assumptions to be made in order to assess them. Several interfacial systems are more transparently analyzed if interpreted in terms of charges rather than of potential. It is recommended to change the notion of "potential-determining ions" into "charge-determining ions".

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Substantia
An International Journal of the
History of Chemistry

Firenze University Press
www.fupress.com/substantia

Citation: H. Bouas-Laurent, J.-P. Desvergne (2017) The Master and the Slave. A glance at the social life of molecules. *Substantia* 1(2): 95-98. doi: 10.13128/substantia-29

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The authors declared that no competing interests exist.

Feature Article

The Master and the Slave. A glance at the social life of molecules

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Abstract. Low energy interactions induce the formation of molecular assemblies that can display a large variety of sizes and shapes such as dimers, oligomers, colloids, gels, helices, cylinders, etc. These grouping modes mimic human relationships, as people generally flock together according to their affinities. Moreover, chemical reactions, undergone under strong energy interactions, that result in bond breaking and formation of new compounds, can also be compared to human behaviour.
The fables usually involve animals but rarely molecules to play the role of human beings. In this article, we report a molecular tale where two different 9-substituted anthracene derivatives compete in a photochemical reaction, simulating the behaviour of a master and a slave, respectively.

Keywords. Molecular sociology, photochemistry, aromatic endoperoxides, singlet oxygen, graduate education.

INTRODUCTION

Oil and water are known to repel each other. Despite shaking a mixture of the two in a bottle, they quickly form two distinct layers. The substances soluble in oil are called lipophilic (vitamines A, D, E...) whereas those soluble in water are said to be hydrophilic (sugars, amino-acids...). Fats cannot be eliminated with pure water, but require the use of surfactants to bring them into solution. These substances have affinity both to oil and water and contribute to form a single macroscopic phase.[1]

Such behaviour results from low-energy intermolecular interactions as compared to much stronger ones governing molecular bonds. Non-covalent intermolecular associations are wide-spread in abiotic as well as in biological systems and are fundamental for the formation of molecular assemblies. These can be very diverse: dimers, oligomers, cylinders, helices, colloids, liquid crystals, cellular membranes, to cite but a few. They form the basis of "supramolecular chemistry".[2]

The affinities between molecules mimic human relationships. An interesting example was reported by Green *et al.* in the form of *sergeants* and *soldiers*.[3] Alkylisocyanates copolymers are known to adopt a rigid helical conformation in solution. The authors observed that, in solutions of copolymers formed from chiral and achiral monomers, even a small proportion (ca 1%) of chiral monomers induced a high enantiomeric excess; thus, a small number of chiral motifs (playing the role of sergeants) can trigger the movements of a large number of achiral motifs (the soldiers).

Apart from the above soft interactions, chemical reactions transform starting materials into products, through bonds breaking and bond formation. *This activity may also be compared to human behaviour.* For example, in his third novel "the elective affinities",[4] Goethe compared acid-base reactions to love affairs between human couples. Amongst other reactions, one of them inspired Cohen *et al.*[5] who compared molecules to *wolfs* and *lambs*, like in story tales. Here, two molecules, reacting fiercely with one another in solution and leading to a mixture of products, become mutually inactive when tightly linked to two different polymers (Merrifield resins); a third reactant, in solution, reacts successively with one of them (the wolf) then with the second (the lamb), to generate a single product with high yield.

In this article, we describe a particularly relevant reaction where two different molecules (M and E) compete in an addition reaction to a special reactant produced *in situ* through light irradiation. The reaction, which is reminiscent of human behaviour, is briefly described below.

MATERIALS AND METHODS

Formation of endoperoxides

9,10-Endoperoxides "AO_2" (Figure 1) are formed by a hetero Diels-Alder addition of singlet oxygen ($^1O_2$) to anthracenes "A".[6,7,8] Singlet oxygen can be generated by several processes. One of them, photosensitization,[9,10,11,12] involves energy transfer from an organic compound in its excited triplet state (T_1). Anthracene derivatives can be good singlet oxygen producers when they have high yields of triplet formation.[8] The energy transfer from the triplet state and dioxygen leads to singlet oxygen $^1O_2$ which can participate in the addition reaction as shown in Figure 1.

The two anthracene derivatives considered here are 9-isopropyl (E) and 9-tertiobutyl (M) anthracene. Although E was found to readily generate $^1O_2$, M was shown to be unable to do so.[8] The primarily reached photochemical state is deactivated much too fast and no triplet state can be formed; therefore M cannot act as a sensitizer.[13,14] Thus, irradiation of E in solution in the presence of dioxygen generates the endoperoxide "EO_2" in high yield. Under the same experimental conditions, M is not transformed into "MO_2" and remains unchanged.

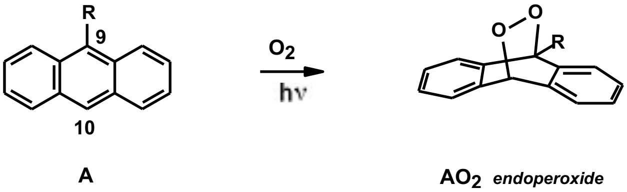

Figure 1. Addition of singlet oxygen to 9-alkylanthracenes (hetero Diels-Alder reaction).

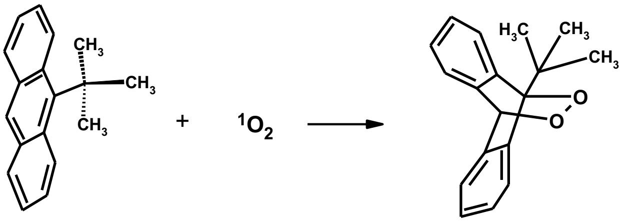

Figure 2. Developed formulae of M and MO_2 respectively, suggesting the steric overcrowding due to the tertiobutyl substituent.

Competition reaction

The irradiation through Pyrex of an equimolecular mixture of E and M in solution in dioxygen-saturated ether, at room temperature initially leads to the exclusive formation of the endoperoxide of M (MO_2), Figure 2. Then, after the complete transformation of M, the reaction of E with singlet oxygen begins, leading entirely to the formation of EO_2.[8] The sequence is illustrated in the following sketches: (1), (2) and (3) of Figure 3.

One observes that M, the most crowded molecule, is considerably more reactive with $^1O_2$ than E. This is called a steric acceleration, due to a relief of strain in the activated complex that is product-like. The same phenomenon was also noted for other anthracene derivatives.[15] The thermal and photochemical stability of the two adducts during the reaction attests to its irreversibility.[8,16]

CONCLUSIONS

Master and Slave

The above molecular behaviour is suggestive of human attitudes. Singlet oxygen might be compared to food, produced only by E, the slave. As soon as the food is available,

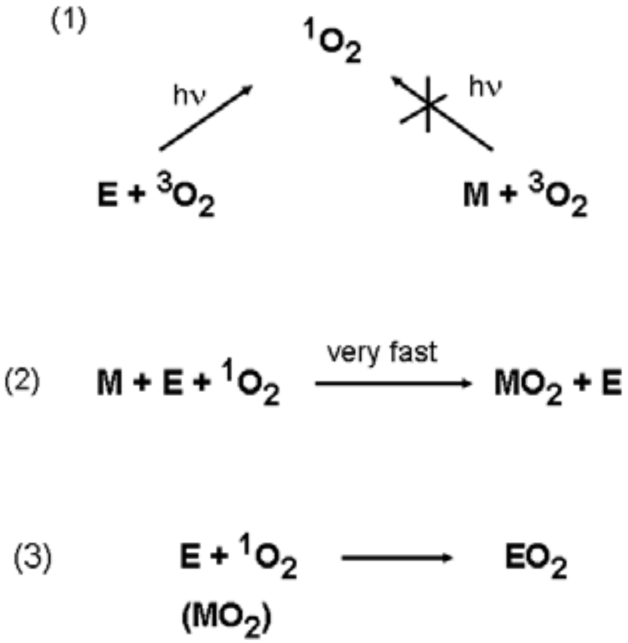

Figure 3. (1) A solution of M and E in equal amounts is irradiated under dioxygen bubbling; E produces singlet oxygen (the food) in contrast to M, which is unable to do so. (2) M swallows and consumes all the food available. (3) M being entirely transformed into MO_2, E can in turn eat the food and generate EO_2.

M (the master) rushes at it in a gluttonous manner until he has eaten his fill. When he has gorged himself, then the poor slave is allowed to eat. The story stops there because after the meal, both master and slave are in a peaceful longstanding state. The nasty master is not punished, in contrast to what generally happens in fairy tales.

One could imagine other scenarios:

1) instead of an equal number of E and M, an excess of M would lead to an accumulation of MO_2; thus a single slave would work for many masters. This would delay the meal time of E.

2) if the irradiation is stopped after M's hunger is satisfied, then in the dark, E would no longer produce the food and be doomed to be starving for ever.

Today, slavery has been abolished on earth. However, it seems that some inactive people are prompt to eat what others have strained to produce. This observation might be extended to relationships between countries.

It could be argued that human beings have common ancestors in the Mendeleev table, especially carbon, hydrogen, oxygen, etc., and that their reptilian brain keeps traces of their molecular constitution; this might partly explain their shocking deeds. However, the extreme complexity of human behaviours cannot be traced back to simple chemical reactions.

Let this short tale contribute to inspire to everybody with a humble attitude.

ACKNOWLEDGEMENTS

The authors are grateful to Dr Esther Oliveros for her precious information about singlet oxygen and Prof. Dr Herbert Dreeskamp for perceptive comments. We warmly thank Dr Dario Bassani for valuable linguistic assistance.

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Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Citation: S.C. Rasmussen (2017) The Early History of Polyaniline: Discovery and Origins. *Substantia* 1(2): 99-109. doi: 10.13128/substantia-30

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declared that no competing interests exist.

Historical Article

The Early History of Polyaniline: Discovery and Origins

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Abstract. Prior to the discovery of its conductive properties in the 1960s, polyaniline was studied and applied as a variety of colored materials and dyes. The history of the discovery and origins of polyaniline are presented beginning with the initial oxidation of aniline by F. Ferdinand Runge in 1834 and concluding with the first electrochemical oxidation of aniline by Henry Letheby in 1862. In the process, the reports of aniline oxidation products between 1834 and 1862 are evaluated and discussed in light of modern knowledge, highlighting the various historical contributions to the current field of conjugated polymers. Finally, an initial argument for polyaniline as the first synthetic organic polymer is presented.

Keywords. Polyaniline, aniline black, emeraldine, conjugated polymers, oxidative polymerization.

INTRODUCTION

Modern society is largely a plastic-based culture in which organic plastics have become more ubiquitous than other common materials such as metals, glass, or ceramics. As a result, some have postulated that there is sufficient justification to refer to the period beginning with the 20th century as the Age of Plastics.[1] The bulk of commercial plastics are made up of various saturated organic polymers that are primarily electronic insulators. In contrast, conjugated polymers (Figure 1) are a less common class of organic plastic materials that are native semiconducting materials. In addition, these materials are capable of enhanced electronic conductivity (in some cases quasimetallic) in either their oxidized (p-doped) or reduced (n-doped) state.[2,3] Conjugated polymers are thus organic materials that combine the conductivity of traditional inorganic materials with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs.[2,3] This unique combination of properties has led to considerable fundamental and technological interest in these materials over the last few decades, resulting in the current field of organic electronics. In the process, a variety of modern technological applications have been developed, including sensors, electrochromic devices, organic photovoltaics (solar cells), field effect transistors, and organic light-emitting diodes (OLEDs).[2,3]

ISSN 2532-3997 (online) | DOI: 10.13128/substantia-30

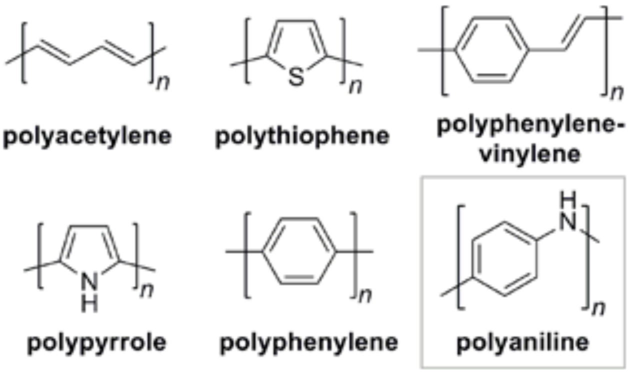

Figure 1. Common parent conjugated organic polymers.

Discussion of the history of these materials typically begin in the mid-to-late 1970s with the collaborative work on conducting polyacetylene by Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger,[4-7] for which they were awarded the 2000 Nobel Prize in Chemistry. The common view that their work marks the historical origins of these materials is further supported by the language of the award which states that it is "*for the discovery and development of electrically conductive polymers*".[8] More recently, however, a number of reports have begun to reveal a more accurate and complete account of the history of these materials, highlighting in particular the documented efforts that predate the commonly cited polyactylene work of the 1970s.[9-16]

The first report of the conductive nature of these materials was by Don Weiss in 1963,[17-19] but the general study of these polymeric materials far predates even this pioneering work. Of the core parent polymers given in Figure 1, the oldest of these materials is generally considered to be polyaniline, although exactly when this material was first studied is often a point of debate. Various authors have credited different figures with the origin and discovery of this material, originally known as aniline black.[20-22] These figures have included F. Ferdinand Runge[20-23] (1794-1867), Carl Fritzsche[9,20] (1808-1871), John Lightfoot[24,25] (1831-1872), and Henry Letheby[11,26] (1816-1876). The current report will attempt to evaluate the work of these figures in light of current knowledge and thus present the first detailed account of the discovery, origins, and development of polyaniline up through the 1860s.

CURRENT KNOWLEDGE OF POLYANILINE PRODUCTION AND CHARACTERISTICS

In order to be able to evaluate the work of the researchers above, it is first necessary to briefly review our modern understanding of the chemistry and characteristics of polyaniline. Polyaniline is readily produced by oxidative polymerization, via either chemical or electrochemical oxidation of aniline.[21,22,26,27] Most often, such oxidations are carried out in acidic aqueous environments with a pH below 3-4, which is most favorable for the production of the polymeric product.[21,22] A significant excess of oxidant is required due to the fact that polymer product undergoes oxidation at a lower potential than the initial aniline, thus consuming oxidant that cannot contribute to polymerization. As a consequence, the polymer product is also always isolated in its oxidized (p-doped) form. Neutral, non-doped samples are possible, but must be obtained via reduction following the oxidative polymerization process. Polyaniline can thus occur in a number of well-defined oxidation states, of which isolated polymer samples are viewed to exist as averages of these forms.[22,27] These states and their corresponding names were initially proposed by Arthur G. Green (1864-1941) and Arthur E. Woodhead in 1910,[28-31] and range from the fully reduced *leucoemeraldine* through the partially oxidized *protoemeraldine*, *emeraldine* and *nigraniline*, to the fully oxidized *pernigraniline*. The three primary forms are given in Figure 2. It should be pointed out that the terms *emeraldine* and *nigraniline* predate the

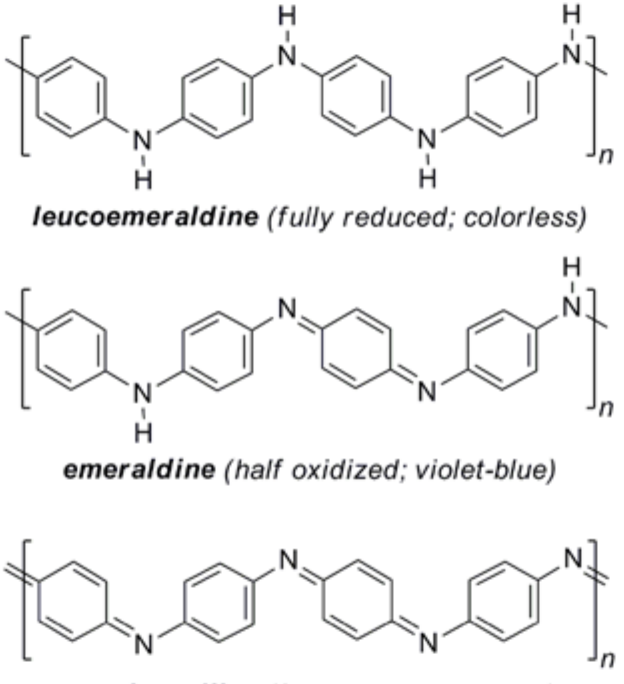

Figure 2. Primary oxidation states of polyaniline.

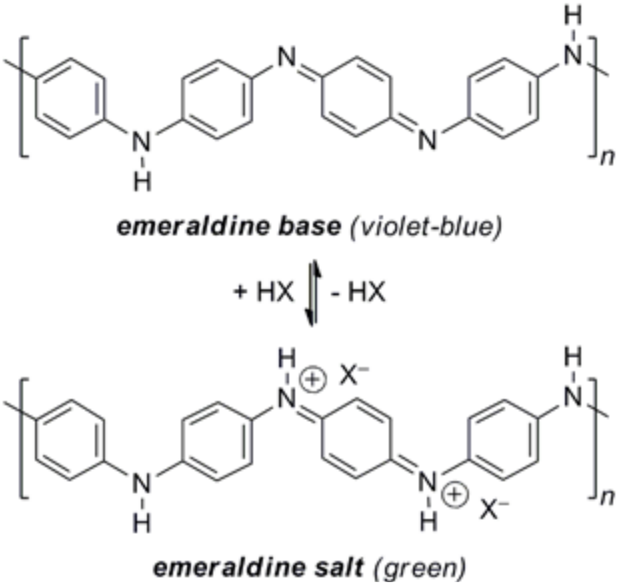

Figure 3. Protonic equilibria of polyaniline's emeraldine form.

work of Green and Woodhead, with nigraniline originally referring to true aniline black and emeraldine representing a green, reduced form of the material.[23,32]

Unlike the other parent conjugated polymers shown in Figure 1, the electrical conductivity of polyaniline is affected by both traditional doping via oxidation, as well as the extent of polymer protonation.[21,22] This protonation effect is often referred to as protonic acid doping[21,22,27] and the acid doping level can be tuned simply by controlling the pH of the dopant acid solution. As such, each of the forms given in Figure 2 can exist as either its base or protonated salt. The most common forms of polyaniline, however, are either the emeraldine base or emeraldine salt (Figure 3).

