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Research Article

Hydration of Silica and Its Role in the Formation of Quartz Veins – Part 1

JOHN ELLISTON

Elliston Research Associates Pty Ltd, 10B The Bulwark, CASTLECRAG 2068, New South Wales, Australia

E-mail: john.elliston@ellistonresearch.com.au

Abstract. The crystalline forms of quartz and that it is insoluble are well known. The hydrolysis of silica and formation of polymeric silicic acids in slightly alkaline (pH 8.1 - 8.3) sea water is less well known and not recognised by many geologists. Silica is one of the most abundant components of ordinary sediments and the amorphous forms, the silica gels, have been closely studied. Their properties and behaviour are perhaps better known than those of many other colloids. Quartz veins are abundant in all types of sediments and in rocks and mineral deposits derived from them. Clearly if we study how silica is mobilised into these veins and lodes, how it silicifies wall rocks, forms opal, replaces shells and tree trunks, etc. then we may have a better basis for understanding how sulphide particles might similarly be mobilised into veins and lodes, permeate shales, form framboids, replace fossils and plant fragments or fine shale bands, etc. This article briefly summarises recent developments in the aqueous chemistry of silica. It emphasises the particulate nature of the amorphous silica species in order to update rather simplistic views that quartz veins and many other natural forms of quartz “crystallise directly from solution”. A number of features of quartz veins which are due to the particulate nature of natural polymeric silica are illustrated.

Keywords. Sediments, accretion, concretion, charged particle, surface energy, porphyroid, granite.

INTRODUCTION

Quartz veins and silicification are the simplest and most frequently encountered of all mineral concentrations. However, current geological theory is still unable to explain: -

- 1) The occurrence of insoluble oxides of iron and silica in large intrusive and brecciated quartz-magnetite lodes. Chemically, iron silicates should have been formed from soluble silicates and ferrous or ferric salts, or similarly if the oxides had been fused together.
- 2) The suspension of heavy brecciated wall-rock fragments or angular magnetite fragments in quartz veins and lodes.
- 3) Quartz veins and veinlets or occasionally large lodes of quartz which arise and die out locally in the rock in which they occur without any

sign of the passage of large volumes of “hydrothermal fluid” such as would have been needed to dissolve “precipitated” silica.

- 4) The multiple injection and re-injection of quartz in the same vein channel.
- 5) The occurrence of crystal lined cavities in quartz veins.
- 6) The occurrence of chert veins in granite.
- 7) The less frequently observed but very real occurrences of ptygmatic quartz veins, colloform banding in quartz veins, oolites and concretionary structures in quartz veins, or spherulitic structures, rosettes, axiolitic overgrowths, and acicular crystals in vein quartz.
- 8) Quartz oolites found in granite and in porphyroids.
- 9) Fluid inclusions containing brines, petroleum, biogenic organic matter, or carbonates in quartz veins.
- 10) Boehm lamellae or lines of fluid inclusions that extend across crystal boundaries in quartz veins.
- 11) Silicification of wall rocks, vein margins, and occasional shells, tree trunks, etc. by silica which appears to be associated with and occur contemporaneously with quartz veins.

This paper provides adequate explanations for all these observations. They are a logical and expected outcome when current hydrolysis reactions and the physical chemistry of polymeric particulate species of silica are applied.

Simple quartz veins are the most common of all mineral deposits. They are found in all rock types with the exception of congealed molten lava flows and associated pyroclastic debris. They mainly occur in sediments, metamorphics, porphyroid and granite related intrusives.

Quartz veins are so commonplace with such a wide variety of associations and vein types and encountered in every field situation that questions relating to details of their genesis and to the mechanism of their emplacement are seldom raised.

It is clear that most geologists don't really understand how quartz veins are formed. One cannot go straightforwardly to a standard textbook and look up the genesis of a quartz vein. All textbooks contain abundant references to quartz, its mineralogy, varieties, crystallography, properties, features, and associated minerals. Information has been published relative to the solubility of quartz under various conditions of acidity, temperature, pressure, etc., and analyses of the silica content of various natural waters can also be found.

Why then is the classical origin of quartz veins, the most common and abundant of all mineral deposits, shrouded in mystery? Generally, in geological teaching,

quartz veins are attributed to “hydrothermal solutions”, which are supposed to have deposited the crystalline silica from solution. All experienced geologists know that this is too simplistic. Quartz veins occur in many situations where this direct crystallisation from solution does not explain the observations. In fact, most commonly, the quartz of the veins appears to have been intruded or injected (as discordant squirts) into the enclosing rock in bulk, as a fluid mass of silica, as if it had been molten except that there is no evidence of temperatures such as would melt quartz. It melts or fuses gradually like glass at 1723°C. Frondel¹, 1962, p. 3; Iler², 1979, p. 15). Molten quartz does not crystallise on cooling but hardens to an amorphous glassy form of silicon dioxide called lechatelierite.

Most field geologists tacitly accept that quartz veins seem to “sweat out of the rocks”. We clearly believe it has to do with the movement of aqueous fluids. In the light of the currently published aqueous chemistry of silica, the earlier reasoning that attributed vein quartz accumulations to vast quantities of solution based on measured solubilities of silica is clearly false. Barnes³, 1967, p. 392 suggests five cubic kilometres of water would be required to deposit 100,000 tonnes of quartz in a moderate sized vein approximately 128m x 75m x 4m.

There is a significant disparity between the modern chemist's and the classical geologist's view of the “solubility” of silica and silicates. This article provides the information to bridge that gap.

THE FORMATION OF POLYMERIC SILICA IN NATURAL SEDIMENTS

Quartz is virtually insoluble in water. Dispersion of hydrated silica is very variable because: -

- (a) it takes a long time as measured experimentally (but very quickly indeed if measured in units of geological time) for equilibrium to become established;
- (b) the solubility of quartz is a function of temperature, pressure, ionic strength, pH, and the presence of complexing ions;
- (c) silica disperses in water to form three classes of solutes (Iler², 1979, pp 172-248; Stöber⁴, 1966, pp 161-163): -
 - i) simple monomeric complexes such as $\text{Si}(\text{OH})_4$ aq.
 - ii) oligomers or polynuclear complexes such as $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$ which represent condensed chains of $\text{Si}(\text{OH})_4$ tetrahedra (Figure 1). These chains appear to grow to a maximum of about six $\text{Si}(\text{OH})_4$ tetrahedra.

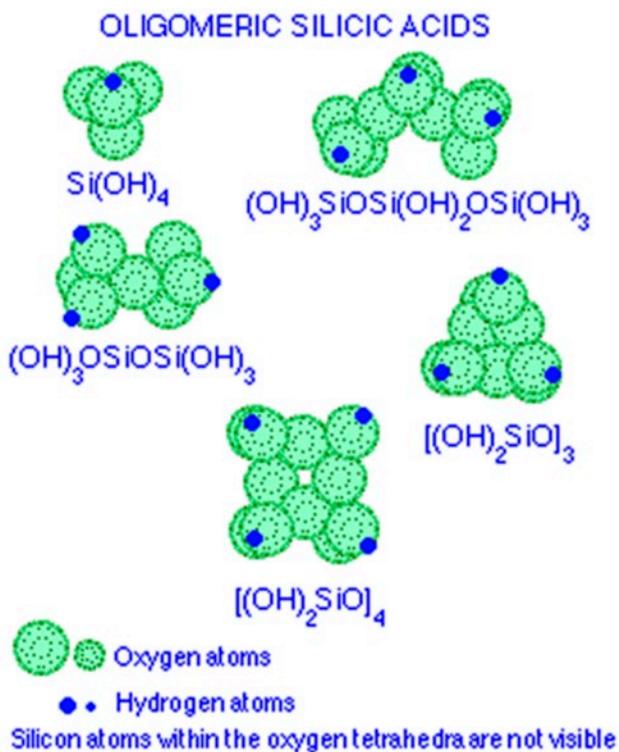


Figure 1. This diagram represents silicic acid molecules. The spheres represent oxygen atoms and the dots represent hydrogen atoms. Silicon atoms within the oxygen tetrahedra are not visible.

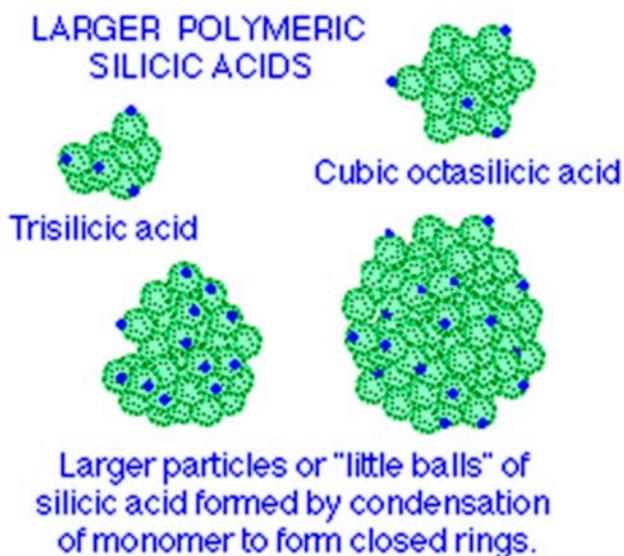


Figure 2. This diagram shows the larger polymers that develop into "little balls". (A) is trisilicic acid, (B) is cubic octasilicic acid that forms larger particles (C) and (D) by condensing monomer to form closed rings until the original species is surrounded by a layer of deposited silica bearing silanol groups. Different kinds of incompletely condensed oligomers are thought to form the cores of colloidal particles but above pH 7 the inner silica contains relatively few silanol groups.

- iii) poly silicic acid where very long chains are produced with cross-linking to yield partly condensed three dimensional networks. These polymeric species are 'colloidal' in that they are frequently loose spherical aggregates of the size that produces scattering of light or gives a "milky" appearance (Figure 2).
- (d) the higher polymeric forms of silicic acid tend to occur in solution, re-adsorbed on surfaces, or in suspension as colloidal sol particles, depending on hydrolysis and ionisation.

Surface charge

All solid and crystal surfaces are charged including very small gelatinous natural sediment particles such as clay and the minute globular particles of polymeric silica. Figure 3 is a TEM image (from Stumm⁵, 1992) that shows the "bumps" due to charge sites where additional molecules would join the surface to result in crystal growth. These electrical charges are arranged in miniscule steps on the crystal surface. The surface reactivity differs according to the way the units of the lattice are exposed at its surface.

If we are to understand why the globular particles or "little balls" of silica interact with each other and form the precipitates, chains, coatings of adsorbed particles, and gel mesh-works as described by Iler², it is necessary to consider the basic hydrolysis of the mineral-water interface. Similar equilibria relate to a great many

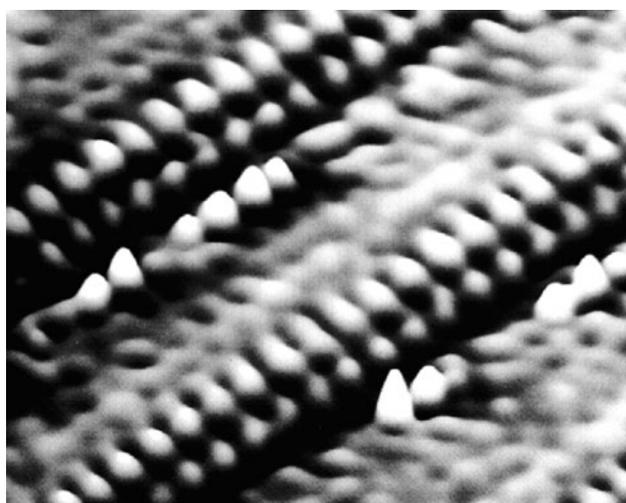


Figure 3. On anhydrous crystal surfaces the lattice units are arranged in layers terminating in 'steps'. This STM image shows the step-like layers on a crystal face at which further crystal growth or dissolution are believed to occur. (From Stumm⁵, 1992.).

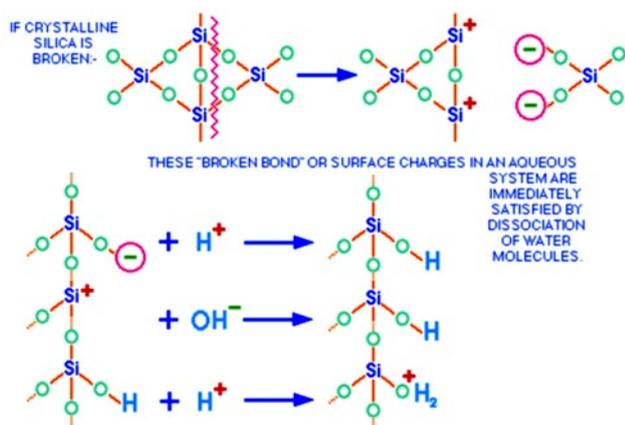
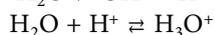


Figure 4. If crystalline silica is broken the "broken bonds" or exposed surface charges in an aqueous system are immediately satisfied by dissociation of water molecules. If the surface is large it will carry an 'overall' or residual charge which adsorbs polar water molecules as an adsorbed water monolayer.

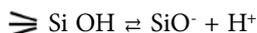
surfaces and certainly to silica and the rock-forming silicates. It is also important for sulphide minerals. It applies as soon as precipitating insoluble sulphides are able to form a lattice. This surface hydration occurs on the minute 'curds' or crystallites that develop when sulphide particles are first precipitated.

In the simplest case, if quartz or a grain of sand is broken, the silicon - oxygen chemical bonds that form the lattice are exposed as indicated in Figure 4.

If the surface is large it will carry an 'overall' or residual charge which adsorbs polar water molecules as an adsorbed water monolayer. This effect can be considered as 'wetting' or it can be manifest in the development of a meniscus like that in a test tube. If the surface is small as in $\text{Si}(\text{OH})_4$ or the oligomeric silicic acids at equilibrium, there is a situation very like that of water dissociation which is:-



Therefore for silica the dissociation is:-



and the net charge on the surface is controlled by the equilibrium for:-



Only a few sediments like BIF's, deep sea oozes, quartzites or cherts have silica as the dominant component. Clays are the major component of most ordinary basin sediments. However, the surface of most clay particles is the tetrahedral layer or net-like Si-O-Si linkages with Si-OH terminations to the exterior surfaces of these large plate-like macromolecules. The net charge on clay particle surfaces is due to 'unsatisfied' or 'broken bond'

irregularities but in natural basin sediments clay minerals present really enormous areas of Si-OH terminations to equilibrate with pore fluid sols and solutions. These immense surfaces are fully loaded with adsorbed ions and charged particles. They all carry adsorbed water monolayers and diffuse charge layers in which the co-ions and counter-ions reside in a narrow zone out from the surface (Hemholtz double layers - see Glossary).

The growth of natural polymeric silica particles

Silicic acid polymerises to discrete particles which then aggregate into chains and mesh-works. As Iler² (1979, p. 173) points out, three stages are actually recognised.

- 1) Polymerisation of monomer to form particles.
- 2) Growth of particles.
- 3) Linking of particles together into branched chains, then mesh-works, finally extending throughout the medium thus bestowing a certain degree of rigidity upon it.

Below 200°C amorphous silica precipitates from supersaturated solution under various conditions and in several physical forms. These range from colloidal particles so small that the suspension or sol remains transparent or so large that it looks milky. Depending on par-

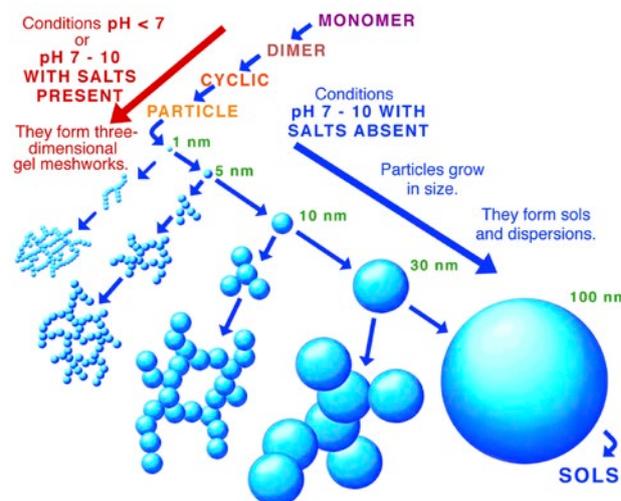


Figure 5. This diagrammatic representation of the polymerisation behaviour of silicic acid indicates the general conditions under which the colloidal particles develop and 'chain' into three dimensional gel meshworks. In alkaline solution the particles are negatively charged and remain discrete as they grow in size and decrease in number. Below pH 7 or in the presence of electrolyte (as in sediment pore fluids) precipitates or gels are formed. [From Iler², 1979, p. 174].

particle size, it precipitates as gelatinous masses or as hard glassy films.

Figure 5 (from Iler², 1979) shows diagrammatically the polymerisation behaviour of silicic acid in the pH range 7-10 and in relation to the presence of salts (the conditions which exist in most pore fluids).

Polymerisation is slowest at about pH 2 and increases in proportion to the hydroxyl ion concentration up to about pH 10. Higher polymers are formed mainly by the further addition of the monomer. It must be emphasised that the ionisation constants of the polymers are greater than that of the monomer. Thus, the monomer reacts more rapidly with the dimer and higher polymers than with another monomer. This is the reason why the natural precursor silica gels in veins are “infilled” and densified and can be regarded as “collectors” of additional silica from the seepage of pore fluids draining from sediments or sheared sedimentary materials that form metamorphic rocks.

The cohesive matrices of consolidating sediments, or those which form the precursor silica gels in vein, dyke, breccia pipe, and lode outflow systems are essentially mixed gels. Figure 1 shows molecular models of the various short chain silicic acids which are small enough to permeate through these porous systems. These short chain acids grow by condensation of the monomer to form closed rings until the original species is completely surrounded by one layer of deposited silica bearing silanol groups. Different kinds of incompletely condensed oligomers may form in the cores of particles as these silica polymers aggregate to colloidal dimensions.

THE NATURE OF ADSORPTION PHENOMENA

The elementary surface chemistry of the mineral-water interface is simple but basin sediments are largely comprised of clays and other components that consist of small colloidal particles with a very large surface-to-volume ratio.

If these basin muds were dispersed in river water as when they were transported to the sea, they may form suspensions and metastable sols. But suspensions settle and sols coagulate in sea-water so that the resulting sediment is a semi-solid three-dimensional meshwork of high porosity containing solvent.

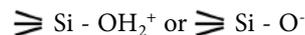
Such three dimensional semi-rigid, largely amorphous, heterogeneous mesh-works are technically gels which are produced by:-

a) polymerising small molecules [like $\text{Si}(\text{OH})_4$] into random, cross-linked network structures of high

water content. Such polymerisation reactions into semi-rigid gels are often promoted by increased electrolyte concentration and slightly decreased water content. They may be strongly sensitive to pH.

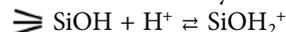
- b) disordering or hydrolytic degradation of crystal lattices into high porosity mesh-works with which the solvent, water, is intimately associated. Ionic diffusion at 20 - 30% of its rate in pure solvent is often observed in such gels.
- c) the ‘stacking’ or aggregation of colloidal sized plate-like, rod-shaped, or globular particles into random, house of cards-like, or semi-ordered mesh-works and networks.

A similar electrical potential gradient exists within gels as that on the planar surface (the surface potential). On its internal surfaces where water molecules interface with oxide or silicate surfaces, centres of charge develop such as:-



These sites exist on the surface of the gel and within its pore structure. The attraction-repulsion due to surface charge on colloidal particles has now been measured. In 1998 a team of researchers led by Professor T. W. Healy (personal communication) at the Particulate Fluids Processing Centre, University of Melbourne, were successful in adapting an atomic force microscope to measure the interparticle forces in relation to minute distances between them. This brilliant work confirms DLVO theory (Figure 6).

As for the simple planar surface of a broken crystal, the net charge on the gel surfaces or the surfaces of its component particles is controlled by the equilibrium for:-



This equilibrium defines the net surface charge.

As in the case of water where:



and the concentration of H^+ equals the concentration of OH^- at pH 7, so for oxide and silicate surfaces a pH will define for each oxide a condition where the concentration of negative sites equals the concentration of positive sites. This pH is called the point-of-zero-charge or p.z.c.

Figure 7 (from Healy⁶, 1972, p. 38) is a diagram representing the electrical double layer on colloidal particles and the variation of their net surface charge with pH. These particles may be dispersed as a sol but the same net surface charge to solvent equilibria apply when particles are coagulated. In a gel some of the charge sites are satisfied by mutually near-contacting or interacting particles.

Where pH values are more alkaline or greater than the p.z.c., the particles have a net negative surface charge and where pH values are more acid or less than the p.z.c. the net surface charges are positive. The p.z.c. values of

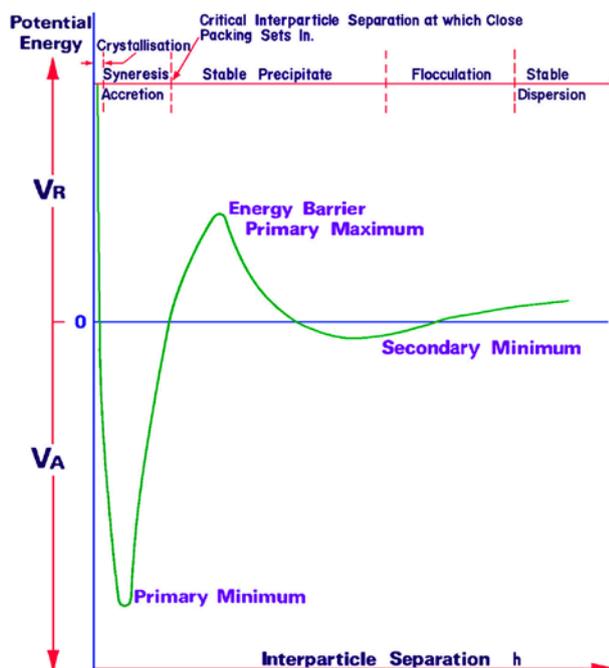


Figure 6. The general form of the curve of potential energy is plotted as a function of particle separation (interparticle distance or concentration of the paste) for interaction between particles in a colloidal system. V_r and V_a are repulsive and attractive energies respectively and the curve represents their sum at a given interparticle distance. This is characteristic of sediment particle interactions. The general behaviour of particles at various distances from each other is indicated at the top of the diagram. Note the critical interparticle separation at which accretions begin to form. This curve describes the general behaviour of particles resulting from the interaction of these forces and is not specific to any particular type of colloidal particle. This succession of repulsion, strong attraction and resistance at exceedingly close proximity is called the DLVO theory that has now been confirmed by direct measurement with an adapted atomic force microscope.

simple oxides vary from pH 2 for SiO_2 , pH 6 for TiO_2 , and pH 9.1 for Al_2O_3 . Some p.z.c. values for common minerals are listed in Table 1 (From Healy⁶, 1972, p. 39).

The existence of surface charges means that surfaces in contact with a solvent must take up or adsorb ions from solution. This occurs on all sediment grains but mainly on the clays and other sediment colloids where surface-to-volume ratios are very much larger.

It follows that:-

- Positive ions adsorb strongly above the pH of the p.z.c. and negative ions adsorb below the p.z.c.
- The larger the valence or size of the ion the more strongly it adsorbs.
- Metal ions which hydrolyse such as Fe^{3+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , etc. adsorb most strongly at a pH value where hydrolysis of the metal ion begins.

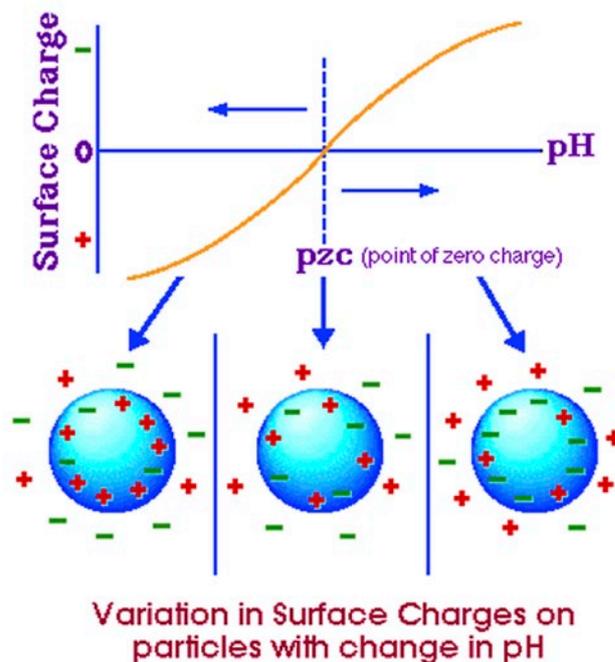


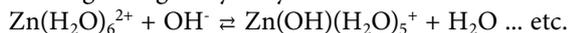
Figure 7. This is a schematic representation of the electrical double layer on colloidal sol particles and the variation of net surface charge with pH. [From Healy⁶, 1972, p. 38].

Table 1

MINERAL	p.z.c.
SiO_2 , silica gel	pH 1 - 2
SiO_2 , a-quartz	pH 2 - 3
SnO_2 , cassiterite	pH 4.5
ZrO_2 , zirconia	pH 4
TiO_2 , rutile	pH 5.8 - 6.7
Fe_2O_3 , haematite (natural)	pH 4.8 - 6.7
Fe_2O_3 , haematite (synthetic)	pH 8.6
FeO.OH , goethite	pH 6.8
Al_2O_3 , corundum	pH 9.1
AlO.OH , boehmite	pH 7.8 - 8.8
MgO , magnesia	pH 12
CaCO_3 , calcite	pH 9.5
$\text{Ca}_5(\text{PO}_4)_3(\text{F,OH})$, fluorapatite	pH 6
$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, hydroxy apatite	pH 7

For example, for SiO_2 where the negative charge persists above pH 2 and is constant from pH 2 to 8, it is found that zinc adsorbs from solution onto the silica

surface more strongly at pH 7 than at pH 4. At pH 7, Zn^{2+} is beginning to hydrolyse:



It appears that the strongly charged and un-hydrolysed ion is so heavily solvated that it cannot approach the interface. On hydrolysis, the average charge per ion decreases and desolvation upon adsorption is more readily achieved.

Similar principles apply when small charged particles are adsorbed on surfaces of sediment substrates and the hydration or strong solvation of the more highly charged surfaces of very small particles is quite significant. It is believed that such highly solvated surfaces prevent or impede such particles closely approaching the surfaces on which they are adsorbed until desolvation is achieved. This is the reason why very small hydrated metal sulphide particles or hydroxy-carbonate particles form “soft” framboids and oolites when these concretionary precipitates first develop.

Colloidal chemists have closely studied adsorption phenomena and many more details are available in standard texts. The main conclusions which are relevant to the behaviour of silica particles migrating and re-depositing in basin sediments are:-

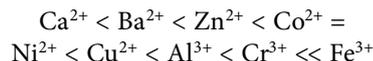
- 1) Higher valent ions carry a higher charge, hydrolyse at pH levels usually encountered in basin pore fluids, and adsorb more strongly on substrate surfaces.
- 2) Adsorption is concentration dependent. Surfaces adsorb more charged particles or ions per unit area from higher concentrations of sols and solutes.
- 3) Diffuse (Helmholtz) double layers thin at higher concentrations of electrolyte. Colloids readily coagulate because van der Waal's attractive forces more easily exceed repulsion between like charges. Aggregation and accretion are more readily achieved.
- 4) Ions or charged particles can have a chemical or a 'site' affinity for certain surfaces or sites on a surface. This so-called 'specific adsorption' is expressed mathematically for the free energy of adsorption ΔG_{ads} as:

$$\Delta G_{\text{ads}} = Z_+ e (\psi_\delta - \varphi_{\text{chem}})$$

Where Z_+ is the valency of the adsorbing ion adsorbing on a surface where the potential at a distance δ out from the surface is ψ_δ volts, e is the electric charge, and φ_{chem} is the adsorption potential of the ion concerned. If there is a strong chemical or 'site' affinity ions can adsorb on like-charged surfaces. For example, SO_4^{2-} adsorbing on Al_2O_3 in water lowers the positive charge through zero to negative so that SO_4^{2-} must then adsorb on surfaces of moderate net negative charge.

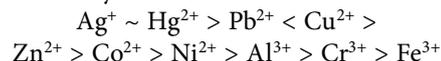
- 5) From solutions at about pH 8 and equi-molar con-

centrations with SiO_2 as the adsorbent, ions where φ_{chem} has a finite numerical value adsorb in order:



The order of adsorption of ions and charged particles at given concentrations of electrolyte determines the order in which species will be desorbed or exchanged if the electrolyte concentration is slowly increased as it is at increasing depths in diagenetic basin sediments.

- 6) There is a change in the adsorption characteristics at pH values and concentration of species just below that at which precipitation occurs throughout the bulk sol or solution. Species tend to 'coat' or preferentially precipitate on surfaces. $Fe(OH)_3$ coating on silica, smectite coating on illite, $Si(OH)_4$ on quartz grains, successive layers on botryoids, etc., appear to be manifestations of this phenomena.
- 7) Polyelectrolytes, that is polymers where repeating units are ionised or ionisable in water, are strongly surface active. They may show some preference for adsorption on oppositely charged surfaces but more usually they adsorb on any surface. This is due to entropy considerations in that one adsorbing polymer frees to solution many previously bound water molecules to yield a net increase in the number of kinetic units in the system.
- 8) The simplest way of desorbing species, and particularly metal species, is to lower the concentration of the surrounding solution. Dilution simply washes most surface adsorbed species off (eg. soap).
- 9) Swamping adsorbing surfaces by increasing the electrolyte concentration or concentration of competing ions in the surrounding solution is equally effective in desorbing species. Increasing electrolyte concentrations within particle aggregates due to syneresis, or simply by the increase of salinities at depth during diagenesis, are important mechanisms for releasing ionic and charged particle species from basin sediments. With metal ions the desorption by this exchange process as salinity steadily increases is in approximately the order:



The order of desorption for charged metal hydroxy-sulphide species which determines the order of their mobility in the outward seepage of pore fluids (the paragenetic sequence) has not been confirmed experimentally and is far less certain because of the complex mixture of substrates. The adsorbed metal sulphide species also remain undefined but it is clear that the hydration is variable and that a complex

series of double sulphides is involved. The original paragenetic sequence suggested by Lindgren⁷ and his contemporaries before particle - ion interactions and DLVO theory had been developed was based entirely on field observations. They studied the order of deposition of sulphide minerals in veins and lodes. Lindgren⁷ refers to sulphides and says (1937, p. 361) that on the whole the order of deposition of the ore-metal sulphides seems to follow:

Hg, Ag, Cu, Pb, Zn, Ni, Co, Fe

Despite lead and cobalt being displaced when these lists are compared, Lindgren's⁷ suggested order of sulphide deposition from observations many years ago does seem to have much more than a coincidental resemblance to the order which has now been determined for base metals to be desorbed by increasing salinity.