As detailed in Figures 2 and 3, the color of the polymeric material is dependent on both its state of oxidation and protonation. Thus, the most common emeraldine salt is green to green-black, while the emeraldine base is violet-blue to blue-black. In both cases, the observed color is dependent on concentration. The state of the polymer also affects its relative solubility. Thus, while the emeraldine base is soluble in organic solvents such as *N*-methylpyrrolidone, polyaniline protonated by common mineral acids is only soluble in aqueous acids.[22,27]

RUNGE, KYANOL, AND ITS OXIDATION

The oldest of the figures to which the polymerization of aniline is first attributed is Friedlieb Ferdinand Runge (Figure 4), who was born in Billwärder, Germany (near Hamburg) on February 8, 1794.[33-36] The son of a pastor,[33-35] Ferdinand (he went by his middle name) was the third of seven children.[35] His mother died in 1806 and his father later remarried, with an additional child from the second marriage.[35] His family was quite poor and could not afford to send the children for further education beyond the local primary school.[34,35] Thus, he was apprenticed at age 15 to his uncle, studying pharmacy at the Ratsapotheke in Lübeck.[34-36] He then moved to Berlin in 1816 in order to study medicine, but transferred to Göttingen after two years, where he attended chemistry lectures by Friedrich Stromeyer (1776-1835).[34,35] After only one semester, however, he transferred again to Jena. At Jena, Runge studied analytical chemistry under Johann Wolfgang Döbereiner (1780-1849)[34,35] and finished his *Dr. med.* with a dissertation on belladonna in 1819.[33-36] Wanting to become a professor, Runge then returned to Berlin that same year to habilitate as *Privatdozent*.[33-35] This required him to first acquire a *Dr. phil.* degree, which he completed in 1822 with a dissertation on indigo.[33-35]

Figure 4. Friedlieb Ferdinand Runge (1794-1867). [Edgar Fahs Smith Memorial Collection. Kislak Center for Special Collections, Rare Books and Manuscripts. University of Pennsylvania].

He remained in Berlin where he lectured on phytochemistry and technical chemistry until October of

1823, after which he traveled Europe with the primary goal of visiting Paris.[34,35] Upon his return, he joined the University of Breslau as *Privatdozent* in 1826. He was promoted to extraordinary professor of technical chemistry in 1828,[34,35] but this was not a permeant position and he found his conditions unfavorable for development of his practical ideas. He finally ended his academic career in 1831.[34,35] He moved to Berlin where he was offered a position in the chemical works of the Königliche Seehandlungs Societät (Royal Sea Trade Society) at Oranienburg (small town near Berlin) in 1832[33-35] or 1833.[36] It was here that he began the most fruitful period of his career. Among his accomplishments, he discovered a number of species from coal-tar, including pyrrole, quinoline, phenol, and aniline. He then became the technical director of the chemical plant in 1840.[33] Runge constantly clashed with his superiors, however, and he was ultimately dismissed in 1851,[36] with his last day of employment December 31, 1852.[34,35] He was granted a small pension, however, providing that he resided locally where his advice could be sought if needed.[35,36] He thus remained in Oranienburg where he died on March 25, 1867 at age 74.[33-36]

Shortly after the start of his new position at Oranienburg, Runge began the investigation of distillates of coal-tar, which he separated into acidic and basic fractions.[37] From the basic fraction, he isolated a volatile oil with a scarcely noticeable, but peculiar, odor. When treated with acid, the oil formed colorless salts, and both the oil and its salts became aquamarine when treated with chlorine of lime. Because of this color response, he named this oil *kyanol*, from a combination of the Greek *kuanós* ("blue") and the Latin *oleum* ("oil").[37] This oil was later shown to be identical to the product *krystallin* isolated from the dry distillation of indigo, which had been previously reported by Otto Unverdorben (1806-1873) in 1826. These materials are now both known as aniline.[33]

Runge then found that treatment of aniline with other oxidizing agents resulted in the formation of various dark insoluble dyes. These efforts began with the application of a hydrochloric acid solution of gold oxide to a porcelain plate, followed by a drop of aqueous aniline. Heating the combination to 100 °C then resulted in purple-colored spot, which became blue-gray when dried.[38] He then went on to show that if one first coated a hot porcelain plate with a solution of copper oxide in hydrochloric acid, and allowed it to dry, an added drop of aniline nitrate solution heated to 100 °C then resulted in a dark green-black spot.[38] Using copper oxide in nitric acid and aniline hydrochloride gave the same result. In order to confirm that it was the metal oxidant that was causing the color change, he then showed that heating just aniline nitrate or aniline hydrochloride gave no decomposition or reaction. However, the addition of any copper salt then caused the formation of the black material.[38] Lastly, he showed that the addition of aniline hydrochloride to a hot porcelain plate coated with potassium bichromate also produced a dark black spot.

In the process, Runge noted that if sufficient amounts of the aniline nitrate or aniline hydrochloride salts could be produced, the colored products resulting from their treatment with metal species could provide a practical use.[38] To illustrate this, he first treated cotton with lead chromate, after which he printed the fabric with aniline hydrochloride to give green patterns within twelve hours. If more concentrated solutions of the aniline hydrochloride were used, black patterns developed rather than green. Both developed patterns remained unchanged by rinsing in water.[20,38]

Runge had a strong interest in dyeing and the coloring of fabrics, as illustrated by his publication of a three-volume series entitled *Farbenchemie*. The first of these was published in 1834,[39] the same year as his initial aniline publications, and these volumes summarized the technical methods and state of the coloring field at the time.[33] Due to this interest and the results of his studies from various coal tar species such as aniline, Runge approached his superiors in 1836 to propose that the chemical works at Oranienburg could produce such synthetic dyes from coal tar, but such efforts were never approved.[33,36] Runge moved his focus onto other studies and it was only much later that the merits of his discoveries with synthetic dyes were recognized. Following Runge's initial reports, further related studies on aniline did not appear until 1840 with the efforts of Carl Fritzsche.

FRITZSCHE AND ANILINE FROM INDIGO

Carl Julius Fritzsche was born on October 29, 1808 in Neustadt, Germany (then within the Kingdom of Saxony).[40,41] His father was a physician and the town where Fritzsche grew up had no grammar school, so he was educated through private lessons until he was 14. He then moved to Dresden, where he was employed in the pharmacy of his uncle for five years.[40] After that, he moved to Berlin where he became an assistant to Eilhard Mitscherlich (1794-1863) in 1830.[40,41] As Fritzsche took a doctorate in botany at the University of Berlin in 1833, Mitscherlich is credited with all of Fritzsche's chemical training.[40-42] His initial papers focused on botanical subjects, but with chemical character, and his following papers began to take on greater chemical content.[40] He then emigrated to Russia in 1834,[40-42] where he became the manager of Struve's mineral-water works in St. Petersburg.[41] He became an adjunct member of the St. Petersburg Academy of Sciences in 1838, becoming an associate member in 1844, and a full member in 1852.[40,42] His chemical work, most of which appeared initially in publications of the St. Petersburg Academy of Sciences,[40] touched on uric acid derivatives, various oxides of nitrogen, and most critical of the discussion here, indigo and its derivatives. All of the efforts discussed below were carried out in a small laboratory next to his house, but he later shared the new, spacious chemical laboratory of the St. Petersburg Academy with Nikolay Zinin (1812-1880) beginning in 1866.[40,42] Fritzsche enjoyed good health until he suffered a stroke in 1869.[40-42] Although he recovered from it, he suffered from paralysis on one side, and his speech and memory suffered.[40,42] Nevertheless, he continued working until his death on June 20, 1871.[40,41]

In 1840, Fritzsche published a paper detailing the isolation of a new species from the decomposition of indigo.[43] Treating indigo with a hot, highly concentrated solution of base gave a salt mass of reddish-brown color, from which was then distilled a brown oil. Further purification isolated a colorless oil, which he called *anilin* after the Spanish name of indigo, *añil*.[41] This material was a base which formed light and highly crystalline salts and was isolated as 18-20% of the original indigo.[43] During the publication of this paper, the editor of the *Journal für praktische Chemie*, Otto Erdmann (1804-1869), recognized the similarity of *anilin* with Unverdorben's *krystallin*, and highlighted this in a note following Fritzsche's paper.[44] Two years later, Nikolay Zinin reduced nitrobenzene to give a species that he called *benzidam*.[45] In a short note directly following Zinin's paper, Fritzsche identified *benzidam* as his own *anilin*, stating that there can be no doubt about its identity.[46] The following year, August Hoffmann (1818-1892) then presented evidence that Unverdorben's *krystallin*, Runge's *kyanol*, Fritzsche's *anilin*, and Zinin's *benzidam* were all the same compound,[47] which ultimately became known as phenylamine or aniline.

Fritzsche found that aniline reacted with exposure to air, taking on first a yellow color and then turning into a brown mass. Continuing his 1840 study of the oil, he found that under 'certain circumstances' treatment with HNO_3 caused the production of a blue or green material, which he thought might be indigo, but he was only able to generate it in small quantities.[43] He then found that dissolving aniline salts in chromic acid (H_2CrO_4, typically as a H_2SO_4 solution) produced a dark green precipitate, which ultimately became black-blue in color.[43] Combustion analysis of the precipitate revealed a significant amount of chromium. Lastly, he treated aniline salts with potassium permanganate, which resulted in a brown precipitate containing manganese oxide.

Fritzsche admitted that he had not been able to study these color-forming reactions in much detail and planned to return to these in later publications.[43] Thus, while he did not follow up on the direct results reported in 1840, he did return to the treatment of aniline with oxidants in 1843, this time applying potassium chlorate.[48] Mixing an alcohol solution of aniline salt with potassium chlorate in HCl resulted in a blue precipitate, which turned green upon washing with alcohol, and became dark green upon drying. Analysis of the composition of the solid revealed an empirical formula $C_{24}H_{20}N_4Cl_2O$, which is in near perfect agreement with the structure of the emeraldine salt given in Figure 3 ($X = Cl^-$).[48] Although this seems to be Fritzsche's last report on the oxidation of aniline, the green aniline materials introduced by Runge and Fritzsche were later applied to commercial dyes by Frederick Crace-Calvert (1819-1873), Samuel Clift, and Charles Lowe.

CALVERT, CLIFT, LOWE AND EMERALDINE

Frederick Crace-Calvert was born near London on November, 14, 1819.[49] In 1835, he moved to France where he studied chemistry at the University of Rouen under Gerardin. After two years, he then moved to Paris to continue his studies at the Sorbonne and the College de France. He then became the manager of the chemical works of Robiquet and Pelletici at the age of 21, but soon left to become an assistant to Michel Eugène Chevreul (1786-1889) in 1841.[49,50] He returned to England in late 1846, where he was appointed as a honorary professor of chemistry at the Royal Institution, and later as lecturer on chemistry at the School of Medicine in Manchester. He became interested with the properties of carbolic acid and built works for its manufacture in 1865. Due to his various contributions, he became a Fellow of the Royal Society and of the Chemical Society, as well as other societies both at home and abroad. He was seized with a fatal illness in 1873, and died in Manchester on October 24, 1873.[49]

Sometime prior to the summer of 1860, Crace-Calvert, Samuel Clift, and their assistant Charles Lowe developed green and blue dyes from the oxidation of aniline for the coloring of cotton, for which they filed a joint patent on June 11, 1860.[24,51,52] These methods involved the application of an aniline salt (either the hyrdochloride or tartate) and potassium chlorate to give a green color after 12 hours. This green color was given the name *emeraldine*,[24,50-55] which ultimately became the name adopted for the most common form of polyaniline (Figure 3). If the initially produced green dyed fabric was boiled in an alkaline or soap solution, the green color could be converted to a blue color, which was given the name *azurine*.[24,51-54] Both the blue color and the method of its production from emeraldine is consistent with the formation of the emeraldine base as outlined in Figure 3. Crace-Calvert presented these results as part of an address before the Society of Arts, which was then published in the February 7th issue of the *Journal of the Society of Arts* in 1862.[52] Later that same year samples printed by these techniques were exhibited in the chemical section at the London International Exhibition of 1862.[55] The following year Crace-Calvert also included this in his book *Lectures on Coal-Tar Colours, and on Recent Improvements and Progress in Dyeing and Calico Printing*.[53]

Crace-Calvert, Clift, and Lowe induced the printers Wood and Wright to apply their methods to generate green and blue colors in the end of 1860.[53] Wood and Wright considered the resulting colors good enough to be commercialized and introduced improvements resulting in a dark shade that could be considered black.[25,53] The improvements were achieved by either adding iron salts or other oxidizing agents to the potassium chlorate, followed by treating the color produced on the fabric with either a weak solution of potassium bichromate or bleaching powder. It was also found that copper nitrate could be mixed with aniline hydrochlorate, without the addition of potassium chlorate, and the mixture could be printed on the fabric to gradually give a dark green or black. These two methods gave either a green or blue color, but one that was so dark that it could be viewed as black.[53] About the same time, black dyes produced from the oxidation of aniline were introduced by John Lightfoot and Heinrich Caro (1834-1910).

LIGHTFOOT, CARO, AND ANILINE BLACK

John Lightfoot, Jr. was the son of Thomas Lightfoot (1811-1866), but was named after his grandfather John Lightfoot, Sr. (1774-1820).[25,50] His grandfather, father, and uncle were all colorists and connected with the Broad Oak Print Works of Accrington, about 20 miles north of Manchester.[24,25,50] As part of his practical education, Lightfoot traveled to France and Alsace in 1854.[50] He then continued the family tradition by joining Broad Oak in ca. 1855.[25] At Broad Oak, Lightfoot played a leading role in the use of madder, archil (or orchil), and indigo colors. He also began experimenting with the semisynthetic colorant known as murexide, the behavior of aniline colors, methods of fixing new dyes to wool and cotton, and imitations of madder and aniline colors.[25]

According to Lightfoot, it was November 1859 when he first observed that aniline hydrochloride in the presence of potassium chlorate imparted a fast and brilliant black to cotton during printing.[25,51] Initial efforts in the application of this aniline hydrochloride and potassium chlorate mixture produced little to no color after 24 hours, but he found that when the same formulation was printed with copper rollers, a green color was produced within 12 hours. Believing that the copper was a critical factor, he then added a copper salt to the mix to ultimately give an intense black.[24,51] The conclusion that the copper was a necessary factor is not consistent with the previous reports of either Runge[38] or Fritzsche,[48] both of which produced either green and black materials by treating aniline hydrochloride with chlorate salts alone. In reviewing the formulation given by Lightfoot,[51] however, it is clear that he used too little potassium chlorate to sufficiently oxidize the aniline salt and thus an additional oxidant such as copper was required for him to generate the color in sufficient intensity. Of course, prior to the addition of the copper salts, Lightfoot's process of printing cotton with the green or black aniline dyes was nearly identical to that originally reported by Runge.[38] In fact, from a chemical standpoint, the methods only differed in the chlorate salt utilized. Although Lightfoot recognized that the high price of aniline in 1859 was a disadvantage, he continued with experiments in July 1860 and had produced a few samples by 1861.[24,25]

In 1862, he reported his discovery as a letter to the Editor in the December 6th issue of *Chemical News and Journal of Industrial Science*, along with some sample swatches.[56] At the end of Lightfoot's letter, the editor added a note that the color was not a pure black, and as with the previous cases of either Runge[38] or Wood and Wright,[53] was most likely so dark a blue or green as to appear black. However, Lightfoot's black was considered superior to that of Wood and Wright.[25] Patents for this process were filed in early 1863,[51] with the US patent granted in May of the same year.[57] In this patent, Lightfoot describes the dyeing of fabric with mixtures of aniline hydrochloride and potassium chlorate, followed by the addition of copper chloride.[24,55,57] The patent, however, also covered the use of other copper salts or even salts of other metals.[57] The rights were then sold to Jakob J. Muller-Pack of Basle.[25]

A significant limitation in Lightfoot's printing process was that it caused severe corrosion to the rollers of the printing machines, which also led to streaking on the cloth.[24,25,55] This limitation was solved by Charles Lauth, who registered a patent in 1964 that specified the use of insoluble copper sulfide. The insoluble salt was inactive at the time of printing and later converted to soluble copper sulfate by action of the chlorate salt during development of the aniline black, which dramatically reduced the damage to the rollers of the printing machines.[24,55] Lauth's process was sold to Muller-Pack, who combined it with Lightfoot's process in an effort to dominate the European and US markets.[25]

During this same time period, a second black aniline dye was produced by Heinrich Caro (Figure 5) in 1860.[24,25] Born on February 13, 1834 in Posen, Caro attended the Realm Gymnasium in Köln from 1842-1852.[58] From 1852-1855 he attended the Königliche Gewerbeinstitut (Royal Trade Institute), which trained students for industry, while also attending lectures at Berlin's Friedrich-Wilhelms-Universität (now the Humboldt University of Berlin).[58,59] In April 1855, Caro took a modest appointment in the Troost factory in Mülheim, where he mainly performed analytical work outside the printing shop.[58] In March 1857, Caro was then sent on a study trip to England in March of 1857, where he visited a large number of printing and dyeing factories, in particular that of John Dale and Roberts. Upon his return to Germany, he then carried out his military service in 1857-1858.[58]

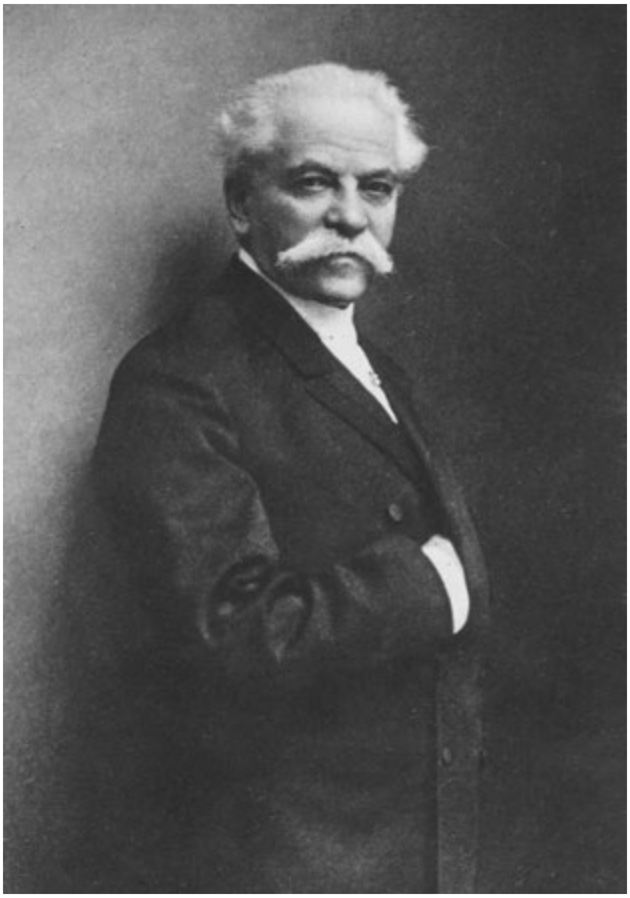

Figure 5. Heinrich Caro (1834-1910). [Edgar Fahs Smith Memorial Collection. Kislak Center for Special Collections, Rare Books and Manuscripts. University of Pennsylvania].

In November, 1859, Caro moved to England to try his luck there. Although his initial efforts were in vain, he was finally able to obtain a job with John Dale, co-owner of the Cornbrook Chemical Works of Roberts, Dale & Co. in Manchester.[58-60] He later returned to Germany in 1866, and on November 1, 1868 he became the coordinating technical director for the Badische Aniline and Soda Fabrik (BASF).[24,58-60] There he oversaw development of new colors including artificial alizarin, eosin, methylene blue, and azo dyes, as well as the initial stages of the indigo synthesis, and contributed towards the structural elucidation of the triphenylmethane dyes.[59] He was appointed to the company's board of directors in 1884 and continued to serve on the board until 1890.[60] Caro died after a short illness on September 11, 1910 in Dresden.[58]

In 1960, while working for Roberts, Dale & Co., Caro developed a process for making aniline purple by the oxidation of aniline with copper salts. After alcoholic extraction of the desired purple dye, a black residue remained which provided an excellent fast black dye for printing on cotton. Roberts, Dale & Co. then commercialized this dye for sale to printers in 1862.[24,54,59] As with Lightfoot's original formulation, this residue played havoc with the printing machinery, but it could be successfully printed with wooden hand blocks.[24] The efforts of Roberts, Dale & Co. established the advantages of aniline black over other black colorants of the time and it has been proposed to have been the motivating factor for Lightfoot to patent his process in 1863.[24] As discussed above, the color found more widespread application in British printworks following the introduction of insoluble copper sulfide by Charles Lauth in 1864.[59] By 1871, these black dyes from aniline became known as *aniline black*.[51] Aniline black later became the first real general term for polyaniline. Following the introduction of aniline black dyes, the next major innovation came from the physician and chemist Henry Letheby.

LETHEBY AND THE ELECTROLYSIS OF ANILINE SULFATE

Henry Letheby (Figure 6) was born in Plymouth, England in 1817,[61-63] and received his early education

Figure 6. Henry Letheby (1816-1876) [by W. & D. Downey albumen carte-de-visite, 1860s © National Portrait Gallery, London].

there.[61] He continued his chemical studies in the laboratory of the Royal Cornwall Polytechnic Society in Falmouth,[61,62] where he eventually became assistant and did some lecturing.[61] He then moved to London in 1837 to attend the Aldersgate Medical School, where he became assistant to Jonathan Pereira (1804-1853), professor of chemistry at the London Hospital.[61,62] Letheby became a licentiate of the Society of Apothecaries in 1837, and then received his M.B. (Bachelor of Medicine) from London University in 1842,[62,63] after which he succeeded Pereira as the chair of chemistry and toxicology at the London Hospital in 1846.[61,62] He was elected as London's medical officer of health in 1855,[61-64] while also serving as the city's public analyst.[62-64] In addition, he served as the city's chief gas examiner [62-64] and as a consulting chemist to the Great Central Gas Company[61,64] In 1858, he received a M.A. and Ph.D. from an unknown German university.[62] He was a fellow of both the Linnean Society of London and the Chemical Society of London.[62,63] Because of failing health, Letheby resigned his city posts in February 1874.[62] After a brief illness, he died at the age of 60 on March 28, 1876, at his home in London,[61-64] and was buried in Highgate cemetery on March 30th.[62]

After the investigation of two cases of fatal poisonings by nitrobenzenes, Letheby began investigations into chemical tests for the presence of aniline, as he had found that nitrobenzene was reduced to aniline after ingestion. Thus, he reported the study of acidic solutions of aniline with various oxidizing agents to produce blue-to-purple colors in 1862.[65] Continuing his investigations, Letheby then oxidized sulfuric acid solutions of aniline via a Pt electrode at the positive pole of a small Grove's cell (an early high current battery) to generate a deep blue to bluish-green pigment that adhered to the electrode as a fine powder.[65] As with many of the previous reports of chemical oxidation, the exact color observed depended on the concentration of the aniline solution used.

He then prepared the material on a larger scale, using greater quantities of aniline and two larger Grove's cells connected together for intensity.[65] Using this setup, a thick layer of dirty bluish-green pigment quickly covered the large platinum sheet (4 × 6 in) acting as the positive electrode. The pigment was then removed from the electrode, washed with water and dried to give a bluish-black powder. The powder was insoluble in water, alcohol, ether, or ammonia, and was only soluble in sulfuric acid. Immersion in ammonia did cause the powder to acquire a brilliant blue color, but the resulting blue pigment still did not dissolve.

When dissolved in concentrated sulfuric acid, the solution formed was either blue, green, or violet depending on the degree of concentration. Diluting the resulting acid solution with water then resulted in the precipitation of a dirty emerald green powder, which could be made blue with treatment of concentrated ammonia or blue to purple with the addition of concentrated sulfuric acid. The blue pigment generated by any of the means above could also be partly decolorized by various reducing agents, and in this condition, it became soluble.[65]

ANALYSIS AND DISCUSSION

Although the various studies presented above included little to no structural or compositional data, all of the reaction conditions and resulting properties reported are completely consistent with the modern knowledge of the oxidative polymerization of aniline, as well as the chemistry and characteristics of the resulting conjugated polymer, polyaniline. In addition, it is clear that all four of the historical figures that have been previously credited with the origin and discovery of polyaniline did indeed play critical roles in the early history of this material. However, if we are to assign priority to any of these figures, the credit must be properly given to Runge. Not only was he the second to discover aniline itself after Unverdorben, but he was the first to report its oxidative polymerization and the first to document the successful application of these products as both green and black dyes for printing on cotton.[38] Although Runge's contributions were not usually recognized during the time periods discussed above, Heinrich Caro paid tribute to Runge during the celebration of his own 70th birthday in 1904, crediting Runge with various discoveries including the first formation of emeraldine by copper salts.[33] While Caro does not go so far as to credit Runge with the discovery of aniline black, author Emilio Noelting (1851-1922) begins his 1889 book *Scientific and Industrial History of Aniline Black* with the statement that the history of aniline black can be traced to the "very old researches of Runge".[20]

The proper recognition of Runge should not diminish the contributions of the remaining three gentlemen, however, all of which left their mark on the history of polyaniline. Although Fritzsche did little to advance the oxidative polymerization of aniline beyond what was previously reported by Runge, he was the third to discover aniline and more importantly gave it the name by which we recognize it today.[43] Needless to say, there would not be the current term *polyaniline* without the contributions of Fritzsche! Also of significant importance is the fact that Fritzsche was the first to analyze the elemental composition of the polymerized product to reveal an empirical formula in near perfect agreement with the structure of the modern emeraldine salt of polyaniline.[48] Of course, the work of both Runge and Fritzsche may have been lost as academic curiosities if it had not been for the efforts of Crace-Calvert, Lightfoot, and Caro to develop these materials into commercial products. In addition, it is their application of this material as a black dye that resulted in the longstanding name *aniline black*, the primary common designation for this material until the ultimate use of the modern *polyaniline*. It is hard to quantify how much impact their work had on maintaining interest in polyaniline until its more critical electronic properties were ultimately discovered in the 1960s.[9,10,16] Lastly, one cannot overlook the contributions of Letheby. Although he most certainly was not the first to report the oxidation of aniline to polyaniline, as is often claimed, he was the first to demonstrate its electrochemical oxidation and the very first to report on this method for the production of conjugated materials.[65] The electrochemical generation of conjugated polymers was the most common route to conductive films of these materials prior to the 1990s, and this still is the most common method utilized for the production of polyaniline.

In closing, I would like to postulate a final question for further consideration. If the work discussed above places the first report of the polymerization of aniline to polyaniline with the work of Runge in 1834, *is polyaniline then the earliest known synthetic organic polymer?* I am not the first to propose this possibility,[26] but I still feel that this is worth bringing to light once more and to provide at least initial support for such a claim. Although the term *polymer* was first coined by Berzelius in 1832, it did not have the same meaning as its modern usage and did not originally refer specifically to macromolecules.[66,67] In addition, none of the studies above ever used the term to refer to the oxidation products of aniline and the modern concept of macromolecules was not accepted until the 1920s, after which it was decades before Staudinger, Carothers, Flory, and others could convince the scientific community that these unusual molecules were real.[9] The earliest man-made polymer is generally considered to be polystyrene, whose polymerization was first observed in 1839[68] in which freshly distilled storax resin produced an oil (styrene, but then called styrol) that converted into a rubberlike substance in the presence of air, light, and heat.[66,69] Of course, from the discussion above, Runge's conversion of aniline to green-black materials predates the observed formation of polystyrene by five years. In addition, unlike the spontaneous polymerization of styrene, aniline was polymerized via the purposeful addition of an oxidizing agent and its polymerization was carried out under a number of different conditions. A complicating factor in this argument is that what made polystyrene interesting was its obvious changes in physical properties, while the obvious changes in the polymerization of aniline was the resulting color produced, rather than any particular physical change. As such, in that time period of the early 19th century there were no related properties to connect the two materials and polyaniline was not recognized as what we would call an oligomer or polymer until 1910.[28-31] Still it is clear that polyaniline represents not only an important beginning in the path to conducting organic materials, but to organic polymers in general.

ACKNOWLEDGEMENTS

I would like to thank Tony Travis for sharing some of his publications on Lightfoot, Caro, and anline black, as well as for a number of helpful discussions. Thanks also to Dave Lewis for the helpful discussion on the relationship between Fritzsche and Zinin. I would also like to thank the Department of Chemistry and Biochemistry of North Dakota State University (NDSU) for continued support of my historical research, as well as the NDSU Interlibrary Loan Department, who went out of their way to track down many elusive and somewhat obscure sources.

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Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Citation: F. Naso (2017) Mario Betti: a Giant in the Chemistry Scenario of the Twentieth Century. *Substantia* 1(2): 111-121. doi: 10.13128/substantia-31

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declared that no competing interests exist.

Historical Article

Mario Betti: a Giant in the Chemistry Scenario of the Twentieth Century

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Abstract. The life of the chemist Mario Betti (1875-1942) is presented by focusing on the activity performed at the University of several Italian cities. Born in Bagni di Lucca, a small town in Tuscany, in 1897 he graduated in chemistry at the University of Pisa, under the supervision of Roberto Schiff, nephew of the famous Ugo. In 1900, he moved to the University of Florence, where he published a three component reaction which became known world-wide *as the Betti reaction* and, nowadays, represents a synthetic tool of increasing use. The product deriving from the reaction can be easily obtained optically resolved and used as ligand in catalysts of nucleophilic attack on carbonyl compounds. Since then, stereochemistry was the subject in which the most relevant achievements of the Italian chemist were made. After working in Florence, Betti spent a ten years long period at the University of Siena, where he covered the role of faculty dean and rector. In 1922 he was hired by the University of Bologna as successor of the famous Giacomo Ciamician. In this article the many merits of this open minded and farsighted man will be presented against a background with chemistry and chemists of the 20th century playing on the scene. The conclusion is reached that the chemical heritage of Mario Betti, after a long time from his death, appears richer than previously thought.

Keywords. Betti reaction, Betti base, Mannich reaction, chirality, asymmetric synthesis.

1. INTRODUCTION

Chirality (the existence of a couple of compounds that are non-superimposable mirror images, *i.e.* enantiomers) is a wide topic of paramount importance in chemistry. Several features of interest concerning this type of stereoisomers, and, especially, the maniacal preference shown by mother nature towards one of them, are still unclear. The chemist-writer Primo Levi was attracted by this "beautiful and fertile"[1] theme ever since he started to prepare his degree thesis on the stereochemical problems connected with the Walden inversion.[2] Later on, after becoming very famous for his literary masterpieces, he wrote an article where his enthusiasm for the enigmatic subject appears unchanged.[1] As for me, stereochemistry, including chirality, was one of the areas in which I enjoyed working since the early stages of my scientific career. During this activity, reading literature papers I met the name of Mario Betti and eagerly studied his work, thus becoming aware of the importance of his ideas and achievements. At the same time, I got convinced that the scientific potential generated by the Betti's chemistry was far from being fully developed. As a consequence, my dedicated co-workers and myself decided to embark on a journey with the aim of expanding the Betti's chemistry and to use it as a tool for developing our interest in stereochemistry.[3,4] Furthermore, we wrote a review[5] in order to increase further the attention towards the work of the Italian scientist. The present contribution, that is mainly of biographical nature, aims to go in the same direction, hopefully, with the same success.

2. MARIO BETTI: THE LIFE[6-10]

2.1 The Betti Family and the Pharmacy in Bagni di Lucca: Music and Drugs[6,7]

Mario Betti and his twin brother, Adolfo, were born in Bagni di Lucca on March 21, 1875 from Adelson and Dalmanzina Amadei. Bagni di Lucca is a small town in Tuscany, situated about 60 miles northwest of Florence. The town is rather well known for its thermal baths, that attract visitors from Italy and foreign countries. It seems also worth noting that the celebrated chemist Davy visited frequently the town with the aim of studying some hydrological problems. Adelson Betti was a chemist who owned an antique pharmacy, that had been established in 1709 and, after being run by generations of descendants of the first owners (the Ghiareschi's), in 1833 was inherited by Adriano Betti, son of Ippolito and Maria Teresa Ghiareschi. Along the years, the place reached a high level of professionalism and attractiveness, also due to an uncommon library endowed with rare books. The pharmacy was also known by the inhabitants of Bagni di Lucca as "the English pharmacy". The unusual adjective derived from the fact that around 1870 the pharmacy was awarded by the Queen Victoria the title of "Pharmacy of the British Embassy", with the right of using the royal English coat of arms.

Adelson Betti, son of Adriano, was the subsequent owner of the pharmacy. Being fond of music, he used to play organ in the Bagni di Lucca church. Often, another young musician was playing there and the same man was frequently welcome as a guest at the Betti house, located at the upper level of the pharmacy. One may imagine a place enveloped within a cloud of dream melodies, especially upon hearing that the young musician was Giacomo Puccini (1858-1924). The excellent hospitality of the Betti's was reciprocated by Puccini who, gladly accepting an Adelson request, composed the hymn *Vexilla regis* for the local church. This musical background greatly influenced the two Adelson's twins. One of them, Adolfo, after studying in Italy and Belgium, became a famous violinist, teacher and music editor. In particular, he is known for having led for years (1923-1929), as a first violinist, the Flonzaley Quartet. The ensemble, that was considered as the earliest top-notch American string quartet, gave approximately 2500 performances in the United States and another 500 in Europe. When the quartet disbanded, Adolfo Betti taught music in New York for several years, receiving in 1933 the Coolidge Medal for eminent services to chamber music in the United States. Later on, he returned to Italy, becoming the mayor of Bagni di Lucca at the end of World War II. Adolfo Betti died on December 2, 1950.[7,11,12]

The twin brother Mario was also culturally inclined towards humanities, especially music and painting. However, he was afflicted by deforming arthritis and, on the other side, his presence in the pharmacy was badly needed by his father. At the time a pharmacy located in a small town represented an aggregation centre for the most important cultured men of the place. Discussions on politics, social problems and other topics went on with a high frequency. This sort of cenacle was beneficial for the formation of the young Mario. Needless to say, a pharmaceutical path was planned for him.

2.2 The Pisa Period[9,13]

In 1892 Mario Betti registered as a student at the Chemistry School of the University of Pisa. The school had a high reputation, thanks also to the presence in previous times of well known chemists, such as Raffaele Piria (1814-1865), Stanislao Cannizzaro (1826-1910) and Cesare Bertagnini (1827-1857).

At the beginning, Betti chose to follow the course that, eventually, would have allowed him to obtain the "Diploma in Farmacia", that he needed to direct a pharmacy and, as a result, a quiet future in Bagni di Lucca was easily predicted. However, after the first year, the university student realised that his growing interest in chemistry could have been hardly satisfied upon reaching this target. Therefore, he changed his plans by asking to the faculty to be transferred to the second year of the course in Chemistry and Pharmaceutical Sciences. The faculty was very reluctant to express the necessary opinion in favour and the transfer procedure stopped at a dead end. The young student, who had plenty of drive, decided to grasp the nettle by lodging complaints in a letter addressed directly to the Minister of Education in Rome, who happily solved the problem within a short time.

Most frequently, the research performed at the Institute of Pharmaceutical Chemistry of Pisa dealt with synthesis and behaviour of heterocyclic compounds or with relationship between structure and physical properties. At the same institute Betti became a pupil of Roberto Schiff (1854-1940), son of the famous physiologist Maurizio (1823-1896) and nephew of the great chemist Ugo (1834-1915). The Betti's supervisor was of high intellectual level, but unhappy with his teaching duties (pharmaceutical chemistry), that he never liked. Roberto felt much more attracted by the passion of collecting artworks, a field in which he had a rare expertise, luckily associated to a large availability of money deriving from his marriage with Matilde Giorgini (1860-1940), a rich girl who was a granddaughter of Alessandro Manzoni (1785-1873), one of the most famous Italian writers and poets of all time. In spite of this distraction, Roberto was able to establish with his student a fruitful co-operation, in which his fanciful ideas were driven into the real world by the experiments of the younger co-worker.[9,13] In 1897, Betti obtained his degree with a thesis on the reaction of methylisoxazolones with aldehydes and co-authored with Roberto Schiff the first two papers of his career.[14,15,16]

2.3 The Florence Period

In 1898, Betti moved to the University of Florence as an assistant of Ugo Schiff, who was founder and director of the Institute of Chemistry. The famous chemist, well known for his bad tempered character, was not adequately friendly with his colleagues and showed a severe behaviour towards his students. A few anecdotes will suffice to understand the man.