AGGREGATION OF GLOBULAR POLYMERIC SILICA PARTICLES IN NATURAL SEDIMENTS

Liquefaction and flow or intrusion of natural sediments provides the shear to aggregate the sediment particles into close packed clusters as in Figure 8. The extremely small size of the ultimate particles in this form of silica must be kept in mind. A small granule of typical silica gel about 1 mm in size contains about 50×10^{12} particles.

Silica spheres forming 'close packed' accretions in re-liquefied natural sediments probably involve both large and small particles, but as Iler² (1979, p. 372) points out, a strong dense gel is formed from a mixture of large and small particles (Figure 9). The 'active' silica, the $\text{Si}(\text{OH})_4$ molecules and the oligomeric silica (Figure 1), are much smaller again. These can pass through the

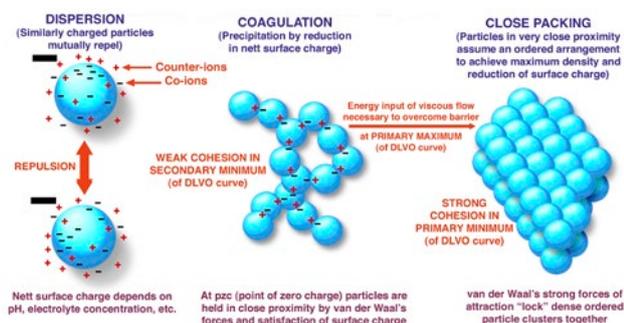


Figure 8. This diagram shows the way natural polymeric silica globules closely pack together in the shear regime to reduce surface energy and form denser, physically stronger clusters that aggregate to accretions.

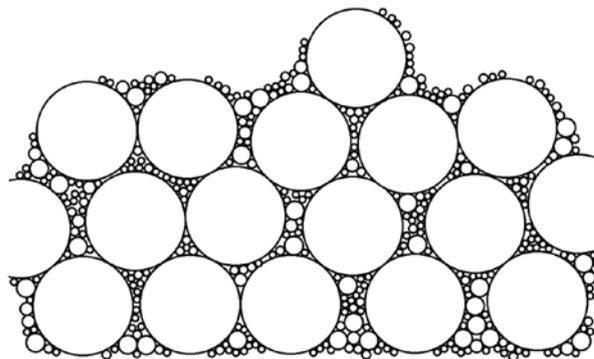


Figure 9. Generally larger particles form weaker gels. However, mixtures of large and small particles form very strong dense gels. The infill 'necking' and silanol linkages are not so well developed between larger particles. Smaller intergranular particles in the interstices act as strong 'bridges' linking the whole into a denser mass. [From Iler², 1979, p. 372].

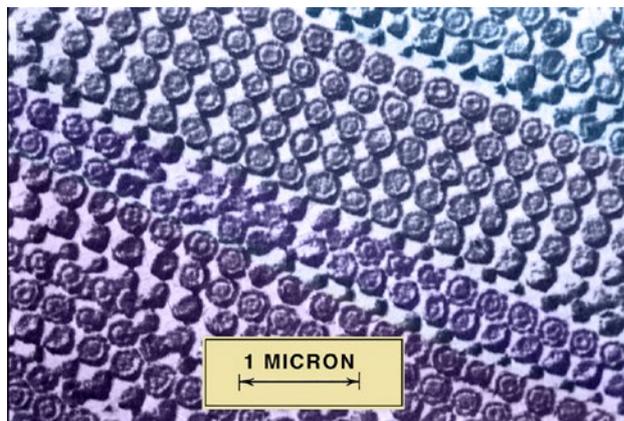


Figure 10. An electron micrograph of opal structure that has been lightly etched with hydrofluoric acid shows internal rings within the ordered silica spheres. Iler² (1979, p. 401) records as many as five internal layers. The size of the particles comprising the layers is 50nm but the opaline spheres have to be over 300nm before the interplay of colours can be seen.

finest membranes. It is important to recognise the wide size range of the colloidal silica spheres and the ability of the monomeric and oligomeric species to diffuse through the finest pore spaces.

In 'close packed' and ordered structures of silica spheres such as opal (Figure 10), this 'active' silica can diffuse in to fill the spaces between particles. The opaline spheres themselves are in fact, built up from much smaller silica particles or spheres. Concentric rims round a central nucleus can be seen in the lightly etched opaline spheres in Figure 10 but Iler² (1979, p. 401) records as many as five shell-like layers on cross sections of opaline silica spheres which show their growth from

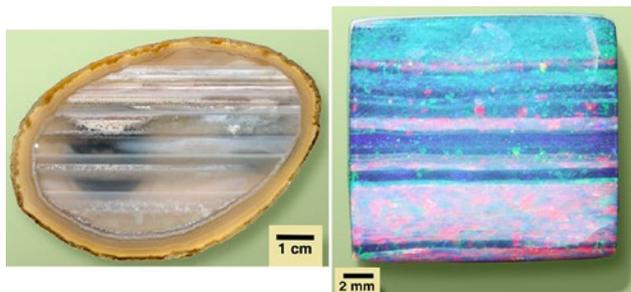


Figure 11. Silica accretions in porphyroid are usually about half to 1 cm in size but in some fluid muds they aggregate to much larger chert or agate nodules. These are called geodes. As they condense and loose water a peripheral region may loose water to form a much denser porous media. Similar to that in the opaline cavities, the polymeric silica particles settle into horizontal layers to form Uruguay banding as illustrated.

much finer particles like tree rings. These minute opaline spheres apparently build up like small concretions, framboids, or oolites and with the aging of the gels the build-up continues to infill the ‘necks’ in the chains of silica spheres or the interstices in the ordered opaline-type ‘close packed’ structures.

Opal is usually formed in irregular cavities in the soil profile where the ground water is alkaline. Smaller silica gel particles filling the cavities finally dehydrate to form chert, potch or ‘milky’ opal. The concretions of some gem quality opal appear to develop in dilute mobile gels. In some cavities the opaline spheres settle in horizontal layers to Uruguay Banding as Illustrated in Figure 11.

The accretion of polymeric silica in mobile sediments

The development of polymeric silica accretions in mobilised sediment is illustrated in Figures 12 to 14. Figures 15 and 16 also show how impure silica accretions break up and divest impurities as they are kneaded when the sediment is further re-liquefied and involved in flow.

The development of siliceous accretions can be seen in many rock exposures and drill cores and in a wide variety of rock types. Unfortunately, many geologists remain unaware of current developments in colloid and surface chemistry and remain unable to correctly interpret the porphyroid or small globular quartz accretions or larger synerectic quartz ovoids that are commonly found in sediments that have been mobilised during diagenesis.

Figure 17 is a typical example of a “quartz clot rock” from drill core at the Dalgara Prospect in Western Australia. Some of the small quartz ovoids can be seen to be aggregates of smaller pieces. A very good example

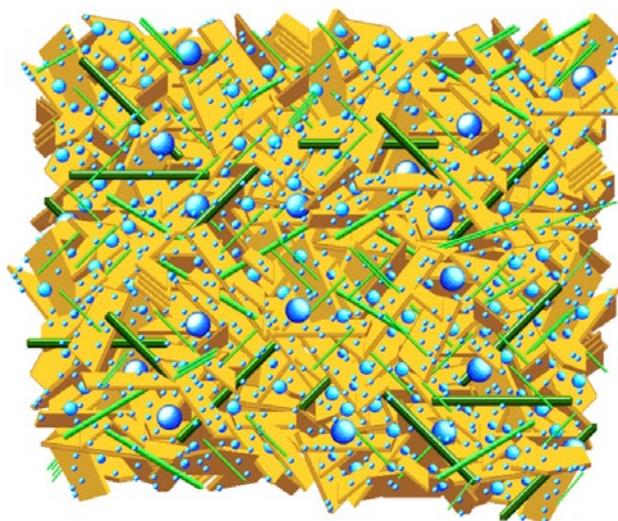


Figure 12. Sediment as initially flocculated has its silica particles ‘coating’ other sediment particles and interspersed as random linking chains (From Elliston⁹, 2017, p.101).

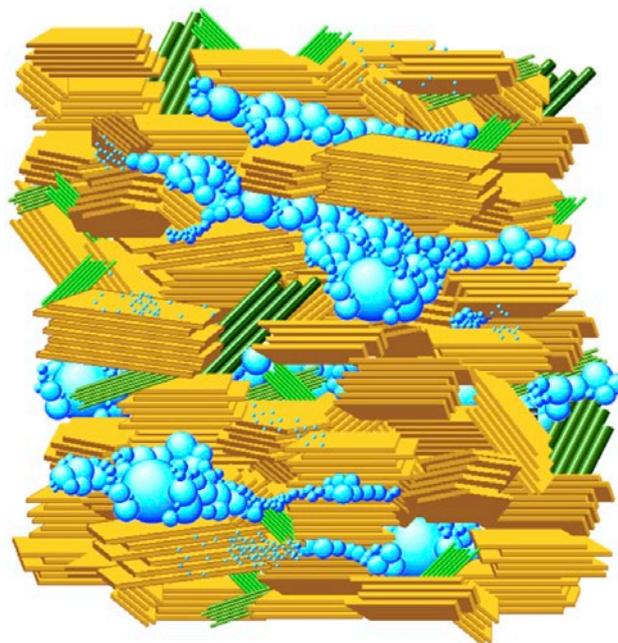


Figure 13. Liquefaction or shear by pasty flow of the sediment allows some ‘close packing’ of silica particles into micro-accretions and orientation of the clusters and chains of particles to result in a schistose or “tuffaceous-looking” greenstone texture as in Figure 18 (From Elliston⁹, 2017, p.101).

of the accretion of very small polymeric silica globules aggregating to quartz ovoids was found in drilling the Olive Wood Prospect at Tennant Creek NT. This is illustrated in Figure 18.

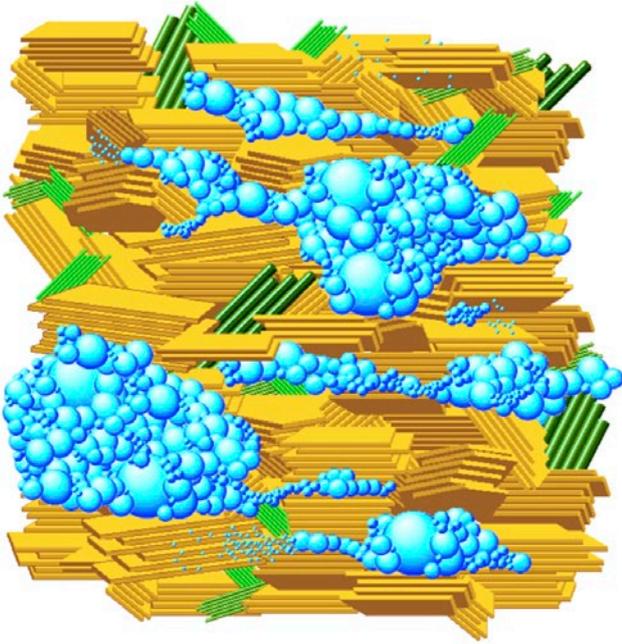


Figure 14. With continued laminar flow the micro-aggregates of silica spheres combine to form larger macro accretions that survive in the shear regime in accordance with their internal cohesion. This is dependent on their ‘purity’, the degree to which they have been “kneaded” (broken and re-formed) in the laminar flow (From Elliston⁹, 2017, p.101).

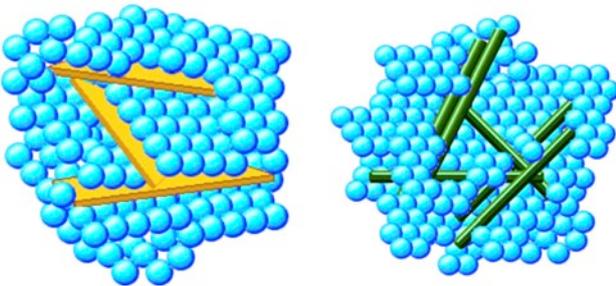


Figure 15. Accretions of silica spheres containing impurities tend to break up in the shear regime during laminar flow (From Elliston⁹, 2017, p.101).

Siliceous accretions develop in various types of sediment containing polymeric silica gel particles that have been liquefied or sheared by pasty flow. Mobilised beds in the Western Australian banded iron formations form accretions of gelatinous ferric hydroxide (crystallises to haematite ovoids) and denser silica gel that crystallises to white quartz ovoids. Accretionary chert ovoids occur in some of the porphyroids at Tennant Creek and those at the Black Angel Prospect initiated research into the longstanding problem of porphyroid and granite genesis.

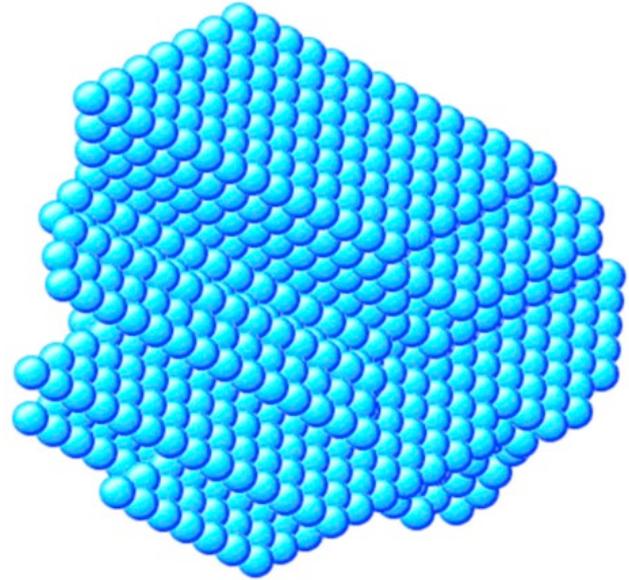


Figure 16. Accretions comprising only silica spheres can form dense ‘close packed’ aggregates. In this configuration each silica sphere is densely packed in contact with twelve others such that the accretion has sufficient internal cohesion to survive in the shear regime (From Elliston⁹, 2017, p.101).



Figure 17. This shaly porphyroid intersected in drilling at the Dalgaranga Prospect west of Mt Morgan in Western Australia contains small ovoids of quartz. Some of these can be seen to be aggregates of small ovoids or fragments of the pre crystalline polymeric silica. This is clear evidence of their accretionary origin (From Elliston, 2017, p.129).

Shear by slight lateral movement in a highly siliceous sediment intersected by drilling at the Wagga Tank prospect near Mt Hope in NSW has developed the shreds and small round accretions of khaki chert illustrated in Figure 19. Similar shear in a jasper bed intersected in the Explorer 7 prospect drilling at Tennant Creek, NT, has developed small white quartz accretions. These shown in Figure 20, have been ‘kneaded’ or rolled to a greater extent to divest the larger ferric hydroxide particles that form the bright red pigment in jasper. Very small clay particles or muscovite flakes are the usual colouring impurity in khaki chert but the very common

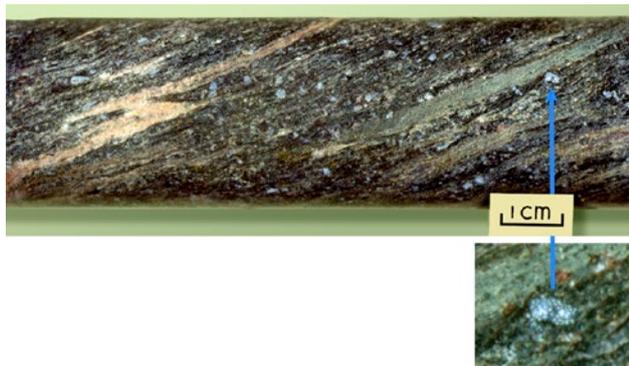


Figure 18. The accretionary origin of the small quartz ovoids in the Olive Wood re-liquefied sediment lens at Tennant Creek, NT, is clearly indicated by the many examples of the aggregation of sub-units of former polymeric silica. The enlargement shows this aggregation but most small accretions in this rock have crystallised to small round globules of quartz (From Elliston, 2017, p. 153).



Figure 19. Slight lateral movement or shear in former siliceous ooze from the Wagga Tank drilling Mt Hope, NSW, has developed an obvious 'porphyroidal' texture. The elongation, distortion, and aggregation of the ovoids indicate deformation and plasticity occurred at the soft stage in consolidation of the ooze. Wisps and shreds of cherty sediment are similarly deformed. Some quite large (1cm) accretionary nodules or 'gel balls' have developed (From Elliston, 2017, p.311).

and abundant white quartz in accretions and veins is usually a dispersion of exceedingly small inclusions of water or even residual hydroxyl groups trapped in the crystal lattice.

Before measurement of interparticle forces with an adapted atomic force microscope had confirmed DLVO theory in 1998, Professor T. W. Healy at the Particulate Fluids Processing Centre, University of Melbourne, in 1973 was commissioned to demonstrate the formation of accretions experimentally in a range of colloidal pastes and slurries. His denser silica gel accretions, similar to those in mobilised siliceous shale (Figure 17) or jasper (Figure 20) are illustrated in Figure 21.

Tubular syneresis crack patterns, plastic distortion, aggregation of sub units, chert and jasper in the



Figure 20. Formerly fluid (thixotropic) jasper bands were found in the lode section when drilling the Explorer 7 prospect at Tennant Creek, NT. During flow the fluid jasper gel developed denser accretions of paler 'blue' (leucoxene tinged) and white quartz (From Elliston⁹, 2017, p.159).

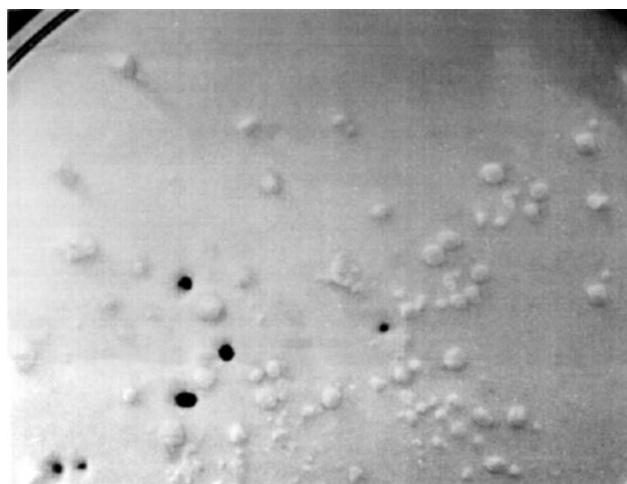


Figure 21. These siliceous accretions were formed experimentally in a gel paste and were also produced in a number of other colloidal materials. The formation of accretions requires thick pastes and achieving steady rates of uniform shear throughout concentrated thixotropic gelatinous materials that are normally gelatinous solids. This imposed some limitations to the laboratory work [From Healy¹¹, 1973 Accretion of colloidal material, p.9, fig 2(c)].

so-called phenocrysts, irregular fluidal contacts with feldspar and central shrinkage cavities filled with chlorite characterise the siliceous accretions that occur in the porphyroids at Tennant Creek, NT. From these and similar features in the feldspar ovoids it became quite clear that these ovoids had hardened or crystallised from common components of ordinary sediments. They were accretions of clays, hydrous ferromagnesian mineral and polymeric silica particles. The rather irregular interbedded and formerly fluid layers and lenses of porphyroid had been mudflows. The Caroline mudflow conglomerate, Mammoth intrusive sandstone and the True Blue and the Plum Mine slip complexes outcropping in the turbidite sequences at Tennant Creek contained clay and

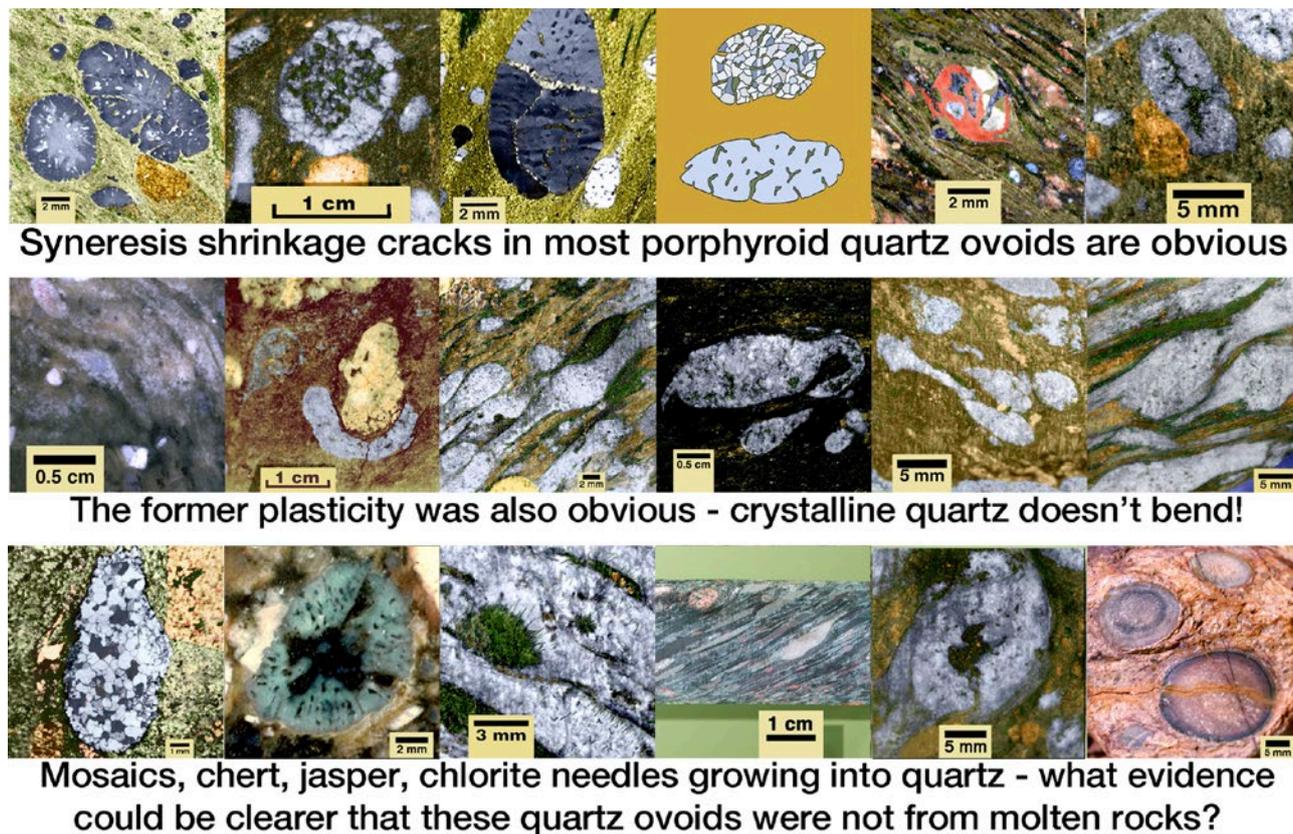


Figure 22. This illustrates the characteristic features of siliceous accretions in the Tennant Creek porphyroids. They include tubular syneclitic crack patterns, plastic distortion, aggregation of sub units, chert, jasper, white and 'blue' quartz rolled together, irregular fluidal contacts with feldspar and central shrinkage cavities filled with chlorite. This evidence for a non-molten or volcanic origin is conclusive (From Elliston¹⁰, 2014, p. 69).

quartz accretions like those in the porphyroids. A selection of quartz accretions from the Tennant Creek porphyroids is illustrated in Figure 22.

THE CRYSTALLISATION OF QUARTZ FROM MONOMERIC, OLIGOMERIC AND GLOBULAR POLYMERIC DISPERSIONS

Quartz is virtually insoluble and quartz crystals do not grow directly from solution. They grow through a disordered solvated surface layer (coating of polymeric silica particles) that are replenished by diffusion from the surrounding fluid as polymeric silica particles adsorbed at the surface charge sites loose water and become part of the crystal lattice.

In the geological context equilibrium between the monomeric, oligomeric (Figures 1 and 2) and polymeric silica globules is maintained according to the pH and concentration of other salts present in the surrounding solution as shown in Figure 5. Figure 3 is a TEM image

of the charge sites on a crystal surface. These charge sites are arranged in 'steps' and Figure 23 (from Stumm⁵, 1992) is a highly simplified model of a surface to which lattice units are added as cubes. It indicates the different activation energies that would pertain at the five possible surface sites. Sites 1 and 2 are most reactive and face site 5 is least reactive. Since precipitation/solution will occur preferentially at sites 1 and 2, the surface configuration is continuously converted towards 3 and 4 giving a 'stepped' growth to the crystal face.

Crystallographically oriented striations on the faces of natural quartz crystals reflect this "stepped growth" of the respective lattices. This is commonly observed on large hexagonal quartz crystal faces but it is also responsible for "hopper structures", internal growth layers, compound crystals, negative and pyramidal forms, etc. in a variety of natural crystals like pyrite, galena, quartz, etc.,

Details of textures observed in the Waitara Sinter on the Coromandel Peninsula, New Zealand, are illustrated in Figures 24 and 25. They are from a student honours

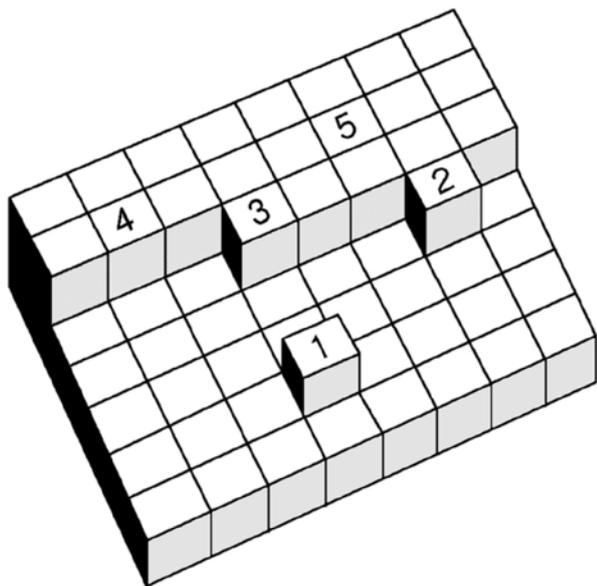


Figure 23. This is a diagram of a simplified square crystal lattice model. It shows the five possible types of surface exposure for the unit cells in such a lattice. The activation energies for each site differs as the units are bonded to 1, 2, 3, 4, and 5 surfaces respectively. Sites 1 and 2 are most reactive and site 5 is least reactive. Since precipitation or solution will occur preferentially at sites 1 and 2, the surface configuration tends to be continuously converted towards site 3 giving a 'stepped' growth to the crystal face.

thesis by Z. J. Newton¹², University of Auckland, in May 2000. Euhedral quartz crystals are observed projecting into vughs, miarolitic cavities, central cavities in geodes, and into a cavity in the Waitara Sinter illustrated in Figure 24. Water is a product of the silanol-siloxane condensation by which natural polymeric silica crystallises. Water pockets, fluid inclusions or cavities that are still or were formerly filled with fluid are therefore found in most occurrences of natural quartz. Such cavities are mainly due to the syneresis of the surrounding polymeric silica but while the particulate gel remains porous, additional $\text{Si}(\text{OH})_4$ diffuses inward as the condensation reactions proceed. The syneresis cracks and various forms of shrinkage or fluid cavities can be filled with 'secondary silica'.

The euhedral crystal of clear glassy quartz illustrated in Figure 24 has grown in a fluid cavity in the Waitara Sinter. "Little balls" (about 70 to 80 nm) of amorphous polymeric silica have been deposited from the last stages of dilution in the surrounding sol. The actual silica globules that can be observed in the SEM image form an incomplete coating on the crystal surfaces. The polymeric silica globules are irregular in size but they tend to be arranged in 'chains' or lines along the crys-

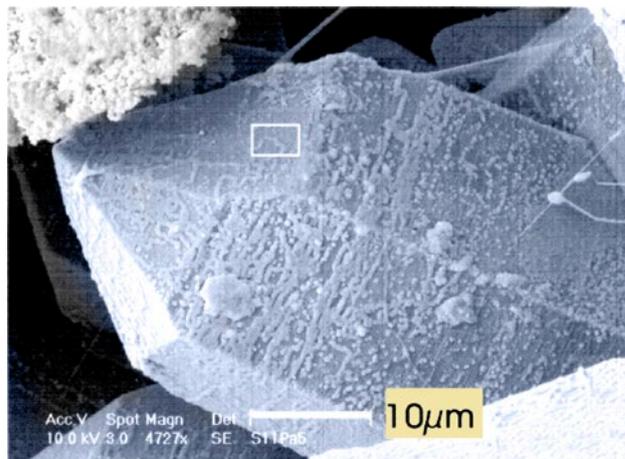


Figure 24. This euhedral crystal of clear glassy quartz was formed in a cavity in the Waitara Sinter, Coramandel Peninsula, New Zealand. It is coated with "little balls" (about 70 to 80 nm) of amorphous polymeric silica. The silica globules are irregular in size but they tend to be arranged in 'chains' or lines along the crystal striations and they form a crude linear pattern on the crystal surface in accord with the atomic geometry of the crystal lattice (from Newton¹², 2000).

tal striations and they form a crude pattern on the crystal surface. The atomic geometry of the crystal lattice has resulted in a pattern of electric charges distributed on the crystal surface to which the much larger charged particles coagulating from the sol both as short chains of globules (flocs) and as individual charged particles have been attracted. The globular polymeric silica particles can be directly observed to be coating the crystal surface and the charge they carry can be inferred from the crude pattern in which the charged particles have linked to each other in 'chains' and to the crystal surface.

Figure 25 at 10 times greater magnification shows a small part of one of the non-striated faces of the quartz crystal in the Waitara Sinter. Without the alignment of 'steps' the polymeric silica globules have been deposited in more random patterns on the surface and this enlargement also illustrates the wide variety in size of the "little balls" of polymeric silica. Colloidal particles range in size over 4 orders of magnitude from molecular dispersions (2 to 7Å) to about 1,500 nanometres.