When a student started to work towards his thesis in the lab, Schiff was used to play always the same scene. He gave to the student a low quality match box warning him with these words:

> *You must keep in mind that you descend from Berzelius because Berzelius taught chemistry to the old Wöhler and the old Wöhler taught chemistry to me. A school can be honoured by its pupils, but it may be also stained: think it over.*[9,13]

Schiff was a follower of the classic approach to organic chemistry without any enthusiasm towards physical chemistry "interferences". With his caustic style he liked to express the following opinion:

> *One day some chemists lost their wish of working and for this reason they invented physical chemistry.*[9]

The Schiff's behaviour towards people of other disciplines was even more drastic. In 1879 the physicists and the chemists of the University of Florence had to move to the same building. Once they had moved there, Schiff got in contrast with the physicist Antonio Roiti (1843-1921), an expert of electrology, who had to run his experiments during the night, due to the interferences caused by the trams passing in the neighbourhood during the daytime. At night, with the aim of disturbing the experiments of his colleague, Schiff enjoyed moving metallic masses in the corridors of his floor located below the level of the physicist labs.[13]

The chemist Augusto Piccini (1854-1905), who in 1893 was professor of pharmaceutical chemistry in Florence, is considered the author of a witty classification of the Schiff family group. Such a classification, related with oxidation state of the elements and nomenclature, required the definition of *schiffico* for Maurizio, *schiffoso* for Ugo, and *iposchiffoso* for Roberto. Even without inventing an English translation of these terms, the tricky joke is easily understood by taking into account that *schifoso* in Italian means *nasty*.[9,17]

These funny tales have been reported here with the intention of emphasising the difficulties that Betti expected when he entered the Institute of Chemistry in Florence. He was going to face a supervisor who had a diametrically opposite character. Fortunately, a miracle occurred because the two men shared the high sense of

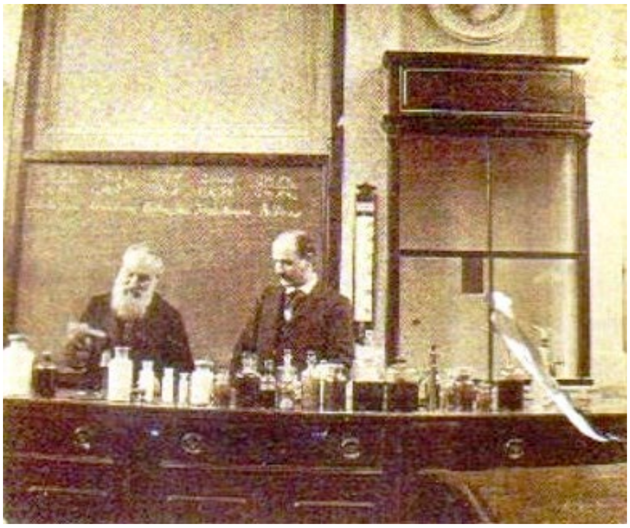


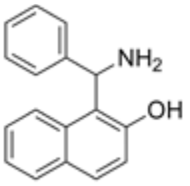
Figure 1. Ugo Schiff and Mario Betti during a lecture in a classroom (Courtesy of "Ugo Schiff" Chemistry Department of Florence University. Chemical Heritage Project DCO155).

duty and the passion towards research. This was sufficient to establish the character compatibility needed. The driving forces towards a fruitful coexistence were strenghtened by the fact that the behaviour of the younger scientist was paved with a constant serenity, a convincing reasoning, and a kind way of acting.

After a short time, due to a simple incident, Schiff was obliged to take a long sick leave, during which Betti became responsible for all research and teaching activities. On his return, Ugo Schiff deeply appreciated the work that had been made by his worthily substitute. His hearth became less hard, since he realised that, after all, his co-worker was inspired by the same ideals.[9]

On the other hand, the chemistry environment was very sparkly and this had a beneficial effect on the scientific productivity. In the Florence laboratories, Betti developed his interests in stereochemistry with important studies on the relationship between optical rotatory power and the structure of groups connected with the stereocentre.[18] On performing these studies, a great advantage was achieved by the synthetic versatility of the reaction, nowadays known as the Betti reaction, that in the original version produced 1-(α-aminobenzyl)-2-naphthol **1** (scheme 1), starting with 2-naphthol, benzaldehyde, and ammonia.[19a] The product begun to be known with the name of the author (*i.e.* Betti base, 1) and the multi-component process was published in Organic Syntheses,[19b] a prestigious international book series, where only independently checked synthetic procedures are reported. Finally, the base was also easily resolved into his optical isomers by means of tartaric acid.

Meanwhile, Betti had gained high scientific reputation. The Italian chemistry community had a clear sign that a new shining star was rising in Italy during an important meeting held in Parma (*i.e.* Congresso della Società per il Progresso delle Scienze, September 27, 1907). Betti gave a speech on his research in a session chaired by Emanuele Paternò (1847-1935). At the end of the talk, the great chemist Giacomo Ciamician (1857-1922) expressed his enthusiasm and appreciation to the speaker in front of the audience.[8,9]



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Scheme 1. Structure of 1-(α-aminobenzyl)-2-naphthol.

2.4 The Siena Period

In the same year Betti won a public selection for the chair of Pharmaceutical Chemistry in Cagliari, where he worked two years and founded the Institute of Pharmaceutical Chemistry. At the end of his stay in Sardinia, another public selection led him to the University of Siena. The time spent in this University was ten years long and fruitful and Betti kept forever pleasant memories of this period. His professional experience was enriched by highly qualified management roles. Indeed, he became first dean of the Faculty of Sciences and afterwards, at the age of forty, the youngest rector in Italy.

2.5 The Bologna Period

Two subsequent competitive examinations occurred in the Betti life. In 1921 he became professor at the University of Genoa. In this city he met a young chemist who appeared to him very eager to explore the exciting world of molecules. Giovanni Battista Bonino (1899-1985), this was the name of the enthusiastic fellow, impressed professor Betti to such an extent that within a couple of weeks the young chemist was called to cover a temporary position as a technician at the university, in view of a more rewarding research oriented job.

In January 2, 1922, Giacomo Ciamician died in Bologna. The top level University, to which the famous chemist had contributed his highly qualified chemistry, stimulated the interest of many Italian professors, who were eager to move to Bologna. The success at the competition appeared soon an up-hill task. The Italian term for "public competition" is "concorso", but people of the community invented a whimsical neologism by making the "absolute superlative" of *concorso*, *i.e. concorsissimo*, and, besides this grammatically amusing term, nothing appeared more appropriate to convey to the interested people the idea of "the most difficult public competition of the century".[6] Eventually, a prestigious *ad hoc* committee was formed. The group included authoritative chemistry professors, such as Nicola Parravano (1883-1938) and Guido Pellizzari (1858-1938). The merits of each of the many applicants were scrutinised and Mario Betti was unanimously selected.[6]

Meanwhile, a new building was ready to host the chemists of the University of Bologna. The direction of the new institute was entrusted to Betti, who had to face financial problems that appeared exceedingly severe. Updated instrumentation as well as furniture for the wide space were badly needed. On the other hand, the money granted was not sufficient even for the basic activity of the structure. The university fund that was allotted each year amounted to 25,000 Italian lire, a sum that, converted in today value, should roughly corresponds to 20,000 euro. Nevertheless, Betti undertook the uphill task and was able to give the start to the institute, that was called " Istituto di Chimica Giacomo Ciamician" to honour the great chemist, who had made well known world-wide the top level chemistry performed at the university.

During the early years of his stay in Bologna, Betti started to show his deep interest in the relation between *in vitro* chemical reactions and biochemical transformations. He realised that the boundaries between the two areas could be more blurred than commonly thought at the time. He wrote up his ideas on the matter in a book where topics connected to his stereochemical interests (*e.g.* asimmetry and life, enzymes) were dealt with.[21] Furthermore, he presented a communication on the same subject at the "Congresso della Società per l'Avanzamento della Scienza", Bologna, (from October 30 to November 5, 1926). The talk was scheduled for October 31 at the "Archiginnasio", one of the most important buildings of the city. In the same day, the leader of fascism, Benito Mussolini, was visiting Bologna where the day before he had inaugurated the new stadium of the city ("Stadio del Littoriale"). Mussolini wanted to attend the meeting and to listen some lectures of special interest, including the talk of Betti.[6,22] The meeting proceeded as expected. Mussolini gave a talk in which he urged chemists to do both fundamental and applied research. Furthermore, he was proud to mention the cases in which his government had spent a consistent amount of money to support scientific projects. The reader of this article will soon understand that this is the standard type of talk that even today any important politician would give at a scientific meeting. However, a difference does exist. Luckily enough, in Italy and in many other countries no politician would dare to share the opinion that Mussolini expressed by encouraging chemists to work in areas of interest for the needs of war-time.

At the end of his participation to the meeting, Mussolini left the building in a procession of cars. After a stretch of road, he was shot by a teenager, Anteo Zamboni (1911-1926). The Italian "Duce" remained uninjured, whereas the shooter was immediately captured and lynched by a crazy crowd. Lieutenant Carlo Alberto Pasolini was the first to identify and to catch Zamboni. The lieutenant was the father of Pier Paolo, (1922-1975), the famous Italian writer, poet, movie director and intellectual.[23]

The comparison between man and mother nature in the matter transformation continued to be a fascinating topic for Betti. Meanwhile, his ideas were conveyed also to the man at the street. In some case the Betti's thoughts were not fully understood. In one article, the Italian newspaper "La Nazione" (April, 26-27, 1942) wrote: *At other times a man like professor Betti could undergo the risk of being sent to the stake.*[6]

A critical point was the fact that Betti oriented his interest not to philosophical problems concerning the reasons *why* things occur in nature but rather he wanted to know *how* they occur. In particular, due to his expertise, for Betti one of the most important questions was how the chirality problem might be brilliantly solved with one enantiomer selection in reactions involving asymmetric natural agents, whereas a chemist working with common reagents is inevitably bound to obtain only mixtures containing equivalent amounts of antipodal isomers. Indeed, several literature papers had shown the possibility of obtaining optically active material from a racemic mixture just by using the intervention of an enzyme as a catalyst that, due to its chemical nature, has many resolved stereo-centres. The process went through the preferential "destruction" of the faster reacting of the two isomers leaving unchanged and recoverable the slower reacting one.

Betti chose to evaluate a revolutionary innovation. The reaction of a normal Grignard reagent with aldehydes was performed to produce an alcohol, but instead of a common solvent he used optically active dimethylbornylamine. As a result, the alcohol showed a small but significant optical resolution, thus evidencing the first asymmetric synthesis based on the use of a chiral ligand.[24]

We shall deal with this process in more details later on. For the moment, it seems more convenient to focus on the milestones of the route followed by Betti in his attempt to imitate mother nature. Indeed, almost at the same time, he wanted to check the possibility of using circularly polarized light as physical agent to induce asymmetry in the formation of an optical active compound. Attempts had been made by using racemic mixtures to effect an asymmetric destruction, reporting cases of success. Betti reasoned that chances could be higher by working in the gas phase, where intermolecular forces are weaker. For this reason, he chose to perform the reaction of addition of chlorine to propene. This process had also an additional advantage since it leads to a liquid product that separates from the gaseous reagents, in a way that, if a suitable reactor is used, the effect of the light after the addition reaction is avoided. This would makes unlikely any disturbing post-reaction on the liquid phase, such as an asymmetric destruction of the product. As a result of the actual experiment, a weakly optically active 1,2-dichloropropane was obtained. The first asymmetric synthesis under the influence of circularly polarized light had occurred.[25,26] However, as we shall see later on, this result was considered controversial.

During all his academic activity, Betti showed a great interest also on applied problems for which he used his capacity of innovation. Perhaps due to sentimental ties with his home town, he became a highly reputed expert of thermal water of many Italian regions. In this field he introduced the use of the mobile laboratory with which it was possible to analyse water at the spring. Another topic of interest was represented by chemistry and properties of rubber. The anti-gas mask used during world war one was significantly improved by him.[6]

Towards the end of the year 1941, the health problems of Betti became rather critical. Nevertheless, he continued to do research. A communication on the asymmetric synthesis was presented at a meeting of the Academy of Sciences of Bologna held on April 19, 1942. Mario Betti died on May 13. He was 67 years old.

On May 15, 1942 Bologna honoured the teacher and the scientist. The next day Bagni di Lucca honoured his son. More recently, the citizens placed a slab of marble on the external wall of the Betti's house that still include the antique pharmacy. The names of Mario and Adolfo Betti were engraved in the epigraph together with a few nice words recalling the merits of the two men.[27] Atoms and notes, reactions and scores, chemistry and music are now close together.

The life of Betti was spangled by a variety of honours and a full list would be to long. Just to mention a few, he was a member of *Accademia dei Lincei* and of the *Società Italiana delle Scienze detta dei XL*. In 1939, he was nominated Senator of the Kingdom of Italy. At that time the chairman of the Senate was Guglielmo Marconi, who had already received the degree of Doctor *Honoris Causa* in Physics from Betti, Dean of the Faculty of Sciences at the University of Bologna.

3. THE CHEMICAL HERITAGE OF MARIO BETTI

3.1 The Transition Period

Most of the top papers of the last period of the life of Betti had been co-authored by Elio Lucchi, who also worked at the same University. Unfortunately, due to an accident, he died a few months after the departure of the senior scientist. For this reason, the important work that was going on in Bologna suffered a stop. The passing of the torch had failed and the light on the Betti's chemistry became attenuated.

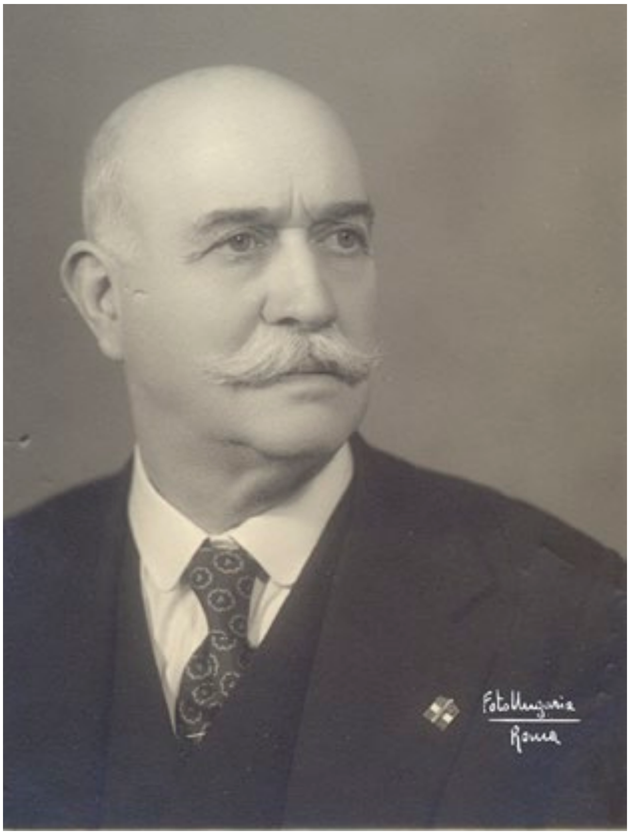


Figure 2. Mario Betti (Courtesy of dr. Massimo Betti).

During the same difficult period another great school of chemistry was rising in Bologna, *i.e.* the school of Industrial Chemistry. When Betti died, his former co-worker Bonino was the dean of the Faculty of Industrial Chemistry. In subsequent years he returned to the Ciamician Institute and the school of Industrial Chemistry was led by another farsighted great chemist, Angelo Mangini (1905-1988).[28] The building with the labs was located on a hill and the chemistry developed there was called "the chemistry of the hill" whereas the Ciamician Institute was downtown in the lowland. Under the leadership of Bonino and Mangini many difficulties deriving from the war times had to be overcame by both the "hill" and the "lowland" school. Eventually, within a reasonable numbers of years they were both able to reach a high standard and a great reputation.

In the years 1961-1968 Bertoluzza and Marinangeli of the Ciamician Institute published a series of papers[29] dealing with one of the Betti favourite themes, *i.e.* correlation between optical rotatory power and the nature of the group bound to the stereogenic centre. Betti had made extensive work and established a correlation between structure and optical parameter. Bonino, who had co-authored several papers on the topic, considered the *Betti correlation* as " the most important contribution to organic chemistry of the earliest part of the 20th century".[8] The merit of Bertoluzza and Marinangeli was represented by the efforts of revisiting the correlation with a new approach that included theoretical calculations, u.v. spectroscopy, and circular dichroism. In my opinion, despite the interest stimulated by his correlation, nowadays the fame of Betti is supported by more solid bases and these will be dealt with in the following sections.

3.2. The Betti Reaction and the Betti Base

Thus far the attention of this article was focused on the "man Betti" and to the scenario where he played, whereas chemistry was only occasionally mentioned. Now, it is time to reverse the approach and to give a deeper insight into the activity of this great chemist, enlightening at least its most highest peaks.

As already said, in its original version the Betti reaction was represented by a multi-component process in which 2-naphthol, an ethanol solution of ammonia and 2 equivalents of benzaldehyde were involved. The product obtained in high yield could be described as deriving from the equilibrium between an imino- and an oxazino form. Treatment of the reaction mixture first with HCl and then with NaOH gave 1-(α-benzylamino)-2-naphthol. Many variations on the amino-reagent were considered, but it took a few decades to read about the possibility of replacing ammonia with a secondary amines. Indeed, in a work reported in 1935 by Littman and Brode,[30] dimethylamine and piperidine were successfully used.

Although commonly the research on this topic is focused on synthetic aspects, it seems reasonable that the reaction proceeds according to the following equations. The mechanism that was suggested as operating depended upon the nitrogen base used.

(i) Reaction with ammonia.

When ammonia is used, as in the case of the prototypal reaction, the first step of the reaction should be the formation of an imine (scheme 2), that would be then attacked by the carbon nucleophile at the 1- position of the naphtol (scheme 3):

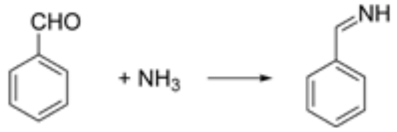
Once the Betti base **1** is formed, benzaldehyde easily leads to the imino-oxazino equilibrium between **2a** and **2b,** from which the final compound is regained by acid-base treatment (scheme 4).

A similar sequence would be followed when a primary amine is used.

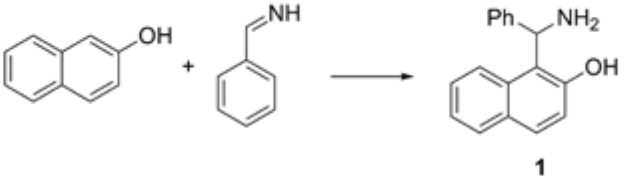
(ii) Reaction with secondary amines

For the reaction with a secondary amine, the production of an aminal **3** as intermediate was suggested by Littman and Brode (scheme 5).[30] The benzylidene diamine would then react with the carbon nucleophile leading to the final product by a substitution reaction.

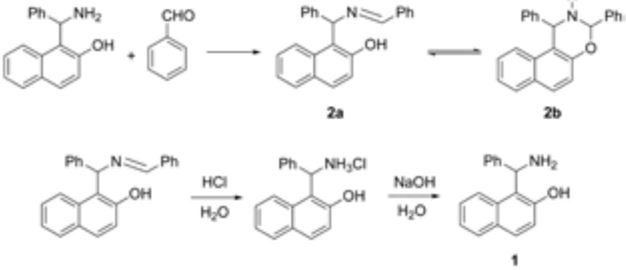
Often, the Betti reaction is referred to as a Mannich or a Mannich type reaction.[31] Indeed, the two reactions are very similar both in a form and with substance. If instead of a naphthol we consider the enol deriving from a carbonyl compound suitable for the Mannich reaction we should envisage a behaviour very similar to the one reported above, provided that the oxazino-imino compounds are considered products deriving from the second attack of an aldehyde molecule. A problem arises when priority and name attribution to the two reactions are taken into account. Betti published his reaction in 1900,[19a] whereas the paper of Mannich appeared twelve years later.[31] Therefore, it is inappropriate to qualify the *Betti reaction* as a *Mannich reaction*. It would be tempting to do the reverse, but, after a century, it seems hopeless to modify a well established terminology practice. Tilting at windmills should be better



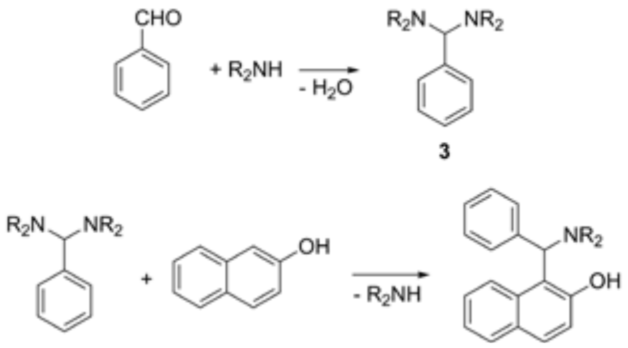
Scheme 2. Formation of the imine.



Scheme 3. Formation of the Betti base.



Scheme 4. Post-reaction and regeneration of the Betti base.



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Scheme 5. Reaction with a secondary amine.

replaced with a factual recognition of the merit of the Italian scientist.

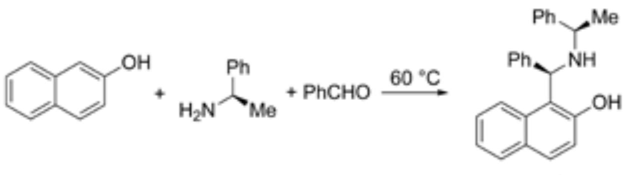
During his activity Betti was able to achieve a variety of optical resolutions and, actually, the first case that he studied was represented by his homonymous base, resolved with the classical procedure involving tartaric acid.[20] Since the possibility of obtaining a compound with high enantiomeric purity in a straightforward manner represents a convenient tool in organic synthesis, in 1998 at the University of Bari we undertook work concerning the preparation of the Betti base and similar structures, that we called using the plural form, *i.e.* Betti *bases*. Furthermore, we repeated the resolution of the prototypal base bringing minor changes to the original procedure and extending the resolution to other members of the family. The absolute configuration of 1-(α-benzylamino)-2-naphthol was established by X-ray experiments and this gave to us the possibility of assigning the configuration also to other bases.

Subsequently, prompted by our work, other research groups published important contributions reporting interesting and useful advances.[5] A significant progress was achieved by Palmieri[32] with the reaction between 2-naphtol, arylaldehydes and (*R*)–phenylethylamine in absence of a solvent (scheme 6). The product **4** resulting from the reaction with benzaldehyde was enriched up to of 99% in one optical isomer with two stereogenic centres.

3.3 Asymmetric Synthesis

The paper of Palmieri and co-workers leads us to the theme of stereodifferentiating reactions,[32] that becomes of special importance when the scientific activity of Betti and his merits are presented.

In 1940 Betti e Lucchi reported that the reaction of benzaldehyde with methylmagnesium iodide in *N.N*-dimethylbornylamine as a solvent gave a 73% yield of 1-phenylethanol showing an optical rotation of +0.30°.[24] The same alcohol was obtained with a rotation of +1.33° by reacting phenylmagnesium iodide with acetaldehyde in the same solvent.



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Scheme 6. Reaction between 2-naphtol, arylaldehydes and (R)–phenylethylamine.

In their work the two authors reported a scheme that clearly suggests the reason why the reaction could lead to optical active product, showing the interaction between ligand and metal in the nucleophilic attack. Such an interaction was fated to be the crucial aspect of a large number of reactions whose synthetic application have mushroomed under a variety of aspects.[33]

Two years after the publication of Betti and Lucchi, their reactions were repeated by Tarbell and Paulson,[34] who were not able to reproduce the stereochemical results. These authors attributed the optical activity that Betti and Lucchi had found to the formation of an optical active impurity as by-product of the reaction. It would be tempting to compare carefully the details of the two papers reporting contrasting results and to search for the origin of the differences between the two couples of scientists. A detailed analysis was performed by Rosini[35] in an engaging paper characterised also by an elegant and enjoyable style. A possible source of the discrepancy could be attributed to a difference in the stereoisomeric composition of the amine used by the two groups, but the inadequate information available does not permit to reach a safe conclusion. Nevertheless, as appropriately commented by Noyori,[33] independently from the contrast existing between the results obtained in the two laboratories, the original concept of Betti and Lucchi remained valid. An undisputed proof appeared in 1953 when Cohen and Wright reported the reaction between ethyl benzoylformate and ethylmagnesium chloride in a mixture of benzene and (+)-dimethoxybutane.[36] The resulting ethyl 2-hydroxy-2-phenylbutanoate showed an extent of asymmetric synthesis reaching about 5%. Since the work of Cohen and Wright, the enantioselective alkylation of aldehydes was produced by many groups. A variety of ligands were used with enantiomeric excesses reaching very high values. The use of a catalyst having two co-ordinating centres, such as aminoalcohols, gave excellent results.

A large part of the merit that led Noyori to achieve the Nobel Prize in Chemistry 2001 derived from this type of synthesis.

In connection with our work concerning the exploitation of the Betti base, we entered the field with success by introducing ligands having the Betti base structural theme.[4,5] After sixty years, the Betti original stereochemical idea was found to work at the best level by using the homonymous base. Rosini noted that the story presents some fascinating aspects.[35] As one would have expected, the work of our research group in Bari elicited (and is still eliciting) many other applications, thus enlarging the arsenal of chiro-methodologies available to the chemist.

3.4. Absolute Asymmetric Synthesis.

In the writing of Rosini a slight sensation of suspense accompanies the reader when the author deals with another paper by Betti and Lucchi concerning the synthesis of optically active substances.[35] The work was presented at the congress held in Italy in 1938, *i.e. X° Congresso Internazionale di Chimica, Roma, Maggio 15-21, 1938*. The theme of the important meeting was rather appealing: *Chemistry at the service of human kind*. A detailed report of the work appeared in the second volume of the abstracts.[25] As usually, in the introduction Betti and Lucchi briefly review previous work made by others on the asymmetric synthesis performed in the presence of *dextro* or *levo-* circularly polarized light. In a few words, a different situation existed between asymmetric destruction of racemic compounds and asymmetric synthesis: experiments on deracemization had led to products showing optical rotation, whereas in the case of asymmetric synthesis no compound with a defined and stable optical activity had been obtained at the time. The experiment set up by the two Italian authors was represented by the gas phase addition of chlorine to propene to produce 1,2-dichloropropane. As already mentioned, a suitable apparatus was devised in order to separate the liquid product as soon as formed, thus avoiding an artefact connected with the possible deracemizazion of the produced chloroderivative. Eventually, in the experiment performed by Betti and Lucchi the dihalogeno-compound produced under the effect of *dextro or levo-* circularly polarized light was found to be optical active with rotations in the ranges from +0.040° to +0.050° and from −0.035° to −0.040°, respectively (the polarimeter sensibility was 0.005°). Three years after the Betti's death, Davis and Ackerman reported the absolute asymmetric synthesis of tartaric acid,[37] thus lending support to the feasibility of absolute asymmetric synthesis. Surprisingly, three decades later Boldt and coworkers failed to carry out the asymmetric cyclopropanation reaction between diazoalkanes and trimethylethene under the effect of circularly polarised light.[38] The authors were then assailed with doubts concerning the possibility of achieving absolute asymmetric synthesis. Their doubts became even more consistent when they decided to repeat the chlorination of propene and the synthesis of tartaric acid. The results previously reported were not reproduced and the sad story was told in a paper in which the scepticism of the authors was made clear even in the title (*Sinde absolute asymmetrische Photosynthesis möglich?*).[38] However, almost in the same period evidence against this excessive scepticism was obtained by the successful absolute asymmetric synthesis of epta- and octa-elicenes.[39] The reason of the difficulty met in the attempts to reproduce the Betti results remains unclear. The enigma appears even more surprising if one considers that in the case investigated by the Italian chemists it is not possible to invoke the formation of an adventitious by-product since the dichloropropane obtained in the reaction was characterised also by transformation into a different optically active compound, *i.e.*propylene glycol diacetate.[26] So no wonder that the mystery that wraps the process stimulates interest even nowadays.[40]

Considering the discussion presented in both Sections 3.3 and 3.4, it seems wise to express the idea that the failure in reproducing results previously obtained by others cannot be taken as a verdict that the results are wrong. When discrepancies arise, extensive experiments should be repeated under strictly identical conditions. This is particularly valid when the expected results are associated to small values.

4. CONCLUSIONS

The end of the 20th century and the beginning of the present century have witnessed a steady increase in the production of work concerning the Betti chemistry, whose importance now is appreciated in its real dimensions. The present article has been written with the aim of reporting together with the life of Betti the peaks of his scientific and academic career. In spite of controversial aspects that inevitably occur in the activity of any great man, the stature of the chemist remains of a high standard. The trend of the impact of the work of the Italian scientist in chemistry reveals that this opinion is even bound to be enforced in the future. The high moral stature of the man revealed by his personal history represents an added value.

ACKNOWLEDGMENTS

I'm indebted to dr. Massimo Betti, the grandson of Mario, for kindly making available to me the couple of the manuscripts mentioned as ref. 6 and 7. It was a privilege for me to meet the ninth Betti generation of chemists and to have "first hand" information on the protagonist of this article. On the chemistry side, I wish to express my gratitude to my former co-workers drs. Cosimo Cardellicchio and Maria Annunziata Capozzi for sharing with me the enthusiasm to revisit the Betti chemistry world.

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Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Citation: I. Bainbridge (2017) Zvi Enrico Jolles Pioneer in Applied Chemistry. *Substantia* 1(2): 123-132. doi: 10.13128/substantia-32

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declared that no competing interests exist.

Historical Article

Zvi Enrico Jolles Pioneer in Applied Chemistry

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Abstract. When I brought to Florence the death mask of Prof. Angelo Angeli, earlier this year, I was greeted most warmly but with some puzzlement as to how it came to be in my possession.
I discovered that my father, a pupil of Angeli and later a rising figure in Florentine chemistry between 1924 and 1938, had been completely forgotten there after he was expelled from Italy to comply with the fascist Racial Laws of 1938.
This biography aims to fill that gap. It was originally written by his son, Joshua Jolles, on the occasion of the dedication of a Meeting Room at the Casali Institute, Jerusalem in 2005, and has been revised in 2017 by his daughter, Irene Bainbridge, for *Substantia*. It is a story of diligence and adventure, tenacity against many odds, and finally the triumph of optimism over adversity, to be celebrated in Florence, his Alma Mater, with the establishment of the Fondo Jolles, for the preservation of many documents relating to his life and work.

Keywords. Applied chemistry, organic chemistry, scientific biography, racial laws.

1. ACKNOWLEDGEMENTS OF FLORENCE CHEMISTRY MUSEUM

Hugo Schiff (Frankfurt-on-Main 1834 – Florence 1915), discoverer of the *schiff* bases and *schiff* reagent, is considered the founder of the Florentine school of chemistry, having been for fifty years Professor of Chemistry in Florence. The school created by him in 1864 developed further under his successor Angelo Angeli and produced chemists of international calibre, whose faces we can to some extent see in the images preserved in the Section of Chemistry of Museum of Natural History of the University of Florence.

In the past few months one of the hitherto unknown faces has finally regained a name: Zvi Enrico Jolles, assistant to Angelo Angeli and "libero docente" in Applied Chemistry, exiled from teaching in 1938 by the disgraceful implementation of the Racial Laws. Thanks to the generosity of the Jolles family the documents that attest to Zvi Jolles' activity in Florence have now been brought to Florence. They will form part of the *Fondo Jolles*, an important endowment for the Chemistry section of the Museum: first, because the donation refers to a person who played a significant role in international chemistry; second, because it fills a lacuna in the academic history of Florence; and finally, because it provides new and completely unedited primary information about Angelo Angeli and his school, in the voice of someone who was very close to him.

So close as to have been entrusted by Angeli with preparing his death mask – a mask Zvi actually took with him in his enforced exile.

Prof. Andrea Goti,
Director of "Ugo Schiff" Chemistry Department of Florence and Scientific supervisor of Chemical Heritage Project of Florence University,

Prof. Antonio Guarna,
founder of Chemical Heritage Project of Florence University

2. INTRODUCTION

Zvi Enrico Jolles was born on 23rd April 1902 in Lvov (Lemberg) in the province of Galicia in the Austro-Hungarian Empire. His life was a remarkable odyssey which reflected much of the history of the 20th Century: from Austria, to British Mandate Palestine, to Italy, to Britain, and then to Israel. He saw incredible technical advances, from the excitement when electric lighting first reached his home, to atomic energy and men on the moon.

He first went to Palestine, travelling on foot or in a donkey-cart, as a young Zionist pioneer to help reclaim the land, where he endured many hardships and survived typhus and malaria; then he returned forty years later by El Al jumbo jet to find the Zionist dream come true - a strong and vibrant modern state of Israel, making great strides in science and technology.

He built up a successful academic career in Italy but had to leave hurriedly as a refugee from Fascist persecution with nothing except the knowledge in his head. In Britain, he was briefly interned on the Isle of Man[1] as an "enemy alien" at the beginning of World War II. He built up his career again in the chemical industry, originating many novel products and processes. He suffered a terrible blow, losing to the Nazi monsters most of his close family who had remained in Europe. He survived the "blitz" in London, life-threatening illnesses, heart attacks, all the time retaining his faith and optimism, his love of family, and devoting himself to the study of chemistry, hoping that one day he would find full scope for his treasury of knowledge and ideas.

On retiring from his post as Head of Research of a chemical company in Britain, he returned to Israel as a scientific advisor to the government and played a leading role in the foundation of the *Casali Institute of Applied Chemistry*. He was appointed to a newly created Chair in *Applied Chemistry* in the Hebrew University and was the first Director of the Institute. Sadly, when he was at last beginning to see his ideas for it coming to fruition, he left this life on 13th June 1971, aged 69 years.

3. LEAVING POLAND FOR THE PROMISED LAND

Bernard Jolles, the father of Zvi, had been a modestly prosperous timber merchant producing pit-props for coal-mines and railway-sleepers for the Polish government. His father's father had been at one time an innkeeper and then a printer. On the whole, they were scholarly people; in the male line there were distinguished scholars and rabbis, some of whom combined enlightenment and secular learning with their study of Torah and Talmud. On the side of his mother (Malka Leiter) was a numerous extended family throughout the province of Galicia who played an active role in community social and charitable activities.

They were traditionally observant, as were most Jews in those parts. They kept the Shabbat so strictly that writing or cutting paper with scissors was forbidden. It was a household of order, discipline and study. At the age of four Zvi was sent to the "cheder" where he learned to read and write Hebrew and study the Torah. By his diligence and concentration he avoided the slapping and ear-pulling which were the regular teaching aids in those classes.

Later he went to a state school, the Gymnasium, where he first encountered anti-semitism. The worst perpetrators were some of the teachers. Three to four centuries earlier the Jews, who had been expelled from Spain and were migrating eastwards across Europe, had been accepted by the Polish kings as they helped to bring development and prosperity to their host country. The family name of Jolles is believed to have originated in Spain but from the 16th century onwards appears to have spread to Holland, Austria, Poland, Russia and even England. Over the course of the 19th Century, the historic territories of the Polish kings had been carved up between Austria, Russia and Prussia. The glory days of Poland had long gone, but there were lingering folk memories of a once great kingdom and noble traditions.

From the moment when an idyllic family holiday in a Carpathian mountain village was cut short by the outbreak of the first World War in August 1914, the region was plunged into turmoil. First the Austrians fought the Russians; then, as the Austrian Empire crumbled and Russia was convulsed by the agonies of the Revolution, the conflicting imperial armies melted away. Polish nationalism revived and by 1917-18 machine-gun fire raked the streets of Lvov as Poles fought Ukrainians for control. None of this was good for the Jewish community, who had enjoyed peace and stability under Austrian rule. For three centuries they had prospered but now they were exposed in quick succession to the endemic anti-semitism of Russians, Cossacks, Ukrainians and Poles who terrorised this once peaceful old town, often venting their frustrations on its Jewish inhabitants.

In his early teens Zvi Jolles had reached the conclusion that Poland could no longer be his country and that as long as the Jewish people did not have their own land they would wander the world for ever, never quite belonging anywhere. The Zionist dream – a homeland for the Jewish people in the land of Israel - gave him hope and inspiration. Zionism was an intellectual ferment among young Jews. Zvi joined the Hashomer Hatzair ("the young guard") and listened eagerly to outstanding speakers such as Hirsch Lauterpacht (much later Professor of International Law at Cambridge University, who memorably expressed the concepts of "Human Rights" and "Crimes against Humanity" at the Nuremberg Trials). Many young people in those days idealised Socialism but Zvi focused his thoughts on returning to the ancestral land of Israel. At the age of sixteen he left school and went to train on a farm, to prepare himself for the hard physical labour that lay ahead.

In 1917 the Balfour Declaration[2] gave a completely new impetus to Zionism and at the age of seventeen Zvi Jolles set off on foot through the chaos and anarchy of central Europe in the aftermath of the Great War, to make his way to Palestine. It was a hazardous adventure. With the help of friends and supporters of the Zionist movement, he crossed the Balkans, often hidden in peasants' hay-carts, sometimes given shelter by Jewish families, until he reached Turkey. Here, he was promptly arrested and imprisoned for having no passport. He was rescued by the British Consul, who provided him with an identity card as a Palestinian resident under the British Mandate. He completed his journey by ship to Jaffa and was sent by Hashomer Hatzair to Degania, a kibbutz in the north. At first, he spoke entirely in the language of the Bible, but soon became fluent in modern Hebrew.