CRYSTALS GROW LIKE CONCRETIONS IN GELATINOUS MEDIA

Surface catalysis or the role of the surface interface in different gel structures does not yet appear to be fully established. It seems that the enhancement of crystal growth operates in a very similar manner to the way

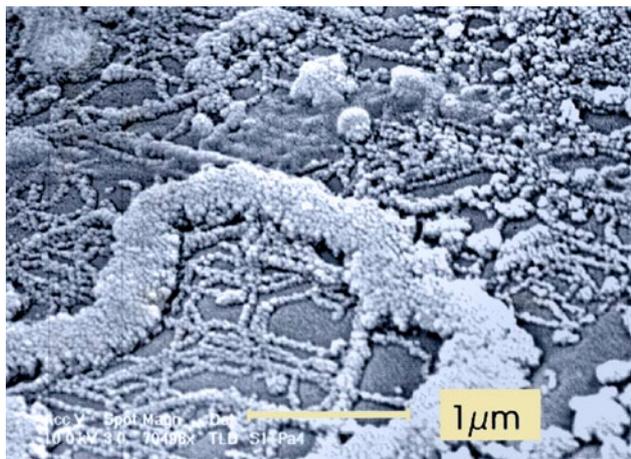


Figure 25. At 10 times greater magnification the polymeric silica globules on one of the non-striated faces of the quartz crystal in the Waitara Sinter are seen to have been deposited in more random pattern. Without the alignment of 'steps' the polymeric silica globules ("little balls") have been deposited in a wide variety in sizes (from Newton¹², 2000).

in which concretions form, that is by entrapment of the mobile particulate species at the surface layer where a higher concentration of electrolyte is maintained by desorption from the particles joining the nucleus. In the case of concretion, oolite, or framboid formation, the particles are presumably larger and retain their hydration. Concretionary nuclei are synergetic, semi-ordered, and 'close packed' denser gels. They exude electrolyte to the surface as Helmholtz double layers impinge due to van der Waal's interparticle attraction.

The enhanced crystal growth in gels or surface catalysis by a 'gel coating' appears to involve the following steps:

- 1) Crystallite formation by coalescence of molecular species.
- 2) Crystals nucleate by coalescence of crystalline molecular clusters of less than unit cell size.
- 3) Enhanced crystal growth (surface catalysis) occurs on crystal faces having a certain orientation in relation to the long-range ordering in the coating gel.
- 4) Solubility in the vicinity of surfaces is greatly reduced and colloids in particular tend to "plate out" on surfaces. This process of "diffusophoresis" is also used in surface coating technologies where colloidal particles are deposited onto substrates like plastics or roofing materials.
- 5) Species added to the surface of a crystal growing in a gel move to the liquid-solid interface by diffusion down a concentration gradient created by their removal from dispersion.

- 6) Particles that diffuse to the growing crystal face are charged hydrated molecular or macromolecular species.
- 7) On surfaces the diffusion rates of particles are increased (Henisch¹³, 1972, p. 56).
- 8) Adsorbed ions and surface hydration water on particulate species joining a crystal lattice must be released in cases where water or these ions cannot become part of the lattice.
- 9) The higher concentrations of nascent water and ions liberated at the surface may be responsible for the increase in surface diffusion rates and destabilisation of the dispersed particulate species.
- 10) Gelatinous media act as 'molecular sieves' where they effect chromatographic separation and banding of particulate species (as in agates, geodes, etc. - see Figure 26). Most large geodes develop cavities where crystals grow from the internal surface. Since the structure of the 'coating gel' in which enhanced crystal growth is occurring has a specific orientation in relation to the crystal face, it suggests that particles with similar non-homogeneous charge distribution (like those dictating the internal ordering in framboids or the radial orientation of chlorite or chamosite layers round oolites) are controlled to approach the surface in a certain way.

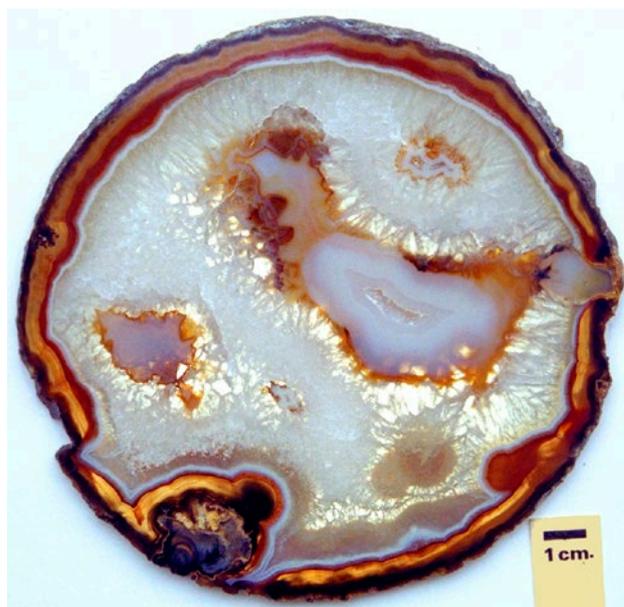


Figure 26. The fine concentric bands of ferric hydroxide stained chert, the growth of coarse crystals into the crystal cavities in the centre and the fluid 'out-burst' channel in this geode are positive evidence for the syneresis of its precursor silica gel. This clear empirical evidence positively supports theoretical work that shows that synergetic aging of a uniformly mixed gel must result in separation of component particles into Liesegang type concretionary bands.



Figure 27. Long slender ‘needles’ of rutile develop in the gelatinous polymeric precursor of a large single crystal of vein quartz. Growth on the small newly nucleated ‘seed crystals’ of rutile in their supporting silica gel medium is enhanced in accord with the orientation of the crystalline surface with the ‘structure’ or meshwork pattern within the gel. This surface catalysis can therefore be confined to one face of the ‘seed crystal’ that grows taking all available dispersed rutile to the exclusion of other faces.

- 11) If the diffusion of particulate species through the surrounding gel and transfer to its internal surface against the growing crystal resulted in their orientation (as it does in certain micelles and concretionary structures) such a favourable orientation in relation to the crystallographic axis and the surface ‘growth steps’ may significantly increase the rate of growth.

Hatschek and Simon¹⁴ (1912), Boydell¹⁵ (1925), Healy¹⁶ (1969), Henisch¹³ (1970) and many others have demonstrated enhancement of crystal growth in gels experimentally. It is developed dramatically in the spectacular needle-like crystal growth of rutile in the precursor silica gel of vein quartz (Figure 27) and similar acicular interlocking needles of tourmaline are occasionally also developed in this type of quartz.

THE FLUID TRANSPORT OF SILICA INTO VEINS

Calculations of water volumes required to transport the tonnage of quartz observed in various vein systems and lodes have tended to discount the oligomeric and polymeric silicic acids (colloidal silica) with which the monomer and ionic acids must be in equilibrium.

It is quite apparent that calculations based on measured solubilities of silica alone give unrealistically large volumes of solution. This leads to the postulation of recirculation or additional quantities of water from deep mantle sources. Unrealistically large volumes of solution would be required to deposit the observed large volumes of vein quartz (Barnes³, 1967, p 392). He assumes depo-

sition at around 300°C, a geothermal gradient of 35°C/km, and a pressure gradient of 100 atm/km. It suggests an unrealistic 5000 cub/m of solution would be required to deposit each tonne of quartz. If temperatures indicated by the fluid inclusion data are assumed, the listed solubilities generally result in a requirement of some 4000 to 5500 cub-m of solution per tonne of quartz deposited. Where would this volume of water come from?

Sediments generally are deposited with average total water content around 75% by weight. In the consolidation of sediment to a rock some 3.5 to 4 cub.m of pore water, surface adsorbed water, and water from chemical dehydration reactions must be released. Each cubic meter of finally compressed and anhydrous rock (weighing 2.7 tonnes) could be expected to express silica during the stage where it could be dissolved and mobilised.

It is suggested that water outflow of this magnitude could be sufficient to accumulate and deposit the observed volumes of vein quartz. However due regard must be given to all classes of solutes of quartz, their mutual equilibrium, and the permeability, thixotropy, rheopexy, syneresis, and enhanced crystal growth properties of the precursor vein gels.

Quartz vein development is related to the water outflow system, crosscutting the sediments initially by clastic diking and hydraulic fracture. The crosscutting fractures start filling first with water, dilute sediment slurry, or watery silica gel, as earthquake shocks or disturbance of the whole pile initiates “outbreaks” from over-pressured entrapped fluids. The crosscutting nature of earlier veins is shown in Figure 28. All these “outbreak” or vein injection phases is followed by a “static” period in which pore fluid seeps through the fabric of the crosscutting, more watery vein gel, introducing new silica both by the fluid seepage and by diffusion (“sweating out of the rocks”).

The polymeric silicic acids of the vein gel remove the monomer by polymerisation. This creates a diffusion gradient in respect of this species. Like the replacement reaction in petrifying wood, monomeric $\text{Si}(\text{OH})_4$ dispersed in sediment pore fluids diffuses into the precursor vein gels during the extended times involved. Examples of silicified wood plainly demonstrate that substantial volumes of silica can be transferred and localised by cumulative diffusion. The polymerisation of the monomer depletes this species within the vein and “draws” in more silica, possibly as much by diffusion as by seepage of solution. Denser and “purer” precursor vein gels are then involved in each successive mobilisation. Later injections are of dense silica gel slurry capable of supporting wall fragments and other minerals as in Figure 29. They involve relatively small volumes of water.



Figure 28. Several types of early diagenetic crosscutting sediment veins ranging from irregular quartz veinlets 'splashed' within the ooze, 'dirty early quartz' veinlets, and later quartz-chlorite veins re-injected beside original veins, illustrate stages in "the birth of quartz veins" in this soft diagenetic siliceous ooze intersected in the Wagga Tank prospect drilling in Mt Hope district, NSW.

Requirements for vein emplacement

Veins and veinlets ranging in all sizes from minute micro-veinlets to large 'quartz blows' constitute the most common of all mineral deposits. Smaller veins persisting for relatively shorter distances through the rocks usually consist only of quartz but many quartz veins contain a variety of other minerals such as sulphides, oxides, feldspars, chlorite, carbonates etc. The veins appear to be emplaced by the injection of entrapped fluid and components from the sediments that these fluids carry with them. Fluids escaping upwards through semi-consolidated sediment piles re-liquefy and mobilise sediment, individual sediment components, or previously re-mobilised sediments. These then rise to higher levels within the pile. Such vein injections are usually episodic and triggered when de-watering basins are disturbed or shaken by earthquake shocks.

To be injected through semi-consolidated sedimentary materials during diagenesis and metamorphism, certain essential requirements for the emplacement of any vein must apply. These are:

- 1) Entrapment of a fluid or a readily liquefied semi-solid at hydraulic pressure that is supporting part of the weight of overlying materials. When disturbed it must be able to flow to effect equalisation of this load.
- 2) If the vein is to intrude upward, its fluid-rich mixture of components must be lighter than any plastic material that it invades or confined within a crack or opening in a cohesive fractural solid.
- 3) If the vein material is to preserve the shape of its injection and suspend wall rock fragments or oth-



Figure 29. A discordant quartz vein in basic rock carries pieces and slabs of wallrock "suspended" in the quartz. Some crystal cavities or vugs are developed near the centre of the vein. If the quartz in the vein were deposited from solution it introduces the problem of suspending the fragments while sufficient quartz is precipitated to support them. Injection of the vein material as thixotropic silica gel is clearly indicated. Rheopexy (instant resetting as gelatinous fluids approach cessation of flow) would support fragments and preserve their delicate projections. After injection and resumption of a gelatinous condition the crystal cavities indicate synerectic shrinkage during dewatering and finally crystallisation. The vein outcrops on the south coast of N.S.W. between Bungen and Goalen.

er mineral masses, it must have some substance or 'body' and be able to rapidly re-solidify.

- 4) The material of the vein must be some component or mixture of components of the local materials from which it originates.
- 5) The host materials injected by veins must be plastic, both plastic and cohesive, or cohesive but readily fractural so that veins can hydraulically penetrate them.
- 6) Veins that show evidence of multiple intrusion or several stages of liquefaction and re-intrusion must be capable of isothermal re-liquefaction by repeated mechanical disturbance such as fault movements, earthquake shocks, etc.
- 7) The mineral or minerals comprising the vein must have simple mobile precursors which can crystallise directly (with only water loss) to the crystals or crystalline assemblage of vein minerals.

Veins are therefore logically part of the diagenetic 'plumbing system', the means by which fluids leave consolidating sediment piles, large re-mobilised sediment masses, or the accumulated precursor mineral gels and sludge which constitute newly deposited lodes and ore-bodies.

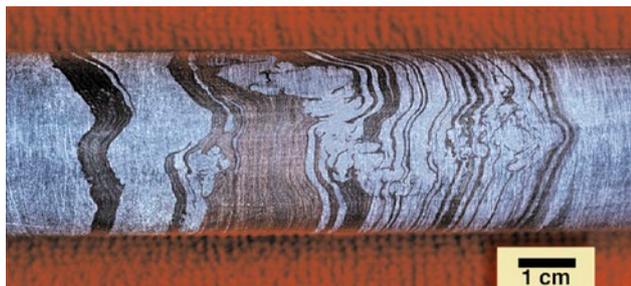


Figure 30. A ptygmatic mud dike is injected into hematite shale at the soft sediment stage. The highly fluid nature of mud between haematite layers is indicated by the irregular folding in its bedding but the dike which has broken across the soft bands is highly contorted into a ptygmatic pattern due to the rheology of the non-Newtonian fluid paste. (From Explorer 8 core, Tennant Creek, NT).

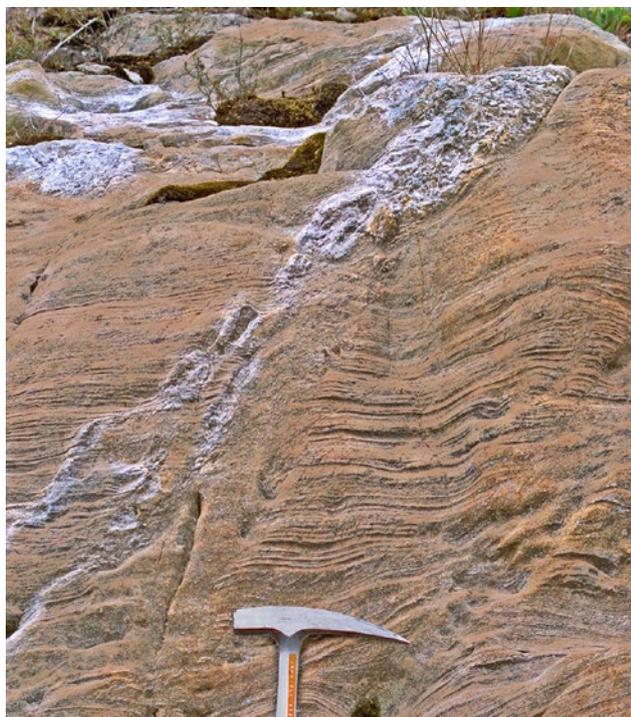


Figure 31. A flow banded mass flow unit, one of the Tasmanian west coast porphyroids outcrops on Whip Spur above South Queenstown. A clastic dyke or fluid outflow channel intruded shortly after its deposition over other wet sediments. This dyke has a ‘sandy’ matrix similar to that of its porphyroid host but it carries rotated pieces of disrupted siliceous flow bands and a ‘jumble’ of these is concentrated in the upper part of the dyke.