From 1919 to 1924 he worked as a Halutz ("pioneer"), harvesting oranges and lemons, draining marshes, ploughing stony hillsides, planting trees, building roads by hand. The pioneers lived in tents by the roadside. In the evenings they sang Hebrew songs round the camp-fire; then guarded the settlements at night. On the road they were building from Haifa to Nazareth he met David Horowitz, afterwards Governor of the Bank of Israel, who much later was able to give first-hand testimony of their experiences to a UN fact-finding mission.

Unknowingly Zvi was one of the very first of the Third Aliyah ("going up") that followed WW1 and the Balfour Declaration: a select group of inspired young people who were prepared to endure all kinds of hardships and privations in pursuit of their pure Zionist ideals. Some of them were to become leading political and public figures in the development of the Jewish state, others distinguished academics in Europe and the USA. A reunion of these Halutzim in London in the 1950s revealed their later achievements in many walks of life.

Zvi returned to Poland briefly in 1922 to take his matriculation examinations for entry to University. All along this had been his intention while working on the land - a textbook always with him in the roadside tent. The occasion to go to University came sooner than he expected or desired, as a result of contracting typhus and malaria that he was fortunate to survive. Polish universities operated a *numerus clausus* for Jewish applicants, so he left for Italy in 1924.

4. IDYLLIC ITALIAN YEARS

The Duce, Benito Mussolini, had thrown open Italian universities to foreign students, free of fees. It was a grandiose gesture which succeeded in attracting many young intellects to Italy. Many were Jews who were glad to leave the anti-semitism of Poland and Eastern Europe for study and work in a friendly and relatively free country. Zvi made his way to Florence where he signed up to study Engineering but switched to Chemistry after a few months because to him it was far more exciting, reaching towards an understanding of the secrets of

Figure 1. Zvi Enrico Jolles (left) with a colleague in a laboratory of the Institutes of Chemistry of the University of Florence (from the private collection of the Jolles-Bainbridge family, now in the Fondo Jolles at Florence University Museum of Natural History).

life. At the same time, he enrolled his younger brother Benjamin to read Medicine and sent him a telegram to come quickly from Lvov. It was for a long time a matter of regret to him that he had not chosen Medicine for himself; but he had been motivated by the length of the courses and the necessity to start earning a living as soon as possible. His father was finding it difficult to continue sending his sons an allowance for their keep in Italy because the newly formed Polish government was unfavourable to Jewish businesses, many of which were in serious decline.

Zvi's brother, Benjamin, had also found difficulty in getting admission to a Polish university because of the restrictive quota. After completing his medical studies in Florence he went on to become an outstanding pioneer of new methods in radiotherapy and palliative care. He was the only one of the immediate family whom Zvi managed to extricate from Poland before the havoc of the Holocaust destroyed the rest of the family along with the whole Jewish community which had flourished in Lvov. The streets and houses are still recognisable today, but there is no trace of the lively communities which once existed. Indeed the Yad Vashem memorial in Jerusalem is grim testimony to the genocide which decimated the Jews of Europe.

Meanwhile, Zvi showed such promise that he was greatly favoured by Professor Angelo Angeli (an

internationally renowned chemist referred to by his pupils as the "Maestro"), who appointed him as his assistant. When Zvi had disembarked in Naples he spoke in his best high-school Latin. Now he

rapidly became fluent in Italian, later delivering lectures and writing many scientific papers in that language. He was an outstanding chemist and soon made his mark. In collaboration with the Maestro, he became expert in the chemistry of nitro-, nitroso- and azoxy-compounds,. He took his Doctorate "Summa cum laude" and was soon guiding and teaching colleagues who had started their studies at the same time.

In 1930 he was awarded the prestigious "Ugo Schiff Prize" in Chemistry[3].

Though dogged by the lack of Italian nationality, Zvi threw himself energetically into appointments such as "assistente volontario" and "supplente" in the department of Chemistry. During Angeli's last illness he took on the burden of most of the teaching duties of the Maestro and supervised many doctoral students' theses[4] and dissertations. Indeed, among them are some now illustrious names such as Giovanni Speroni. Angeli wrote letters[5] to support Zvi's application for citizenship but he died in 1931 and did not live to see it granted later that year.

Figure 2. Zvi with the "Maestro" Angelo Angeli in Pracchia (Pistoia, Italy); (from the private collection of the Jolles-Bainbridge family, now in the Fondo Jolles at Florence University Museum of Natural History).

1n 1937 he created a special course in Applied Chemistry which was attended by a wide range of people beside the undergraduates and doctoral students: industrial and government chemists, military officers and business executives. This new course soon gained official recognition by the University: Professor Passerini, then head of the faculty, wrote commending it[7] and in 1937 Zvi was confirmed Associate Professor of Applied Chemistry[7].

It was in Florence that he met his wife, Nidda Coceani, who was doing a doctorate in Italian Literature of

Figure 3. Zvi (in the centre) with collaborators at Pontelagoscuro, just before the departure from Italy; (from the private collection of the Jolles-Bainbridge family, now in the Fondo Jolles at Florence University Museum of Natural History).

Figure 4. Giosuè and Irene in Italy (1938); (from the private collection of the Jolles-Bainbridge family, now in the Fondo Jolles at Florence University Museum of Natural History).

the "Romance period". She had trained as a schoolteacher in Gorizia and was taking advantage of the offer of free university tuition extended to residents of Venezia Giulia. It was to be seven years before they were able to marry, only when they had achieved financial security: that was how people conducted their lives in those times. They had two children, Giosuè (Joshua) and Irene, and enjoyed a happy family life, often entertaining colleagues and students at their home. During those years, lasting friendships were forged, as is clear from the correspondence with colleagues both inside and outside Italy and now preserved in the *Fondo Jolles* of the "Ugo Schiff" Department of Chemistry of Florence University.

5. ESCAPE TO ENGLAND AND A NEW LIFE

Alas, It was too good to last: Mussolini on his ill-fated visit to Nazi Germany, signed an accord which created the Fascist "Axis"; and in 1938 the Italian Fascist government began to apply its own punitive racial laws[8] in Italy, a country which had traditionally been tolerant of minorities. On 13th October 1938 Zvi received a letter from the Rector of the University[9] informing him that he was dismissed from his teaching posts and any other official appointments "on account of Hebrew race". He had also had his Italian citizenship revoked by the September 1938 legislature.

He did not tarry. On 24th October 1938 he arrived in Folkestone, England, carrying a precious invitation from his sponsor, Professor Robert Robison (of the "Robison ester" in sugar metabolism). They had met briefly at the 10th International Congress of Pure and Applied Chemistry in Rome in 1936, where Zvi Jolles had presented a paper.

His entry to England on an Italian passport was problematic, being on condition that he would be returning to Italy within one month. He worked initially at the Lister Institute for Preventive Medicine in London, where he applied his knowledge of sugar chemistry to carry out research into the protective coat which surrounds certain bacteria. Unfortunately this was temporary, unpaid work and there was an urgent need for a salary to support his wife and family as his meagre savings were rapidly dwindling.

When he arrived in England he spoke the English of Dickens, having read "David Copperfield" in his Polish high school. Now for a third time, he became fluent in

Figure 5. Zvi Enrico Jolles in the passport photo of 1938; (from the private collection of the Jolles-Bainbridge family, now in the Fondo Jolles at Florence University Museum of Natural History).

a new language, writing scientific texts and innumerable letters of application for financial support and permanent work, using his beloved Olivetti typewriter, one of the few possessions he brought from Italy.

Amid the mounting tensions of the 1930s, British men and women of goodwill could see that there was no time to lose. A group of mainly Oxford, Cambridge and London academics, under the leadership of Lord Beveridge, had earlier established the Academic Assistance Council, which then became the Society for the Protection of Science and Learning (SPSL). Its express purpose was to extricate threatened academics mainly Jewish - from the Nazi and Fascist menace in continental Europe. The aim was to help them rebuild their careers.

A key figure in the work of the SPSL was Esther Simpson[10], assistant secretary at the time, who helped scores of refugee academics and their families, whom she came to know personally. The natural empathy she brought to the task was a lifeline through what were very difficult times. For my parents it was a hand-to-mouth existence as the loans from the Society were necessarily small. But they kept us going through those dark years. Much of the correspondence with my parents from that period is preserved in the archives of the SPSL in the Bodleian Library in Oxford[11] . It was with immense gratitude that Zvi accepted ongoing help and moral support from them. It is recorded that he later repaid every penny he received, but the support went far beyond the material help available.

Although in Britain there was an initial reluctance to adopt the newcomers and give them full scope for their professional talents, it is true to say that the virulent anti-semitic policies in Nazi Germany and most of eastern Europe created a veritable “brain drain”, benefiting Britain and indeed the US, who thereby gained a long-lasting lead over the rest of the world in Science, Technology and Medicine.

In the summer of 1940 Zvi was delighted to be offered a place with the Imperial Chemical Industries in their Research Department in Blackley, Manchester, but this was short-lived. Only two weeks later, on 10th June 1940, Italy entered the war, invading France in support of their Nazi allies (to the great reluctance of most Italians who saw Germany as a traditional enemy of Italy and Austria a hated occupying power in important areas of northern Italy). Two policemen came to the ICI Library to arrest Zvi.

Ironically, on arrival in England, Zvi was regarded as an Italian citizen and therefore now became an “enemy alien”. Following Churchill’s famous instruction to “collar the lot”, Zvi was swept up with Germans and Austrians, Nazis, Fascists and anti-Fascists, socialists, refugees from Fascism, restaurant owners, waiters and chefs, ice-cream merchants, businessmen, students, sailors from merchant ships caught in British ports, opera singers and instrumental musicians, Roman Catholic priests and monks, and a sizeable contingent of Jewish academics and students; all interned together on the Isle of Man[1] in what had been, in times of peace, a popular holiday resort. The only common factor to this assorted bunch was their origin from countries now at war. Through the thorough, impersonal, even-handed workings of British bureaucracy they were housed by nationality in the hotels and boarding-houses of the island, surrounded by barbed-wire fences and guarded by the Army.

It was in this incongruous setting that he met an Italian Jewish businessman and engineer, Alberto Casali, who had been sent to Britain by the Stock distillery company of Trieste, owned by his family, to study British distilleries. He, too, found himself interned as an “enemy alien”. Thus began a life-long friendship which, many years later, had far-reaching consequences.

It was not long before there was a veritable university in session! Zvi Jolles very soon began to teach Chemistry to many of the students whose university courses had been interrupted. Zvi was fond of relating how quickly everyone fell into their accustomed professional and occupational habits and attitudes. The chefs cooked, the businessmen organised rotas, the musicians rehearsed and presented recitals and the academics taught the students and discussed the latest theories. Zvi's internment only lasted six weeks – it was not long before the intervention of ICI, in those days a real power in the land, secured his prompt return to their Research Department. When they heard he was leaving, his fellow-internees, fascists, students, priests, sea captains, saved their meagre rations, from which some of London's finest chefs cooked up a banquet in his honour, attended by representatives of all the diverse groups.

He was lucky not to have been selected for transportation to the colonies. The ill-fated "Arandora Star", bound for Canada, with twelve hundred on board, was torpedoed by a German submarine in the Irish Sea. Hundreds went down with the ship. There were only five hundred and thirty survivors, many of whom were then loaded onto the "Donera" bound for Australia!

Back in the ICI Research Department, Zvi Jolles immersed himself in searching for novel chemical compounds which could have useful applications in medicine or technology. From his experience in sugar chemistry, he envisaged the many hydroxyl groups of cellulose and other polysaccharides as rows of hooks to which appropriately reactive molecules could be attached, perhaps as carriers or linking agents for other molecules with desirable properties. Arising from this work it occurred to him that it should be quite feasible to attach dyestuffs chemically to cotton fibres, giving them exceptional reistance to wash and wear. Dyeing of cotton had hitherto depended not very successfully on physical properties such as hydrogen bonding, van der Waals forces, molecular configuration, or on precipitation of the dye within the fibre for instance as metal salts. True chemical bonding was a kind of Holy Grail; it had been investigated but was not seen as a practical proposition for industrial application. Zvi Jolles brought fresh thinking to it, with his expertise in other areas of chemistry.

6. DIFFICULT TIMES - NEW DEVELOPMENTS

The Research Department in Hexagon House lay in a deep valley by a tributary of the River Irwell, just outside Manchester. The village of Blackley had been overwhelmed by the Industrial Revolution; its rows of terraced houses were occupied by the workers who toiled in its sprawling industries. The main road spiralled down into the valley, which was almost permanently shrouded in a pall of acidic yellowish fog with tints depending on the prevailing production process taking place in ICI's plant.

On a cliff high above the valley stood the "Woodlands Club", a substantial Victorian pile which served as ICI's clubhouse, where the senior staff of the Research Department held their monthly meeting with their eminent external consultant, Professor (later Sir) Robert Robinson (later to become President of the Royal Society). Prof. Robinson was sceptical of the notion of dyestuff-fibre combination until Zvi brought to the meeting some extremely wash-fast brilliant orange cotton squares where the colour proved to be in true combination with the fibre. The work was not taken further at this time unfortunately, perhaps because Zvi Jolles now began to suffer serious ill health; but the soundness of the basic idea was vindicated in ICI's later development of a whole range of Procion dyes.

During this time Zvi had received news that his father and two brothers in Lvov had been murdered by the Germans - their hiding-place believed to have been betrayed by a Polish janitor, later hanged as a Nazi collaborator. Externally, Zvi bore the dreadful news stoically, but it must have affected him deeply. As a result of a laboratory accident, he suffered a serious burn to his left hand; from then on he was dogged by illness year after year, no doubt aggravated by the grief within him. He spent many months in hospitals. Supported by his wife and with tremendous fortitude he emerged from this dark period as resolute as ever and went on to write important contributions to major chemical reference books - "Quinones" in Thorpe's Dictionary of Applied Chemistry[12] and chapters on azo-, azoxy- and nitroso-aromatic compounds, diazo-resins, hydroxylamines and others in "The Chemistry of Carbon Compounds"[13] (Elsevier).

In 1954 Zvi was intrigued to read an advertisement by a small chemical company in London seeking to recruit a head of research and apparently having links with Israel - and he was eager to return, this time hoping to contribute to the development of a chemical industry there. In the dark days of 1941 he had already met Dr. Chaim Weizman (himself a chemist and later to become the first President of the State of Israel) in London to discuss this possibility, but had never been able to follow it through then because of health problems. Within three months in this small company, Zvi had developed a novel process for one of their main products. Now came a curious twist: F.W.Berk & Co Ltd., established in 1871 by a family of German immigrants, bought out the smaller company. Berk manufactured a range of bromine compounds and had active links with Israel, specifically with the Dead Sea Works. Zvi , now

Head of Research of the whole company, once again took up the challenge of a new direction.

Since the 1920's bromine had occupied a "niche" market, being used in the manufacture of lead "anti-knock" additive to motor fuel. About 90% of the world bromine consumption at one time was, in fact, just for this use. But by the 1960's public awareness of health and environmental issues was beginning to make a serious impact on the use, in all kinds of applications, of chemicals which contaminate the environment with toxic residues. This was bad news for bromine producers such as Israel which had, in the Dead Sea Works, one of the world's richest sources of bromine. Though there were major outlets for bromine in agriculture and photography, the outlook was not encouraging. Not to be defeated, in 1959, Zvi unveiled a comprehensive programme of work on fire-retardants for a variety of materials based on bromine, (particularly for use on passenger aircraft) a significant innovation in this field. With this project, he had found a circuitous route back to Israel!

He saw that the chemical literature, which had an abundance of information on chlorine and its compounds, was severely lacking it on the analogous bromine compounds as well as on the element itself. He set about compiling a monograph on the neglected halogen. With the assistance of an excellent personal secretary Mrs. Elsie Barrett, wife of a chemist and herself an accomplished landscape painter - he planned and collected material for his book. Then once again, circumstances turned against him and he was struck down by a heart attack in 1963. With his characteristic faith and optimism, he carried on. The book "Bromine and its Compounds"[14] (Ernest Benn, 1966) was widely acclaimed and became a standard reference work.

7. THE REALIZATION OF A DREAM

In 1963 Berk had asked Zvi Jolles to go to Poland to represent them at the Poznan Trade Fair. It was a bittersweet experience for him, his first visit to Poland since he had left in1922 and all the tragic events that followed. He still spoke Polish fluently and was well-received. Then in 1964 he was asked to visit Israel on behalf of the company. How he must have enjoyed that! It had taken him precisely forty years to return to the land he had dreamed about as a boy and worked in as a young man.

When in 1966 he retired from his post as Head of Research at Berk he was invited to Israel as consultant to the National Council for Research and Development (Prime Minister's Office) with special reference to the utilisation of Israel's raw materials. It was then that he thought of creating a Bromine Institute, taking as a model such establishments as the Tin Research Institute in Holland.

Figure 6. Zvi (left) with Alberto Casali; (from the private collection of the Jolles-Bainbridge family, now in the Fondo Jolles at Florence University Museum of Natural History).

Each year in October, Zvi and Nidda travelled to Israel, returning via Italy in April or May, spending a few weeks in Gorizia, Trieste or Venice, and reaching home in England in June, a very pleasant itinerary, which was some compensation for all the hard years. In recognition of the impetus that Zvi Jolles could give to applied chemistry in Israel, he had been invited to the Hebrew University in Jerusalem as a Visiting Professor.

When he travelled in 1966, he took with him copies of the Bromine book, fresh off the press. Taking a train to Trieste, he went to visit his old friend Alberto Casali at his villa in Opicina, in the hills above the town. Alberto was now the head of the Stock distillery company, with factories in Italy, Austria, South America and Israel. He had been for some years the Honorary British Consul in Trieste and had been decorated by the Italian Government for services to industry and exports. Zvi and Alberto talked about Israel's need to develop a lead in technology. The two men found much common ground and Alberto Casali decided to back the vision of an institute of Applied Chemistry.

There followed a year and a half of negotiations with the Weizman Institute in Rehovoth that ultimately stalled; then one day Zvi had lunch with Avraham Harman, formerly Israel's Ambassador to Washington and at this time President of the Hebrew University. Within a week the whole scheme fell into place – the creation of the Casali Institute of Applied Chemistry[15] on the Givat Ram campus was agreed.

By 1969 the Casali Foundation had been established and the Alberto and Kathleen Casali Fellowship Foundation was supporting a number of post-doctoral stu-

Figure 7. Zvi in Jerusalem, 1970; (from the private collection of the Jolles-Bainbridge family, now in the Fondo Jolles at Florence University Museum of Natural History).

dents at the Hebrew University with grants and scholarships. By 1971 the foundation stone had been laid. The work of the Institute was meanwhile taking place in borrowed premises, by kind permission of Professor Shaul Patai. Zvi Jolles had been appointed Professor of Applied Chemistry in the Hebrew University and the first Director of the Institute, a fitting culmination to his career. While always maintaining the highest scientific standards of pure research, he was eager to find practical ways in which his work could benefit the wider community.

Unfortunately Zvi Jolles was now seriously ill, needing an operation, and as he felt he might not be able to see the building of the Institute to its completion, he asked Professor Gabriel Stein to take care of it until his return. Not long after the operation he left this life on 13th June 1971 and was buried on the Mount of Repose (Har Hamenuhot) on the west side, looking towards Tel Aviv, in the section for Professors of the Hebrew University.

8. CONCLUSIONS

It has been our privilege to write about our father, Zvi Jolles. A man of exceptional qualities and culture, he spoke seven languages and understood at least nine. His warm personality and entertaining company, combined with a compassionate and courteous nature, endeared him to all who knew him. Now almost half a century later, we can see how his aim to benefit society by research and development is being successfully achieved in his brainchild of Applied Chemistry in Jerusalem, using modern technology in fields as diverse as biodegradable polymers, biomedical composites, security, forensics, environmental science, energy, water conservation, pharmaceutics, and geochemistry.

9. ACKNOWLEDGEMENTS

We are extremely grateful that Florence University, his old Alma Mater, from which he was so cruelly exiled, should now see fit to house an archive in his name in the "Ugo Schiff" Department of Chemistry, where the first flowering of his life's work began.

We would like to express our sincere thanks to Prof Goti, Head of the Department of Organic Chemistry, to Prof Antonio Guarna and Dr Laura Colli for their invaluable help and encouragement throughout the project, and to Dr. Anna Teicher for her expert historical advice.

I would like to express particular appreciation to Dr. Laura Colli for her dedication and professionalism. She has driven the project forward with determination, gentle firmness and sheer hard work that is now reaping rewards with the establishment and progress of the Chemical Heritage Project at Florence University. We are very fortunate that it is in such capable hands for the time being at least. It is to be hoped that the support and recognition her work deserves will be ongoing.

I owe her my personal thanks for guiding me through the stages of setting up the *Fondo Jolles* in memory of my Father, with the vision and sensitivity she has brought to the task.

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Full Curriculum Vitae of Z.E. Jolles up to October 1969 is held by Fondo Jolles of "Ugo Schiff" Chemistry Department Florence University.

Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

OPEN ACCESS

Citation: J. Lekner (2017) Nurturing Genius: the Childhood and Youth of Kelvin and Maxwell. *Substantia* 1(2): 133-142. doi: 10.13128/substantia-33

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The author declared that no competing interests exist.

Historical Article

Nurturing Genius: the Childhood and Youth of Kelvin and Maxwell

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Abstract. William Thomson and James Clerk Maxwell, nineteenth century natural philosophers, were friends and colleagues (Thomson was Maxwell's senior by seven years). This historical note gives a description of their early lives, with emphasis on the influence of their fathers and of Cambridge on their development.

Keywords. William Thomson (Lord Kelvin), James Clerk Maxwell, genius, childhood, youth, history of physics.

Recent research on electrostatics got me into working contact with the early contributions of James Clerk Maxwell and William Thomson (later Baron Kelvin of Largs, and usually referred to as Kelvin). I read their biographies, and was struck by the remarkable similarities in their childhood and youth. Both were Scots, both lost their mothers at an early age, both had fathers who nurtured them intellectually and were ambitious for their career.

This note is mainly about William's and James' childhood and youth, and comes to a natural stop at their respective completions of the Cambridge Tripos examination. Only a brief catalogue of their later careers is given. Some of their electrostatic researches are discussed in my Author's Note at the end.

WILLIAM THOMSON, LORD KELVIN (1824-1907)

James Thomson, William's father, taught mathematics and geography at the Royal Belfast Academical Institution. William was born in Belfast. His mother Margaret (nee Gardner) died in 1830 when William was six. His father became Professor of Mathematics at Glasgow in 1832, and the family of four boys and two girls moved there. An elder brother James (1822-1892, FRS) trained as an engineer, and became Professor of Engineering at Glasgow.

James Thomson senior was a man of wide interests, 'capable on emergency of teaching the University classes in classics'. His books cover an amazing range: *A treatise on arithmetic in theory and practice* went to seventy-two editions; other titles include *Introduction to modern geography*, *The romance* *of the heavens*, *Elements of plane and spherical geometry*, *Euclid's elements of geometry*, *Algebra*, and *Introduction to the differential and integral calculus* (Ref. 1, pp 6, 7). And this from a farmer's son!

After Margaret died the father taught James and William 'the use of the globes' and Latin (Ref. 1, p 6). James and William were allowed to attend informally their father's lectures at the University. One of those present at the Junior Mathematics Class later recalled to Kelvin 'As a mere child you startled the whole class, not one of whom could answer a certain question, by calling out: 'Do, papa, let me answer.' (Ref. 4, p 5) James and William matriculated at the University of Glasgow at ages 12 and 10, respectively, in October 1834. William '...carried off two prizes in the Humanity Class; this before he was eleven.' In the next session young William got prizes in Natural History and in Greek (Ref. 1, pp 8, 9). And so on. Kelvin recalled (in 1907) 'A boy should have learned by the age of twelve to write his own language with accuracy and some elegance; he should have a reading knowledge of French, should be able to translate Latin and easy Greek authors, and should have some acquaintance with German. Having learned thus the meaning of words, a boy should study Logic'. In Natural Philosophy, under Professor Meikleham, William read *Mécanique analytique* of Lagrange and *Mécanique céleste* of Laplace (Ref. 1, pp 11, 12). In 1839 he attended the Senior Natural Philosophy class taught by the professor of Astronomy, J. P. Nichol, who introduced William to Fourier's *Théorie analytique de la chaleur*. 'I asked Nichol if he thought I could read Fourier. He replied 'perhaps'. ... on the 1st May (1840) ... I took Fourier out of the University Library; and in a fortnight I had mastered it – gone right through it.' (Ref. 1, p 14). William was fluent in French: in the summer of 1839 the family went to London, and then on to Paris, where the boys were left (in the charge of a trusted servant) for about two months to learn French. The father wished them to learn German also; for two months the whole family took lessons in German, and on 21 May 1840 Professor Thomson and his six children (William was 16, the youngest boy Robert was 11) left Glasgow for Liverpool, London and then by steamer to Rotterdam. William's diary has the entry 'Reached the bar at the mouth of the Maas, near Brill, at about 4½ o'clock in the morning, where we had to lie till 10. The vessel rolled greatly from side to side, but the rolling was intermittent, as every two or three minutes it calmed down and then rose again with perfect regularity. This probably arose from two sets of waves of slightly different lengths coming in in the same direction from two different sources'. The family visited the Hague (the diary notes a visit to the Museum to see a stuffed mermaid!), Delft, Düsseldorf, Bonn, Cologne, Frankfurt am Main (where they stayed till 2 August), then onto Baden, from where the brothers James and William went on a walking tour of several days through the Black Forest. The family returned to Glasgow in early September. Certainly an educational trip, much to the credit of Professor Thomson. But young William did not spend all his time practising German: he had taken his Fourier with him, and surreptitiously read it in the cellar. 'When my father discovered it he was not very severe upon me' (Ref. 1, pp 16-18). A text by Kelland, *Theory of heat*, 1837, stated that the Fourier expansions were 'nearly all erroneous'. William found, while at Frankfurt, the cause of the misunderstanding. This resulted in his first publication *On Fourier's expansions of functions in trigonometrical series* (Ref. 8, Vol. 1, pp 1-9).

In April 1841 William entered Peterhouse in Cambridge. (He had purposely avoided taking a degree at Glasgow, so as to be able to enter Cambridge as an undergraduate). The choice of Peterhouse had much to do with the presence there of Dr. William Hopkins, a geophysicist and famous as a Mathematics Tripos tutor. The Maths Tripos was an examination conducted (in Thomson's day) over six days, each with 5½ hours of hard writing, covering mathematics and the mathematical aspects of physics. To be placed high on the list, especially to be Senior Wrangler or Second Wrangler, was the making of a career. Hence the three years of intense preparation and tutoring. Young William, 17 when he entered Cambridge, was mature enough to realize the importance of the Tripos, and organize his life accordingly. He soon saw that there was a separation at Peterhouse into the classes of 'rowing men' and 'reading men'. 'All my friends are among the latter class, and I am gradually dropping acquaintance with the former ... even to know them is a very troublesome thing if you want to read, as they are always going about troubling people in their rooms' (Letter to his father, 12 December 1841, see Ref. 1, pp 32-33). However, together with another undergraduate, William bought a single sculling boat for £7. His father was surprized at not having been consulted, and urged William to 'Use *all economy* consistent with respectability. Be most circumspect about your conduct and about what acquaintance you form. You are young: take care you be not led to what is wrong. A false step now, or the acquiring of an improper habit or propensity, might ruin your life.' (Ref. 1, p 37). William made good use of the boat, and rowed on the river Cam with another 'reading' man, G. W. Hemming of St. Johns, Senior Wrangler in 1844. His sister Elizabeth wrote on 27 February 1842 that 'papa' was reconciled to the purchase of the boat, much to the relief of William, who wrote to his father on 14 April 1842 that 'The sculling is going on with great vigour, and is keeping me in excellent preservation. ... I find that I can read with much greater vigour than I could when I had no exercise but walking in the inexpressibly dull country round Cambridge' (William was used to a more varied topography than the flat land surrounding Cambridge).

During the summer vacation of 1842 the family were at Knock Castle (three miles from Largs, on the Firth of Clyde). There William wrote a paper *On the linear motion of heat* (Ref. 8, pp10-15) in which he discusses solutions of the one-dimensional equation for the flow of heat, namely $\partial_t T = \partial_x^2 T$ where $T(x,t)$ is the temperature, in the form

$$T(x,t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} d\alpha\, e^{-\alpha^2} f\left(x + 2\alpha\sqrt{t}\right), \qquad T(x,0) = f(x)$$

In another paper *On the uniform motion of heat in homogeneous solid bodies, and its connection with the mathematical theory of electricity* (Ref. 9, pp 1-14) was written that summer. Not bad for an undergraduate of 18.

Back at Cambridge in October 1842, William began his training under the tutor Hopkins, with the aim focused on the Tripos examinations in the Senate House in January 1845. He won a mathematics prize of £5, which he proposed to spend on an *Illustrated Shakespeare*, but his father preferred him to buy Liouville's *Journal de Mathématiques*.

James Thomson's paternal care was ever focused on his son's long-term prospects: Dr Meikleham, the Professor of Natural Philosophy at Glasgow, was ill. If only he could last till William had completed the Tripos (and got the laurels of a Wrangler), William might succeed him. A natural wish for the father, to have his son join him as a professor at his University. On 9 April 1843 Professor Thomson writes to William that Dr. Meikleham is better; he adds '...you must take care not only to *do* what is right, but to take equal care always to *appear* to do so. A certain [Professor of Moral Philosophy] here has of late been talking a good deal about the vice of the English Universities, and would no doubt be ready to make a handle of any report or gossip he might pick up.' (Ref. 1, p 53). The next letter detailed the requirements of the chair of Natural Philosophy, which included skill in experiments. This he urges William to attain. William, ever cooperative, replies that in his spare time he is reading *Cours de Physique* by Lamé, 'which is an entirely experimental work'. James Thomson (4 May 1843) writes of the probable votes in an election of Dr. Meikleham's successor, and adds 'Take care to give a *certain gentleman here* (who, as to private affairs, is more nearly omniscient than anyone I have known) no handle against you. Avoid boating parties of in any degree of a disorderly character ... as scarcely anything of the kind could take place, even at Cambridge, without him hearing of it.' (Ref. 1, pp 57, 58). And William did avoid boating parties and any scandal, but he did row in the eights for Peterhouse, and won the single sculls (Ref. 1, pp 58-62). He also played the cornet, and was one of the founding members of the Cambridge Musical Society.

The saga of the chair of Natural Philosophy continued, with Dr. Meikleham becoming ill and recovering. On 20 April 1844 Professor Thomson urged William to 'Keep the matter in mind, therefore, and think on every way in which you might be able to get efficient testimonials ... Do not relax your preparation for your degree. I am always afraid some unknown or little heard of opponent may arise. Recollect, too, that you might be thrown back by illness, and that you ought therefore be *in advance* with your preparation. Above all, however, take care of your health.' William replied on the 22nd: 'I am very sorry to hear about Dr. Meikleham's precarious state ... it is certainly very much to be wished that he should live till after the commencement of next session.'

Preparation for the Tripos was to continue during the long vacation, when Hopkins would go with a party of reading men to Cromer, Norfolk. William wished to go too, entailing extra expense for his supportive father, who agrees to the request. But soon William writes from Cromer (13 June 1844): ' My Dear Father – I have again to write to you on the same pleasant business that I had to write to you about so lately, which is to say that my money is again all gone.' (Details of his expenses follow.) (Ref. 1, p 80). Later (12 October 1844) 'papa' sent his son the halves of bank notes for £100, noting that the three years' expenditure was now £774/6/7, and asked 'How is this to be accounted for? Have you lost money or been defrauded of it ...? ... you *must* exercise the *strictest* economy that shall be consistent with decency and comfort.' Lest the readers think 'papa' a cheapskate, let me remind them of inflation: the value of the pound has diminished by a factor of about 72 between 1844 and 2001,[10] so in present currency Dr. Thomson's £774 is approximately £60,000.

The work of the 'reading party' entailed Dr Hopkins setting examination papers and discussing the students' answers with them. It went on for two months. After the reading party ended, Thomson and a fellow Scottish student 'took a boat and rowed out to sea, and intercepted the G. N. S. steamer *Trident*', which took them to Edinburgh! (Ref. 1, p 82) Railways were only just being established (the Edinburgh to Glasgow line opened in 1845), and travel was a major undertaking.

Let us fast-forward now to the ordeal of the Senate House examinations, set to begin on 1 January 1845. The 'Wrangler' contestants had trained like Olympic athletes for this six-day event. Nor was this the end, because the Smith's Prize (another week of examinations) followed soon after. And the results were: Parkinson of St. John's, Senior Wrangler, Thomson of Peterhouse, Second Wrangler. The disappointment of William's family and friends was mitigated by the fact that Thomson was judged clearly better in the two Smith's Prizes awards, Parkinson second.

Dr Thomson continued to advance his son's education (and the prospects of the Chair in Natural Philosophy at Glasgow) by funding a trip to Paris in early 1845. William went with introductions to Arago, Biot, Babinet, Cauchy and Liouville. He presented himself to Liouville, with whom he met often and became friends. He also met Sturm and Foucault, that is almost all of the living French scientists (Laplace, Legendre, Poisson and Fresnel were no longer). Biot introduced him to Regnault, the professor of Natural Philosophy at the Collège de France, and researcher into the physics of heat engines. William worked with Regnault in his laboratory, met Liouville and Cauchy often, and in his spare time (Ref. 1, p 128) 'I have been reading Jacobi's *Nova Fundamenta* and Abel's 1st memoir on *Elliptic Functions*, but have been rather idle on the whole'. Indeed!

After four and a half months in Paris William returned to Cambridge. At the British Association meeting he met Faraday. Soon after he was elected Foundation Fellow of Peterhouse, this being worth about £200 per annum, with rooms in College. This post he held till his marriage in September 1852. In May 1846 the chair of Natural Philosophy at Glasgow became vacant by the death of Professor Meikleham. The timing was perfect. William and his father quickly gathered testimonials and information about other possible candidates. There were five other applicants. Among the testimonials supporting William Thomson were those from Arthur Cayley, George Boole, J. J. Sylvester, G. G. Stokes, M. Regnault and M. Liouville. To the printed pamphlet of 28 pages containing the testimonials, given to the electors, Thomson added an appendix listing his published papers, twenty-six of them. William was 22 at the time of his appointment in October 1846, and kept the chair till his retirement in 1899.

Our description of young William Thomson's nurture and development stops here. He was not just a mathematically gifted child – he had the great advantage of a highly intelligent and energetic father, dedicated to his son's advancement. In Cambridge he had the support of the best tutor, working in possibly the best environment for mathematics and the natural sciences in Britain. In Paris he met and worked with the foremost mathematicians and scientists of France. And he was sensible enough to make full advantage of these opportunities, through continuous and vigorous use of his exceptional brain.

Professor William Thomson, 1846.

JAMES CLERK MAXWELL (1831-1879)

James' father was born John Clerk, adding the name Maxwell upon inheriting the estate of Middlebie. He practised law in Edinburgh and seemed set on a quiet batchelorhood until he met and married Frances Cay. A child (Elizabeth) died in infancy, and James was born when his mother was nearly forty, at 14 India Street, Edinburgh (Ref. 11, pp 2-3). Frances was of a 'sanguine active temperament', and energised John to develop the estate of Middlebie and enlarge *Glenlair*, their home.

John had a 'persistent practical interest in *all useful processes*'; he made a special last for shoes (square-toed) for himself and later for James, and planned the outbuildings of *Glenlair*, down to the working plans for the masons (Ref. 11, pp 7-9). Even before he was three, little James likewise showed a practical interest in the world. A letter from Frances to her sister Jane Cay gives the picture: 'He is a very happy man ... has great work with doors, locks, keys, etc., and "Show me how it doos" is never out of his mouth. He also investigates the hidden course of streams and bell-wires ... he drags papa all over to show him the holes where the wires go through.' (Ref. 11, p 27). Throughout his childhood the constant question was "What's the go o' that? What does it do?" If not satisfied with an answer he would ask "But what's the *particular* go of it" (Ref.11, p 28). His great love was the outdoors, of streams and ponds and the frogs that inhabited them (Ref. 11, pp 33-34). With his first cousin Jemima Wedderburn, who was eight years older, he produced an animation of a tadpole wriggling from its egg and changing into a swimming frog (Ref. 11, p 37).

James was educated by his mother until she died of abdominal cancer when he was eight. After his mother's painful death in December 1839, Mr. Maxwell hired a local lad to tutor James at home. 'The boy was reported slow at learning, and Miss Cay after a while discovered that the tutor was rough' (Ref. 11, p 41). Just as well she did: his friend and biographer Lewis Campbell describes the 'roughness' (being hit on the head by a ruler, and having ears pulled till they bled), and the lifelong effect this had on James (Ref. 11, p 43).