Veins emerge from partly consolidated sediments at all stages of diagenesis. Some examples of early veins through newly deposited soft sediments and mass flow units are illustrated in Figures 30, 31, 32, and 33.

Veins and sediment dykes could be regarded as the “muddy water” or the more fluid pastes and watery sil-

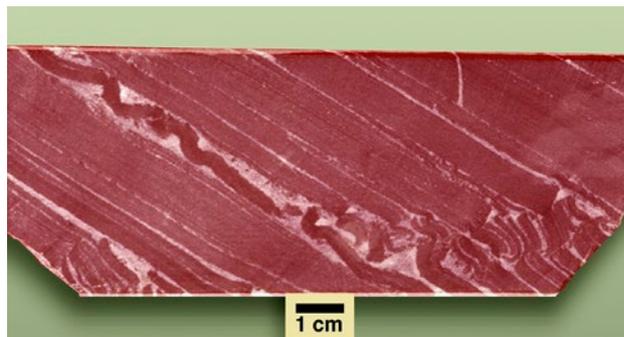


Figure 32. Laminose flow or lateral slippage along overpressured fluid-rich bedding planes during diagenesis has allowed some of the hematite shale bands to fold and disrupt. The suspending ‘fluid’ was probably filled initially with dilute polymeric silica as a “dirty early quartz vein” and then ‘infilled with additional $\text{Si}(\text{OH})_4$ to crystallise as whiter quartz. (From Gecko Mine drill core, Tennant Creek, NT).



Figure 33. A ptygmatic-type clastic mud dyke or “dirty early quartz vein” was intruded into diagenetic soft and banded hematite shales. These early “out wellings” of entrapped fluid through fine oozy sediment are episodic with each successive reactivation becoming more quartz rich until the filling material resembles vein quartz. (From Explorer 8 drill core, Tennant Creek, NT.).

ica gels escaping from normally consolidating sediment piles. They are very much a part of the normal “sediment plumbing system” augmenting the slow seepage and diffusion of the fluids uniformly upward through the sediment layers as a whole.

Once established, crosscutting veins and dykes then become channel-ways by which more fluid seeps round or through their less permeable host sediments. Because of this continuing fluid seepage, veins are often rejuvenated by subsequent movements, effect extensive alteration of adjoining sediments, or act as feeder channels to larger ‘alteration zones’ or overlying mineral deposits. They are often concurrent with, or occupy faults and shear zones which act in the same way to channel fluids and hydrothermal fluids draining from depth.

EVIDENCE FOR THE FORMATION OF QUARTZ VEINS FROM SILICA GELS

Quartz veins formed at low to moderate temperatures

There are many examples of injected, intruded, and “remobilised” type vein quartz in close association with granites, greenstones, andesites, metadolerites, pyroxenites, amphibolites, metabasalts, spilites, and even serpentines and other ultrabasic rocks. This has suggested an origin related to high temperature. Melting has in fact been put forward in the past as the mechanism for mobilising the quartz in some of these settings. However, the clear evidence is that a single and usually relatively pure mineral is involved, a high temperature is necessary to melt quartz itself, quartz veins lack evidence of any extreme temperatures, and molten silica is highly reactive with such things as undersaturated basic rocks, magnetite, haematite, calcite, etc.

The data from homogenisation of fluid inclusions in vein quartz repeatedly indicate low to moderate temperatures usually less than half that assumed for magma melting. This has even led committed magmatists to abandon the idea of molten silica injection to form quartz veins.

For an exploration geologist, observing quartz veins in the field, in drill cores, in granites, in greenstones (even ultrabasic rocks), in andesites, in sediments, in metamorphics, and as massive vein systems in faults and shear zones is so commonplace, and often appears to be of so little relevance to the discovery of major ore deposits, that very seldom is any consideration given to their origin and genesis. In fact, after having worked for so many years in older sedimentary, metamorphic, and granitic rocks, the usual habitat of mineral deposits, it takes something like a visit to the mountains of lava and volcanic debris such as comprise the islands of Hawaii, to realise how impressive and unusual are vast rock exposures totally devoid of quartz veins!

Actual inclusions of calcite, dolomite, haematite, magnetite, rhodochrosite, siderite, chlorite, dawsonite, etc. which are often found in quartz veins preclude the possibility of molten fluidity of the silica. For example, the ferric hydroxide and polymeric silica precursors of jasper do not form iron silicates when intimately mixed together because these substances are already fully reacted with water. The hydroxyl groups saturate and ‘blind’ what would be the normal reaction of these ions to form iron silicates. Mixtures of the gelatinous forms of these materials are stable as manifest by banded iron formations and bedded jaspers. If these same materials were heated so that there is dissociation of the iron and silica hydroxides, in say an

autoclave or an “aqueo-igneous magma”, iron silicates would be formed.

As observed in many highly aqueous environments, very abundant hydrous iron silicates, iron magnesium and calcium silicates, ferric and ferrous aluminosilicates, iron hydroxides, etc. are often associated with sedimentary ‘chemical sediments’ like banded iron formations. But these under-saturated ferromagnesian-rich hydrates and iron hydroxides are stable in the deep ocean and aqueous environments because they are completely hydrolysed (fully reacted with water).

In most cases the concept of minerals such as quartz and magnetite having been deposited contemporaneously from hydrothermal solutions is not possible. Silicates or silicic acid in solution together with ferrous or ferric ions should deposit iron silicates from solution rather than the respective oxides.

High temperature hydrothermal or “aqueo-igneous” quartz veins in serpentines, andesites, metabasalts and dolerites, pyroxenites, amphibolites, etc. must also be somehow constrained to stop what would be their expected reactions with these basic and under-saturated rocks. It is most noticeable that in a true basalt field the molten rocks are fully reacted with all their available quartz. Iron (olivine) or ferromagnesian silicates predominate and there is not a quartz vein in sight!

To fit the case of quartz veins in ordinary sediments, limestone, and marbles there is clearly a need to suggest a low temperature form of mobile quartz. Quartz fluidity due to simple fusion of dry quartz is no longer seriously proposed, even in supposedly igneous rocks. Therefore, in all cases, vein quartz, quartz mobility, and vein quartz crystallisation are envisaged as being from some aqueous phase such as a solution or hydrothermal solution, from silica gel, or from “magmatic quartz” which is thoughtlessly considered some type of higher temperature low-water eutectic.

The entrapment of organic materials and salt in fluid inclusions in quartz veins

The mechanism by which either primary or secondary inclusions of organic liquids and salt could become trapped in minerals such as quartz has always been a problem (Kvenvolden and Roedder¹⁷, 1971, p 1224). The problem arises entirely from the assumption that an ionic solution is the only medium from which quartz, such as the vein quartz in which the inclusions are observed, crystallises.

Kvenvolden and Roedder¹⁷ (1971) review various studies of organic fluid inclusions in vein quartz from sediments and from vein quartz in granites. These con-

tain “vaselinous oil”, possibly olefinic differentiates as dark resinous flakes, and black globules of aromatic differentiate. There is no essential difference between the inclusions in granite quartz veins as opposed to those in veins in sedimentary and metamorphic rocks.

From the fluid inclusions themselves, Kvenvolden and Roedder¹⁷ determined homogenisation temperatures from 70 to 160°C with most in the range 110-150°C. The entrapped material was in most cases a moderately saline aqueous liquid but organic liquids include methane, ethane, butane, n-alkanes and isoprenoid hydrocarbons, and bituminous substances.

The molecular composition and distribution of the hydrocarbons suggest biological precursors for these components.

The problems arising from the studies are:

- (a) the low temperature indicated by the homogenisation of the inclusions, which apply equally to quartz veins in sediments and in granites;
- (b) the biogenic origin of the amines and hydrocarbons, when these were found included in granite veins (Petersilie and Sorensen¹⁸, 1970, p. 59);
- (c) the means by which the inclusions could be entrapped in the quartz crystals when these were assumed to have crystallised from solution.

These problems do not exist for quartz veins having a precursor of gelatinous silica. Since such precursor silica gel accumulates in, and is associated with fluid outflow channels, it is logical that some hydrocarbons and saline pore fluid may become mixed with or included in it. This could occur particularly when such precursor gels may be subjected to periodic re-liquefaction. Entrapped organic liquid or inclusions of saline fluid within vein silica gel are preserved as entities while the gel further densifies and is “infilled” by diffusion into it of additional monomeric and short chain oligomeric silicic acids. These tend to maintain concentrations as exothermic crystal growth depletes and removes the mobile species with release of water.

Silica gel directly observed in veins

One of the earliest excavations in a younger mountain fold belt, the driving of the Simplon tunnel through the Italian-Swiss Alps in the 1890's, encountered gelatinous silica in some of the quartz veins. Spezia¹⁹ (1899) records how in driving this tunnel, over record lengths for that time and deeper beneath the surface above than ever before, “steamy conditions” were encountered and a vein of silicic acid in the gelatinous condition was discovered!

A number of similar quartz veins containing gelatinous silica have been discovered since. Hellm-

ers and Ottemann²⁰ (1952) describe how in the newly laid out Moll Tunnel which supplies the Stau Lakes of the Kapruner Tales with water from the Moll River, Horninger mapped a zone about 1400m from the tunnel mouth which was rather wet and in soft material (1261.6m above sea level). In this zone an oily white mass of silica gel was found in a loamy strongly flowing fault. The water had a temperature of 2.7°C and a pH of 7.5. The main mass of the silica gel was a very fine-grained deposit weakly broken into two tabular masses and spindle shaped white to yellow formations. Some small crystals of calcite and glass-clear or faintly milky opaque columnar prismatic crystals of quartz were found in parts of the gel mass. The quartz was either well-formed single crystals or small radiating clusters of quartz prisms (up to 2mm in length x 0.5mm diameter). Many of these were found entirely suspended within the gel from which they had been formed.

In Australia Levings²¹ (1912) noted gelatinous silica in veins at the Great Australia Mine at Cloncurry and the Victorian Department of Mines issued a report (K. Bowen²², 20th February 1967) on the “mutton fat” which is the gelatinous silica containing aluminium hydroxide found in the quartz veins of the Woods Point district. The “mutton fat” sections of the quartz veins in several of the mines in the Woods Point area are associated with quartz “floors” and fissures in the dykes and are regarded as a good indication of gold.

Analysis of the “mutton fat” solids (the material is 73-75% water) indicate about 53% SiO₂ and 27% Al₂O₃ and although the jelly like material contains small crystals of calcite and quartz it is apparently the dispersion of aluminium hydroxide which has prevented complete crystallisation to quartz. Bowen's²² report indicates that the small crystals of quartz have crystallised in situ within and from the “mutton fat” silica gel and that a dried-out sample preserved in the Mines Department Museum (Reg. No. 15188) had formed a mass of small crystals of calcite and quartz embedded in a transparent film like material. This suggested that the crystallisation occurs on drying out and that the original material in its natural condition in the mine may have been entirely gelatinous.

It is clear that the quartz veins merging to silica gel or with parts of them still preserved in a gelatinous condition are not found very frequently. However, these examples demonstrate that certain quartz veins can and do have this silica gel precursor and that quartz can crystallise within and from such gelatinous precursor material.

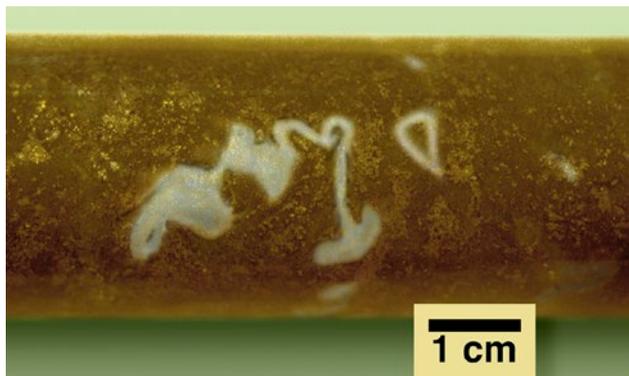


Figure 34. Highly fluid or “poured in” vein quartz or a disjointed plastically contorted fragment of vein quartz occurs in a large mineralised lode intersection. This core is from Woodlawn Mine, NSW, and a number of almost ptygmatic quartz veins and fragments of veins of this type were intersected in this lode.

Plastic quartz in veins

There are many examples of plastic quartz veins or bulbous ptygmoidal plastic folding of vein quartz. This type of folding clearly reflects the plasticity of the precursor silica gel of the vein prior to densification and crystallisation of the quartz.

In the Woodlawn drill core, Figure 34 illustrates some highly plastic quartz that appears to have been ‘poured in’ among the soft precursor lode minerals in a highly mobile condition. It is certainly not intruded along a crack or some sort of fracture and it is quite obvious that this vein quartz displaced its pliable and yielding host at the time that it was intruded. Figure 35 is an example of a “wrigglyite” or plastically contorted multiple quartz vein mass that was deformed while the vein material was in the precursor gel stage.

Figure 36 from a quartz-magnetite-chlorite rock from the lower part of the Peko mineralised complex at Tennant Creek, NT, has concretionary rims developed round siliceous accretionary nuclei. These successive concretionary overgrowths on synrectic nuclei unmistakably indicate the colloidal environment. Later ptygmatic and ‘cleaner’ quartz veins have sinuously intruded the soft precursor quartz-chlorite-magnetite.

Vein quartz as a breccia matrix

Many quartz veins, particularly discordant types, suggest a type of hydraulic fracturing, a movement in bulk of the quartz material itself and its ability not only to fragment the wall rocks, but to entrain pieces of wall rock within the injected quartz. Quartz veins therefore frequently contain angular fragments of wall rock, or



Figure 35. Discordant, ruptured, and re-healed fold patterns occur in this multi layered quartz vein from the Laurentian Shield, near Sudbury in Canada. This plastic deformation is consistent with a polymeric amorphous silica precursor in the vein before crystallisation, but it would remain difficult to explain if it is contended that the vein formation was by “crystallisation from hydrothermal solution” and then subsequent folding of the crystalline quartz. In this type of random discordant folding, analysis of the stress fields that cause the folding, shows it to be isotropic or fluid deformation. Any deformation pattern in a solid phase must be anisotropic.

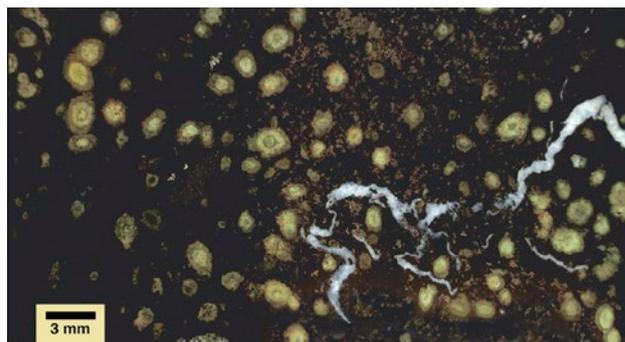


Figure 36. A quartz-magnetite-chlorite rock from the lower part of the Peko mineralised complex at Tennant Creek, NT, has concretionary rims developed round siliceous accretionary nuclei. These successive concretionary overgrowths on synrectic nuclei unmistakably indicate the colloidal environment. Later ptygmatic and ‘cleaner’ quartz veins have sinuously intruded the soft precursor quartz-chlorite-magnetite.

of other associated lode minerals of similar origin to the quartz itself (Figure 37), such that they appear as an injected or intruded breccia (Figures 29, 38, and 39).