And so Mr Clerk Maxwell sent the boy of 10 to the Edinburgh Academy. He lived with his father's sister, Mrs Wedderburn, with occasional stays with his mother's sister, Miss Cay. His first day at school was tough: in his gray tweed jacket and square-toed shoes, he was a target for ridicule and worse. He returned home 'with his tunic in rags ... his neat frill [collar] rumpled and torn ...' (Ref. 11, pp 49-50). His aunts made sure his dress conformed more to the norms, but his nickname 'Dafty' stuck with him. Places in class were allotted according to performance, and James was initially among the rowdy boys, who naturally made things worse for him. For the first two years or so, school was something to endure. Fortunately he had the warm refuge of his aunt's home at 31 Heriot Row, and its good library, plus the occasional visits of his father, when they would explore Edinburgh together. The love between father and son is clear in the letters reproduced in Lewis Campbell's biography. In a letter of 19 June 1844, addressed to 'My Dear Father', and signed 'Your most obt. servt. Jas. Alex. McMerkwell' (an anagram, decoded by numbers underneath), he remarks after news of swimming and other outings 'I have made a tetra hedron, a dodeca hedron and 2 more hedrons that I don't know the wright names for.' (Ref. 11, p 60). Campbell notes that they had not yet begun geometry.

At school he excelled in Scripture, Biography and English, and discovered that Latin and Greek were worth learning. At about this time Lewis Campbell joined the school, and began a lifelong friendship. Lewis lived at 27 Heriot Row, and the two boys were continually together for about three years. 'We always walked home together, and the talk was incessant, chiefly on Maxwell's side. Some new train of ideas would generally begin just when we reached my mother's door. He would stand there holding the door handle, half in, half out ... till voices from within complained of the cold draught, and warned us that we must part.' (Ref. 11, p 68).

By July 1845 young James was coming into his own, with prizes for English and English Verse, and the Mathematical Medal. His father now 'became more assiduous than ever in his attendance at meetings of the Edinburgh Society of Arts and Royal Society, and took James with him repeatedly to both.' (Ref. 11, p 73). A member of the Society of Arts, D. R. Hay, had written a book on *First principles of symmetrical beauty*; one of the problems in it was how to draw a perfect oval. James generalized the equation of an ellipse, $r_1 + r_2 = 2a$ (r_1 and r_2 are distances from the two focal points to a point on the ellipse, $2a$ is the length of the major axis), to curves which satisfy $mr_1 + nr_2 =$ constant. With Mr Maxwell's skilled promotion of this work, the result was James' first paper *On the description of oval curves* (Ref. 12, pp 1-3), which was communicated to the Royal Society of Edinburgh by Professor J. D. Forbes in 1846. Professor Forbes took Maxwell under his wing, and they became lifelong friends. As it happened, the curves were not new, having been described by Descartes, and their optical properties considered by Newton and Huygens, but Maxwell's practical construction by means of pins and string was new. And what illustrious company for a schoolboy of fifteen!

This paper and his other manuscripts on ovals can be found in the *Scientific letters and papers*, (Ref. 14, pp 35-67). Maxwell was now launched into mathematical and scientific inquiry. His second published paper (1849) was *On the theory of rolling curves* (Ref. 12, pp 4-29), in which he already shows a mastery of plane differential geometry. Next, in 1850, came *On the equilibrium of elastic solids* (Ref. 12, pp 30-73), 'an astonishing achievement for a 19 year-old working almost entirely on his own. The mathematics went hand-in-glove with his experiments on polarized light ... He set out for the first time the general mathematical theory of photoelasticity...' (Ref. 15, p 32). By this time James was at Edinburgh University, which he had entered at seventeen. P. G. Tait, who was a school friend of Maxwell's and later a collaborator with Kelvin on their *Treatise on natural philosophy*, was one of James' chief associates at Edinburgh University, but stayed for only one session, going on to Peterhouse, Cambridge in 1848.

Maxwell went to Cambridge also, but not till 1850. Campbell remarks (Ref. 11, p 114) '... it is perhaps to be regretted that he did not go to Cambridge at least one year earlier. His truly sociable spirit would have been less isolated, he would have gained more command over his own genius ...'. Eventually his father was persuaded, and James went to Peterhouse, but transferred to Trinity College to improve his chances of a fellowship. Maxwell's tutor in preparation for the Tripos was the same William Hopkins whom we had met earlier as William Thomson's tutor. Here is Hopkins' view of Maxwell, as recorded by a Cambridge contemporary: '... he is unquestionably the most extraordinary man [Hopkins] has met with in the whole range of his experience; ... it appears impossible for Maxwell to think incorrectly on physical subjects; that in his analysis, however, he is far more deficient; ... a great genius, with all its eccentricities ... one day he will shine as a light in physical science ...' (Ref. 11, p 133).

Unfortunately the letters James wrote as an undergraduate to his father from Cambridge are lost. His father's letters naturally seek his son's advancement: 'Have you called on Profs. Sedgwick at Trin., and Stokes at Pembroke? If not, you should do both. ... Provide yourself with cards.' (Ref. 11, p 150) James got a scholarship from Trinity College in April 1852. At the scholars' table he was in his element, with free debate on almost any topic. He was elected to the Select Essay Club, a discussion group of twelve students who were known as the Apostles. Maxwell's essays delivered to the Apostles (Chapter VIII of Ref. 11) have titles such as *What is the nature of evidence of design*, which begins 'Design! The very word ... disturbs our quiet discussions about *how* things happen with restless questionings about the *why* of them all.' Another essay *Idiotic imps* is about pseudo-science (then called Dark Science), which Maxwell exposes and analyses. Yet another has the intriguing title *Has everything beautiful in Art its original in Nature*? A serious late essay, from February 1856, is on analogies: *Are there real analogies in nature?* We need both data and theory to make sense of the world: 'The dimmed outlines of phenomenal things all merge ... unless we put on the focussing glass of theory and screw it up sometimes to one pitch of definition, and sometimes to another, so as to see down into different depths ...' In the same essay, Maxwell remarks on space and time: '... space has triple extension, but is the same in all directions, without behind or before, whereas time extends only back and forward, and always goes forward.' The arrow of time, which Maxwell's statistical physics was later to clarify!

In the midst of preparations for the Tripos exams, James took a few days of the 1854 Easter vacation, to stay at Birmingham with a friend. His father wrote (Ref. 11, pp 7, 168) 'View, if you can armourers, gunmaking and gunproving – swordmaking and proving – *Papier-mâchée* and japanning – silverplating by cementation and rolling – ditto, electrotype – Elkington's works – Brazier's works, by founding and by striking out dies – turning – spinning teapot bodies in white metal, etc – making buttons of sorts, steel pens, needles, pins and any sorts of small articles which are curiously done by subdivision of labour and by ingenious tools ... foundry works, engine-making ... If you have had enough of the town lots of Birmingham, you could vary the recreation by viewing Kenilworth, Warwick, Leamington, Stratford-on-Avon, or such like.' James began with the glassworks.

Maxwell now faced the trial of the Senate House examinations, in his year five days of 5½ hours each. Ever solicitous and practical, his father wrote 'You will need to get muffettees for the Senate-Room. Take your plaid or rug to wrap round your feet and legs.' James was Sec-

Maxwell with his colour wheel, circa 1855.

ond Wrangler, E. J. Routh of Peterhouse Senior Wrangler. They were declared equal as Smith's Prizemen.

In October 1855 James Clerk Maxwell was elected Fellow of Trinity College. He had supported himself by taking private pupils, but this could now stop. Apart from teaching third-year hydrostatics and optics, he was free to do research. He was now 24. He left Cambridge in 1856 to take up the chair of Natural Philosophy at Aberdeen, then was Professor at King's College, London from 1860 to 1865, when he resigned to live and work at *Glenlair*. After Kelvin and Helmholtz declined the offer, Maxwell became the first Cavendish Professor of Physics at Cambridge in 1871. He had but eight years to live. He died in 1879 of abdominal cancer, aged 48, at nearly the same age that his mother had died of the same type of cancer.

We are fortunate in having a warm and affectionate biography by his friend Lewis Campbell. Especially moving are his depictions of James' childhood and adolescence, and of his early death. We admire his works, and with this biography we can also love him.

EPILOGUE

William Thomson and James Clerk Maxwell both *achieved* greatness; it was certainly not thrust upon them. However, both were fortunate in their fathers, in more than their genetics. And their fathers were fortunate in them: in a letter anticipating James' 21st, Mr Maxwell says 'I trust you will be as discreet when Major as you have been while Minor', quoting Proverbs x.1 [A wise son maketh a glad father.] Both sons showed remarkable good will and cooperated fully with their fathers' guidance and instruction. This in contrast to much modern behaviour, and also to that of the musical genius Wolfgang Amadeus Mozart, who eventually rebelled against his father Leopold. Thomson and Maxwell senior never had to face Leopold's tragedy of having a cherished child spurn them.

In the addition to the wonderful love, instruction and support from their fathers, they each had the support of family, in Maxwell's case particularly the comfort of the Aunts. In the wider sphere, we should also note that Scotland had been important in the European enlightenment and that the rates of literacy were exceptionally high. William and James grew up in a culture with a strong work ethic and widespread respect for knowledge, a powerful combination.

Finally, they both had the great advantage of their Cambridge experience. This environment suited both, matured them, and gave them lifelong connections with some of the brightest minds then living.

AUTHOR'S NOTE

Victoria University physicists Pablo Etchegoin and Eric Le Ru have refined surface-enhanced Raman scattering to such an extent that they are able to detect single molecules.[16] This remarkable feat is accomplished by using the enhancement of an external electric field (provided by an intense laser beam) in the gap between two close conducting particles. The simplest applicable model is that of two conducting spheres in a steady (DC) external field, which had been solved by Maxwell and others.[17-19] The solution is exact, and in the form of infinite series which converge rapidly when the sphere separation s is comparable to or larger than the radii of the spheres. However, the field enhancement is large when the sphere separation is small compared to the sphere radii, and there the series converge more and more slowly as s decreases. This is precisely the physically interesting limit, that utilized by Pablo and Eric to such good effect. So we have the unhappy situation where an exact theory fails to deliver just where it is needed.

I got interested, and spent considerable time investigating the exact series, their integral equivalents and especially the logarithmic terms which appear at small s. What started as an exploration of field-enhancement in the limit of close approach of the two spheres[20a,d] grew to encompass the capacitance of two spheres (at the same potential, or with equal and opposite charges),[20b] and the polarizabilities (longitudinal and transverse) of a two-sphere system.[20c] In all cases terms logarithmic in the sphere separation s appear in the formulae.

Maxwell had approached the problem from the other end: he obtained, for quantities related to the capacitance coefficients C_{aa}, C_{ab} and C_{bb} of two spheres of radii a and b and separation of centres c (with c and s related by $c = a + b + s$ expansions in reciprocal powers of c. There is the remarkable Section 146 of his *Treatise on Electricity and Magnetism*,[17] in which he matches spherical harmonic expansions about the two sphere centres to obtain ℓ, m and n coefficients (defined below) as series in reciprocal powers of c. Section 146 is seven pages of formulae, in which the calculation is carried to the twenty-second reciprocal power of c! As is well-known, series expansions of this type get more complex the higher the order. Maxwell had no computing aids, not even a mechanical calculating machine. I checked all the coefficients in his formulae (using computer algebra, of course) and found all were correct. This attests to Maxwell's amazing ability to carry through very long and intricate calculations, but also raises the question: why did Maxwell do this enormous amount of work? His coefficients ℓ, m and n give the total electrostatic energy of the two spheres, carrying charges Q_a and Q_b, as

$$W = \tfrac{1}{2}\ell Q_a^2 + mQ_aQ_b + \tfrac{1}{2}nQ_b^2 \qquad (1)$$

The coefficients ℓ, m and n are related to the capacitance coefficients C_{aa}, C_{ab} and C_{bb}

$$\ell = \frac{C_{bb}}{C_{aa}C_{bb} - C_{ab}^2}, \qquad m = \frac{-C_{ab}}{C_{aa}C_{bb} - C_{ab}^2}, \qquad n = \frac{C_{aa}}{C_{aa}C_{bb} - C_{ab}^2} \qquad (2)$$

The total energy expanded in reciprocal powers of the distance between sphere centres c begins[21]

$$W = \frac{Q_a^2}{2a} + \frac{Q_b^2}{2b} + \frac{Q_aQ_b}{c} - \frac{Q_a^2b^3 + Q_b^2a^3}{2c^4} - \frac{Q_a^2b^5 + Q_b^2a^5}{2c^6} + \dots \qquad (3)$$

The first two terms are the self-energies of the two charged spheres, the third is the Coulomb energy, the fourth and fifth are due to mutual polarization of the two spheres. Maxwell had the information to give the energy up to terms of order c^{-22}, but he did not do that. Why not? And, why do all that work and give the results in his *Treatise*? My guess is that (i) Maxwell was looking for a pattern in the series, and hoped to sum them completely if he found the pattern; and (ii) he wanted to compare experimental results on the force between two charged spheres with theory, and needed all these terms to do so. There is no hint in Section 146 as to his reasons. Perhaps neither of (i) or (ii) came to fruition, but he wanted the results of his labours to be available to others.

Preceding Maxwell's work were the Kelvin papers of 1845 and 1853.[9] William Thomson was 21 when the earlier of these was published. It deals with the force between an earthed sphere and a charged sphere, and uses the method of images that he invented. He obtained an infinite series for the force $F(c)$, in which successive numerators and denominators of terms in the series are related by recurrence relations. It is now easy to write down the complete expression for the energy:[21] if sphere a carries charge Q_a, and sphere b is earthed, the electrostatic energy, and the force between the spheres, are given by

$$W(c) = \frac{Q_a^2}{2C_{aa}(c)}, \qquad F(c) = -\partial_c W(c) \qquad (4)$$

So, if we know the capacitance coefficient C_{aa}, a simple differentiation will give us the force. Incidentally, the inverses of the relations (2) are

$$C_{aa} = \frac{n}{\ell n - m^2}, \qquad C_{ab} = \frac{-m}{\ell n - m^2}, \qquad C_{bb} = \frac{\ell}{\ell n - m^2} \qquad (5)$$

so the Maxwell coefficients ℓ, m and n could be used directly to give the force as

$$F(c) = -\tfrac{1}{2}Q_a^2\,\partial_c(\ell - m^2/n) \qquad (6)$$

The force is always attractive, as is to be expected since the charge induced on the earthed sphere b has opposite sign to Q_a. The force increases as the separation s between the spheres decreases, and in fact diverges as s tends to zero.

A more interesting but more difficult problem is that of the force between two charged spheres (Kelvin 1853).[9] The Maxwell expansion in reciprocal powers of c fails at close approach, and in particular at contact, when the spheres are at a common potential. They share the charge; the force is clearly repulsive, whatever the sign of this charge. Again Kelvin used his method of images, and again obtained an infinite series for the force. For spheres of equal radii, in contact, his expression for the force is proportional to a double series,

$$\begin{array}{ccccccccccc}
\frac{1}{2^2} & - & \frac{1.2}{3^2} & + & \frac{1.3}{4^2} & - & \frac{1.4}{5^2} & + & \frac{1.5}{6^2} & - & \dots \\
 & - & \frac{2.1}{3^2} & + & \frac{2.2}{4^2} & - & \frac{2.3}{5^2} & + & \frac{2.4}{6^2} & - & \dots \\
 & & & & \frac{3.1}{4^2} & - & \frac{3.2}{5^2} & + & \frac{3.3}{6^2} & - & \dots \\
 & & & & & & \frac{4.1}{5^2} & + & \frac{4.2}{6^2} & - & \dots \\
 & & & & & & & & \frac{5.1}{6^2} & - & \dots
\end{array} \qquad (7)$$

Kelvin notes that adding by vertical columns gives diverging series, while adding by horizontal rows gives a convergent series, which he sums to $\tfrac{1}{6}(\ell n 2 - \tfrac{1}{4})$.

The evaluation of the double sum demonstrates young William's mathematical skill. He expresses the sums of the first, second and third rows respectively as

$$\int_0^1 d\theta \frac{\theta\,\ell n\frac{1}{\theta}}{(1+\theta)^2}, \qquad -2\int_0^1 d\theta \frac{\theta^2\,\ell n\frac{1}{\theta}}{(1+\theta)^2}, \qquad 3\int_0^1 d\theta \frac{\theta^3\,\ell n\frac{1}{\theta}}{(1+\theta)^2} \qquad (8)$$

[For those interested in the mathematics: set $\theta = e^{-x}$ to convert $\int_0^1 d\theta \frac{\theta\,\ell n\frac{1}{\theta}}{(1+\theta)^2}$ to the more familiar $\int_0^\infty dx \frac{x}{(e^x+1)^2}$ then expand in powers of e^{-x} to obtain the sum of the first row.] Noting that $(1+\theta)^{-2} = 1 - 2\theta + 3\theta^2 - \dots$ William writes the sum of the row sums as the integral

$$\int_0^1 d\theta \frac{\theta \, \ell n \frac{1}{\theta}}{(1+\theta)^4} \tag{9}$$

which he evaluates without further comment as

$$\frac{1}{6}\left[\frac{\ell n \frac{1}{\theta}}{(1+\theta)^3}(3\theta^2+\theta^3)+\ell n(1+\theta)-\frac{\theta}{(1+\theta)^2}\right]_0^1 = \frac{1}{6}\left(\ell n 2-\frac{1}{4}\right) \tag{10}$$

A reader who *verifies* each of these steps will appreciate what is involved, but perhaps not the difficulty of its formulation, and certainly not the complexity of the infinite sets of electrical image charges that it is based on.

Without further discussion William takes the convergent result as correct! When I first saw this I wondered how it was that the (mathematically extremely able) young Thomson could be ignorant of Riemann's theorem about conditionally convergent series, namely that they can be summed to any desired result by suitable rearrangement of terms. The answer lay in chronology of course: Riemann (1826-1866) was a student at Göttingen under Gauss (with a spell at Berlin) from 1846 to 1849, and did not teach till 1854. His paper on the re-arrangement of series was completed in 1853, but not published until after his death in 1866.

In fact the Kelvin result is correct. I have obtained it directly from the properties of the capacitance coefficients, and have generalized the result to spheres of arbitrary radii, at arbitrary separation.[21] But young Thomson's choice of one result from the infinity of possible sums of that double series is the boldest move I have seen in theoretical physics.

P. S. From 1854 there was much correspondence between Maxwell and Thomson, who became friends. The Maxwell letters relevant to electromagnetism are reprinted in Ref. 22.

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An International Journal of the History of Chemistry

Vol. 1 – n. 2

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