In many instances the quartz veins merely bifurcate and anastomose round slabs and pieces of wall or host rock such that these slabs become isolated in the vein material. These observations are inconsistent with a hydrothermal solution theory of quartz vein genesis. As calculations of the volumes of water necessary to trans-

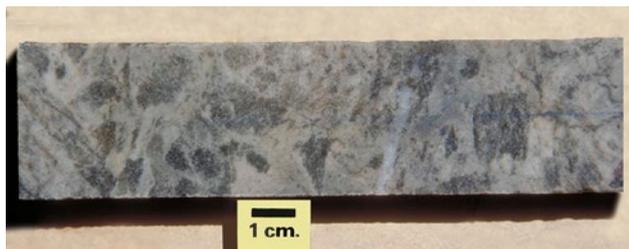


Figure 37. An intrusive siliceous breccia of grey chert containing angular and partly digested fragments of chloritic wall-rock was intersected in drilling near the margins of the gold orebody at the Peak Mine in Cobar, NSW. These earlier grey cherty ‘elvans’ or extensive silicified zones are often found intruded round larger mineral lodes.

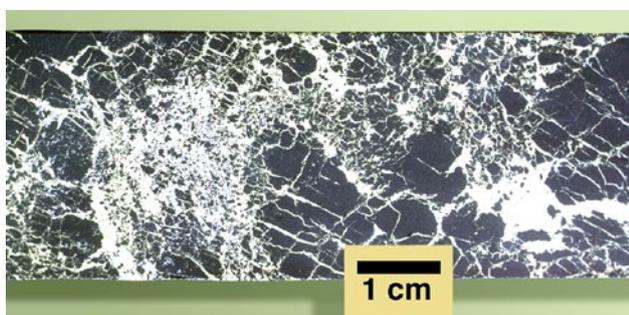


Figure 38. Syneresis of the gelatinous lepidocrocite precursor in the massive magnetite ore envelope at Warrego Mine, Tennant Creek, has developed a strong pattern of shrinkage cracks that have been filled with quartz. There are several episodes of mobility in the siliceous matrix that has suspended the heavy magnetite fragments by its rapid rheoplectic re-setting.

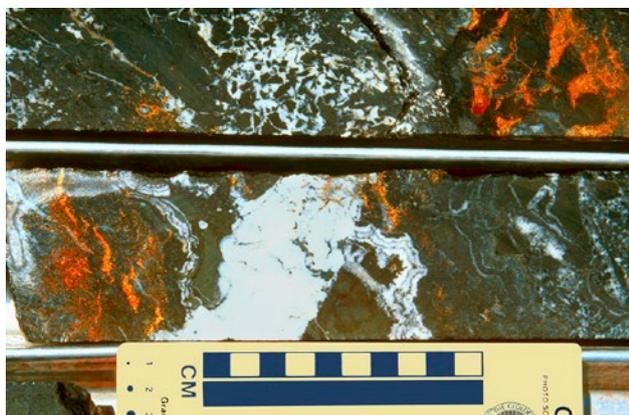


Figure 39. Colloform banding in the quartz magnetite and sulphide lode cored at New Cobar Mine, has been further disrupted at the gel precursor stage. Vein quartz ‘wells’ across the colloform bands and one of the magnetite layers has been brecciated so that highly angular and delicate fragments of now very heavy magnetite are suspended in a matrix of more fluid and rheoplectic silica gel. The rheoplectic re-setting of the precursor polymeric silica has “frozen” the delicate magnetite precursor fragments in place.

port quartz in solution indicate, solutions of silicic acid are very dilute even at optimum conditions favouring solubility. If the resultant quartz vein had been originally injected as a dilute solution, what is to suspend the wall rock slab or the breccia pieces while further volumes of solution arrive to introduce the amount of quartz necessary to “cement up” the entire vein to the point where it could support the fragments?

The observations of angular fragments in quartz vein breccias include basic rocks of density 3.5 (as in Figure 29) and even angular fragments of minerals like magnetite (density 5.0 - as in Figures 38 and 39) which would certainly sink in any opening or hydraulic fracture filled with a dilute solution.

The habit of many quartz veins has been described aptly as “discordant squirts”, a high degree of fluidity involving a very mobile material is indicated by such complex injection structures Figures 40 and 41. How could such a mobile precursor to vein quartz maintain heavy wall rock fragments suspended in it, if it were a solution?

The phenomena of repeated injection or liquefaction, high fluidity and mobility during actual injection, yet “instant refreezing” once in place to “set” the breccia and wall rock fragments suspended within the material, is a clear indication of a silica gel precursor of the vein material. Only a non-Newtonian fluid, that is a material having a Bingham yield point at which it reverts to a fluid isothermally in response to shock or shear (thixotropy) could display this phenomenon. Correspondingly, in order to account for the features commonly observed in quartz veins, it must also revert suddenly to a gel condition (visco-elastic solid) as flow declines to a critical rate when the intrusive flow nears completion (rheopexy).

At the time of injection, the silica gels that are the precursors of vein quartz must have a somewhat similar density to the wet sedimentary materials (like those in the Moll tunnel) that they invade. This means that any wall fragments or slabs isolated by branching and re-joining of veins are able to remain suspended in a fluid of almost the same density while it is mobile and the fluid silica gel slurry would preserve the sharp conchoidal fragments and slivers of the soft fractured wall materials.

Injection of quartz veins is by hydraulic fracture, the materials injected being fractured by the differential pressure or fluid “overpressure” but the incompressible fluids carry the main compressive load of deep burial hydraulically (Phillips²³, 1972). This “hydraulic fluid” is thixotropic polymeric silicic acid accumulating in the normal water outflow or “plumbing system” by which water escapes from sediments during lithification. The silica originates from the natural amorphous silica in the sedimentary materials themselves.

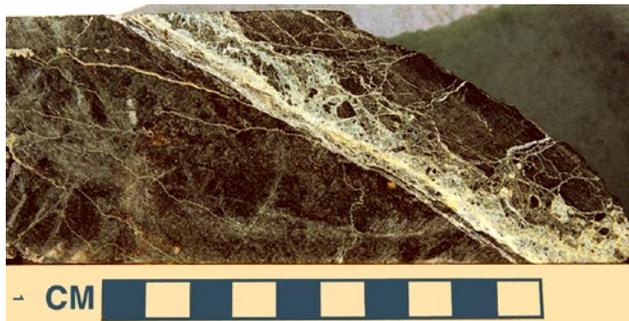


Figure 40. Fluid polymeric silica net veining intrudes a sparsely mineralised section of the Kaiser prospect core near Orange, NSW. It shows a number of features resembling the intrusion of a clastic dyke. It has been formed by hydraulic expansion of the vein space so that angular fragments are rotated and slivers of cohesive sediment parted from the margins. This type of fluid vein is transitional to a clastic dyke.

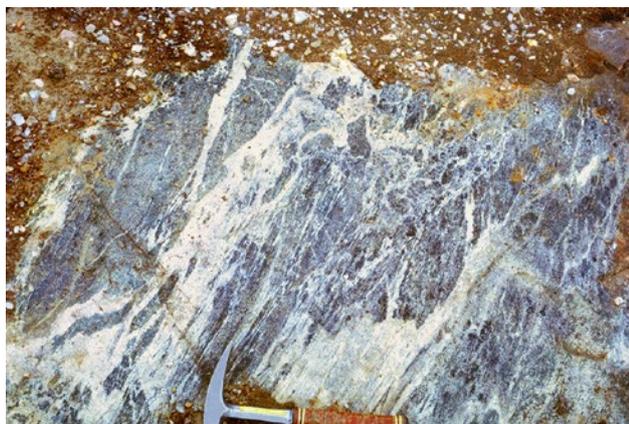


Figure 41. Vein quartz is “splashed in” and partly “soaked into” the host rock mass to give the impression of a very mobile penetrative fluid. However, some wall rock pieces appear isolated and suspended in the vein material. This example is from the Macdonald Mine, Bancroft, Ontario.

Re-brecciated Quartz Veins in Sediments

The water outflow channels from consolidating sediment piles are seen as various types of “dirty early” quartz veins, clastic dykes and sills and pygmatic outwelling in the soft sediments (Figure 30). In many of the clastic dyke type “outflow” structures the hydraulic fracturing breaks and re-breaks the “gelled” semi-consolidated sediments into splintery conchoidal fragments typical of gel fracture, such that they fill the dyke (see Figure 31).

The fluid outflow through the transecting channels and dykes is continuous, being by slow seepage through the fabric of the “gelled” sediments themselves or the “re-gelled” dyke and vein fillings when these are



Figure 42. Several successive ‘layers’ of additional quartz have been injected at the precursor stage beside the first of these quartz veins in the Wagga Tank prospect drill core. Chlorite septa on their margins separate the different additional intrusions but this has largely been disrupted by influx of polymeric silica. This has dispersed and disoriented pieces of the chloritic vein walls through the later intruded silica. Small chlorite ‘needles’ have crystallised in the soft polymeric silica before it finally also crystallised.

in the non-mobilised static condition. Periodic earthquake shocks, slumping, or mechanical disturbance to the sediments, particularly to the wetter seepage zones, episodically re-liquefies those parts of the sediments or lodes that are thixotropically sensitive to that level of disturbance. Each disturbance therefore triggers another episode of reactivation of the dykes, new injections, and extension of existing hydraulic fracture systems. Repeated injection of veins into pre-existing veins results in a “layered” vein complex. They are common (Figure 42).

An early injection of vein quartz precursor fluid along oversaturated bedding planes is illustrated in Figure 32 from the Gecko Mine drilling at Tennant Creek. That these disrupted shale beds were soft and pliable yet cohesive at the time of disruption is indicated by their plastic and random distortion in response to the movement which apparently involved some lateral slippage.

Early clastic diking and “water outflow” structures are closely related to the formation of quartz veins. Such dykes tend to be filled with silica gel that develops an increasing density and purity with each successive sequence of injection followed by seepage. Early quartz veins at their gelatinous stage are similar to and often form part of the clastic dykes. Like the semi-consolidated sediment, the gel of the early vein quartz can be fractured by an episode of mobility and the disrupted fragments or “wisps” of the original gel are often found dispersed in the new matrix.

A large body of discoloured impure quartz occurs in or near the lode zone of the Peak Gold Mine at Cobar, NSW. This ‘elvan’ or peripheral lode quartz was inter-

sected in the 1986 drilling. It is a body of siliceous mineral matter that has been episodically intruded as a diapiric or vein-like mass of wet thixotropic precursor silica gel where the high fluid content of material in the lode zone made it lighter than surrounding semi-consolidated sediments. The soft plastic mobile nature of its precursor silica gel is strikingly indicated by the breccia phases (see Figure 37) in which angular fragments of soft chloritic wall-rock are randomly rotated and dispersed or ‘disintegrated’ in their milky fluid siliceous matrix.

Veins of recognised meta-colloidal silica such as jasper, opal, and chalcedony

Jasper, chalcedony, and chert are among the forms of cryptocrystalline quartz that are regarded as originating from colloidal silica. There is such a strong body of opinion to this effect that when agates are found in supposed volcanic rocks or jaspers found in rhyolites, these are then postulated as secondary or “introduced later infillings”. What the occurrences of agate, chert or jasper imply about the rock in which they occur is not often considered.

Frondel¹ (1962, p 299) records the occurrence of gelatinous silica itself in some so-called “igneous” and sedimentary rocks. He lists occurrences of gelatinous silica in the diabase sills of New Jersey, with hydrophane in porphyry at Hubertusberg, Saxony, in the Chalk formation in England, and in cavities in marly and flinty rocks in France.

Flow banded red jasper forms the main bulk of some parts of the “rhyolite” outcropping in the creek at Box Range Farm, near Lochiel in southern N.S.W. As banded rhyolitic lava under atmospheric or limited confining pressure this rock contains far too much silica for viscous flow other than at very high temperature (near the melting point of quartz - 1723°C). Jasper is not a product of fusion or an “aqueo-igneous magma”.

Chalcedony veins and amygdales containing unweathered pyrite framboids occur in an outcrop of so-called hypersthene andesite at Allendale, 19 km west of Maitland in NSW (Ostwald and England²⁴, 1977, p. 113). Un-oxidised pyrite occurs as irregular patches about 10 mm in size within the chalcedony that also has Liesegang-type banding surrounding the pyrite patches. Both this type of agate banding in the chalcedony and the concretionary framboidal structures indicate diffusion and reducing conditions in the precursor polymeric silica which occurs in this hypersthene andesite as veins.

Opal has been definitely established as a form of colloidal silica with “packed” amorphous silica spheres of about 180 to 250nm in diameter clearly visible in the electron micrographs [Dana²⁵, 1932, p. 475; Iler², 1979, p.

401, and Figure 10 (on page 12)]. Frondel¹ (1962, p. 300) lists its occurrence in a much wider variety of so-called igneous rocks. It is recorded from the basaltic rocks of Northern Ireland, the Faroe Islands and Iceland; from the trachytes of the Siebengebirge in Germany; from serpentine at Kosemutz in Silesia; from cavities in basaltic rocks in the Puy-de-Dome, Plateau Central, France; from reddish brown to pinkish so-called rhyolite in the state of Queretaro, Mexico; and from trachytic rocks near Erandique, Honduras.

One other observation worth noting is that jasper, chalcedony, or chert veins are rarely found in or originating from bedded cherts or massive bedded jaspoidal formations. These are frequently crowded with veins but the mobilised silica is almost invariably white vein quartz. The reason is that the later episodes of mobility, during which the more mobile precursor vein gel is injected into the semi-consolidated parent chert bed, effects a “cleaning” of the silica. As in the development of a white quartz vein in sediment, or a coarsely crystalline galena vein from a fahl ore bed, the thixotropic liquefaction of the precursor gel allows a separation of particles of different macromolecular shapes (discard of impurities by rejection from closer packed aggregates). The “clean” precursor sol is mobilised into the vein. It reverts rheopectically to a gel and most of the silica, which eventually fills the vein with crystalline milky white quartz, is added by diffusion. Further monomeric and oligomeric silica is added into this precursor vein gel during its aging, densification, and crystallisation.

Colloform Quartz Veins

Colloform banding is observed in many quartz veins, often with gold or complex selenide or telluride gold-silver ores (Lindgren⁸, 1933, pp. 497 and 505). The banded colloform quartz frequently contains thin concentric crusts of fibrous quartz (Figures 43 and 44). This fine radial crystallisation is typical of that developed between the concretionary bands in many oolites and orbicules. It can be seen in the orbicules from the Gold- en Plateau Mine quartz vein (Figure 45).

Figure 46 shows colloform banding in a quartz vein from the Abra Prospect core, Jillawara, WA. Some small crystals growing out from some of the colloform bands are over-grown with further gelatinous precipitate. The irregularities, disrupted layers, and ‘oozy’ nature of the precursor silica together with a later small veinlet of similar “pearly” quartz that cuts across the colloform bands, reflect the soft and highly hydrous nature of the original deposition. The textures clearly indicate a gelatinous stage in the accumulation of this vein quartz.

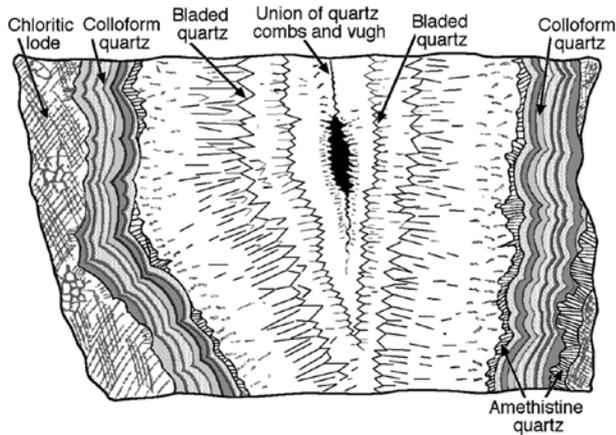


Figure 43. A quartz vein from Creede, Colorado, shows successive crystallisation of bladed quartz towards a central vugh from colloform banded quartz deposited near the vein walls. The history of aging of the polymeric silica in this vein is plainly the same as that in geodes where a similar pattern (Figure 26 on page 56) of cleaner crystals develops. These grow from colloform outer layers toward a central shrinkage cavity. The chain of shrinkage vugs where it occurs in quartz veins, is usually central along the length of the vein but a pattern of crystallisation from colloform banding confirms the initial introduction of polymeric silica gel.

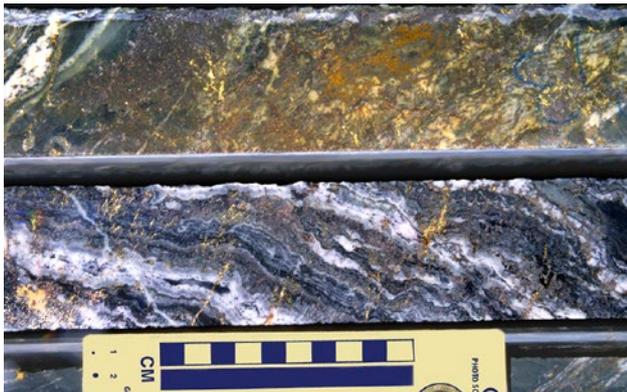


Figure 44. Contemporaneous veining and re-mobilisation of colloform quartz banding occurs in core from the New Cobar Mine, NSW. Three sets of quartz veinlets in the centre bands cut each other and one of them parallels and merges into a colloform layer. Cleaner 'cloudy' white quartz welling out as an expanded band and cutting other colloform layers and the irregular wisps of 'poured in' quartz in the upper core confirm the mobility of the newly deposited silica.

Druse and Miarolitic Cavities in Veins

Miarolitic crystal cavities, vughs, and druse cavities are found in geodes, agates, in the centres of large quartz accretions, in septarian nodules, flint nodules in limestone, and they commonly occur in quartz veins

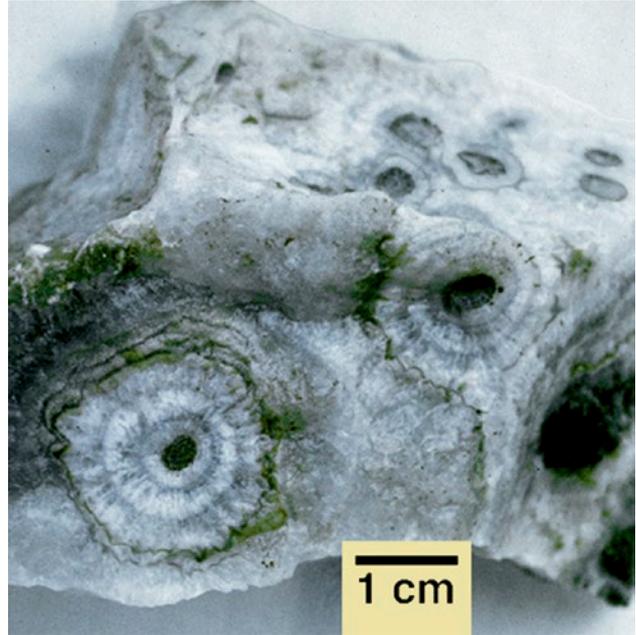


Figure 45. Orbicular spherulites occur in vein quartz from the Golden Plateau Mine at Cracow in Queensland. Concentric zones of radial quartz crystals surround central orbicular cores which are richer in chlorite. These concretionary structures depend on syneresis in the polymeric silicic acid precursor and the radial crystallisation pattern is typical of the outgrowth round nuclei in gels.

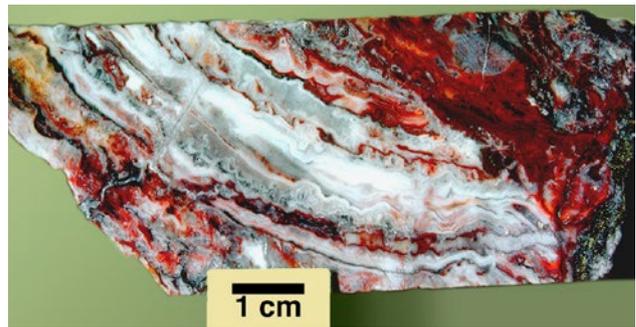


Figure 46. Colloform banding in quartz veins sometimes occupies the whole vein space as in this example from the Abra prospect at Jillararra, west of Mt Morgan in WA. Some post depositional oozy movement can be seen between the bands and towards the left a small dark stylolite-like vein has a pearl-grey branch veinlet outlined by pale silicified margins as it passes up through the colloform layers.

and mineral lodes. In all these cases they reflect the condensation and crystallisation of the original gelatinous precursor. This formerly filled the whole space but on condensation from the 'rind' or outer surface the centres reduce to very watery gels or water pockets (still found in some geodes) from which the remaining

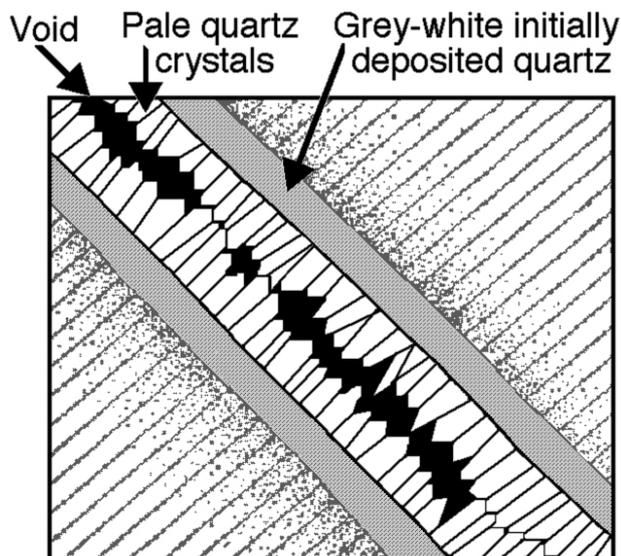


Figure 47. A typical pattern of druse cavities in a quartz vein illustrates how the polymeric silica initially silicifies wall rocks and fills the whole vein space. It then contracts to central watery silica gel into which the large quartz crystals grow until essentially water or salt water is left in the cavities.

silica crystallises in coarse prismatic crystals (see Figure 26).

A similar condensation and crystallisation pattern (usually outward from the wall of the vein) is found in many druse cavities and vughs, lines of cavities, and comb structures in quartz veins (Figures 43 and 47). This reflects the gel condensation and crystallisation of the original silica gel precursor of the vein so that it can also suspend heavy fragments (as in Figure 29 on page 58).

CONCLUSIONS FROM PART 1

The mobile forms of natural silica are the oligomeric silicic acids and short chain polymers. Depending on conditions of pH and other salts present, these tend to establish equilibrium by slow diffusion in pore water and through veins and openings. The monomer $\text{Si}(\text{OH})_4$ is the smallest neutral hydrated form of silica and these molecules can diffuse through the finest pore spaces, gel meshwork, or porous material. Any reaction that removes monomeric silicic acid from the fluid phase creates a diffusion gradient that in time provides the infilling silica to effect replacement or to complete crystallisation.

The observations and diagrams illustrated in Part 1 and in Elliston⁹, 2017, provide completely conclusive evidence that natural crystalline quartz in rocks, quartz veins and mineral deposits has crystallised from poly-

meric silica gel precursors. Exceptions are sandstones, quartzites, gravel beds and conglomerates but these are silicified or 'cemented' to hard erosion resistant rocks by the mobile forms of natural polymeric silica.

Diffusion of monomeric and oligomeric silica 'densifies' and hardens chert, jasper, flint, chalcedony, agate, etc. Quartz in veins and mineral lodes and in accretions in porphyritic, metamorphic and granitic rocks crystallises from gelatinous polymeric precursors.

Part 2 will present further evidence of the features, behaviour and crystallisation of quartz in veins. These provide further support for the conclusions from Part 1 and for the new and revolutionary conclusions from the industrial research programs recorded in Elliston⁹, 2017.

GLOSSARY

Accretion: is rapid formation of clusters of similar shaped particles to form 'close packed' and pre-ordered aggregations at net lower surface energy in any remobilized concentrated fluid paste containing colloids. Crystallisation of these pre-ordered aggregates occurs subsequently to then form a 'porphyroblastic' texture where the large crystals are set in a finer grained matrix of crystallised sedimentary material.

Adsorption: is the adherence or fixation on a surface (usually but not necessarily a colloid because of the enormous area, surface energy, and charge) of an ion or charged particle. The uptake by a surface of a solute or dispersion can occur by electrostatic, dipolar, quadrupolar, linkages or hydrogen bonding, etc. Where a chemical linkage is involved, the surface-controlled reaction is called chemisorption. The dispersed ions and charged particles compete for adsorption sites on all available surfaces. Changes in concentration, pH, in the availability of surfaces, and in the permeability (spacing of the meshwork through which the ions and particles can diffuse) often have quite marked effects in exchanging and replacing surface adsorbed species.

Aggregate: refers to a mass or body of any sub-units such as smaller gelatinous accretions or concretions. These can crystallise as a mosaic of small interlocking crystals, as a composite of complexly intergrown crystals, or in optical continuity as a single ovoidal crystal. Rounded or irregular zones and patches of granular sediment or matrix cemented by infill concretion have also been referred to as aggregates.

Concretion: this 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 medi-

um in which the particles are diffusing. A concretion may be homogeneous, being self-nucleated, homogeneous but nucleated on a foreign body, or heterogeneous (i.e. banded) with or without a specific nucleus. The active process of concretion depends on colloidal particles individually diffusing towards the precipitating surface represented by the boundary of a higher density gel aggregate with the less dense surrounding medium through which the particles are diffusing. Concretion could be considered to represent “adsorption” of ions or colloidal sol particles onto a growing nucleus, and finally onto a growing macroscopic aggregate of particles or a denser gel surface. Removal of such particles from dispersion by precipitation at a nucleus or at an interface between random open meshwork gel and denser ordered gel creates a diffusion gradient (fewer particles in that vicinity). To equalise the concentration, other particles under Brownian motion arrive in turn to precipitate (adsorb) and accumulate on the surface.

Crystal growth: requires particles to move to the surface - Removal of a mobile species from dispersion in the gel by its crystallisation creates a diffusion gradient towards the crystal surface. Henisch¹³ (p. 51) notes that convection currents are suppressed in gelatinous media and therefore movement must be essentially by diffusion but a very important function of the gel media is also to suppress nucleation. Without growth on many closely spaced competing nuclei, the faces of crystals supported in the gel medium are supplied by a steady diffusion of particles or ions so that large and well formed-crystals are able to develop.

Crystal lattice: describes the stable meshwork of chemical bonds that hold the atoms of a crystal together in an ordered repetitive pattern of unit cells so that the compound that has crystallised achieves a low energy state.

Crystallisation of feldspar: a number of natural clays in close packed aggregates react spontaneously with alkali metal ions and monomeric silica to feldspar and water with the liberation of heat. Feldspathoids are sometimes formed as an intermediate product. Reactions are described on page 214 of Elliston⁹, 2017.

Crystallisation of quartz: most natural quartz has crystallised from compact polymeric species to which a further and continuing supply of the monomer is available. Some details are set out on pages 10-13, pages 21-26, pages 126-130, and pages 215-216 of Elliston⁹, 2017.

Gel: a gel is essentially a semi-solid meshwork of fine particles coagulated or flocculated by the inter-tangling of long chained polymers where the particles are linked to form a visco-elastic permeable solid by interaction between electric charges on their surfaces. Synthetic gels of pure clay, silica gel, gelatin, agar, etc. contain

similar particles or macromolecules but natural gelatinous sediments are complex mixtures of charged particles having a wide range of sizes, shapes, and compositions. Hydrolysis reduces most particles to the colloidal size range but these can form a matrix to larger residual grains. Gelatinous ferric hydroxide, hydroxy carbonates, hydrated organic matter and silica gel occur in most sediment and sometimes as major constituents. However, the most common particles in pelitic sediments are clays, amorphous silica, and hydrous ferromagnesian minerals. These common particles are shaped as platelets, spheres, and rods respectively and in the “gelled” or coagulated condition they link together to form ‘house of cards’ or ‘book-house’ structures, ‘strings of beads’, and ‘scaffold-like’ structures of rods. Natural sediment can be thought of as these several types of structures randomly intermeshed and securely cross-linked together by the mutual satisfaction of coulombic charge sites and by van der Waal’s attractive forces where particles are appropriately packed or close enough. It is not surprising that wet sediments have shear strength!

Semi-solid gelatinous sediments are thixotropic and have a definite yield value (Bingham yield point). The strength of the sediment fabric is very sensitive to water content and to the presence of flocculating or deflocculating agents. Liquefaction is isothermal and mechanically induced but the linkages between particles tend to re-form during viscous flow of the mud. The systems are “self-healing” but there is a time delay in reverting to the original gel strength called hysteresis. Cross-links are more readily broken at higher temperatures. Transition from an elastic gel to a liquid of relatively lower viscosity occurs revertably over a narrow temperature range. The more concentrated gels require higher temperatures but the thermal energy “softens” the paste and makes it easier to disrupt the fabric of particle linkages. Gels melt!

Helmholtz double layer: in an aqueous electrolyte solution in the vicinity of a charged surface the aqueous phase is divided into four regions of distinct dielectric behaviour. The innermost region) consists of preferentially oriented water molecules in contact with the solid surface and where specific ions are adsorbed without their hydration shells. This is called the inner Helmholtz layer. The region further from the surface (β in Figure 1.7 in Elliston⁹, 2017) contains both free water molecules and molecules attached to hydrated ions. This is called the outer Helmholtz layer and is defined by the by the closest approach that a fully hydrated charged ion can make to the solid – liquid interface. Further out from the surface the concentration of counter-ions (having a charge of opposite sign to the surface) decreases with increasing distance in the Gouy-Chapman diffuse layer.

The outer and inner Helmholtz layers are referred to as the Helmholtz double layer.

Hydrated silica polymers: a diagrammatic representation of the polymerisation behavior of silicic acid is shown in Figure 5.

Mobilisation: means the liquefaction of a body of semi-consolidated sediment or other particulate material usually by earthquake shock or gravity sliding downslope.

Rheopexy: is the accelerated resetting to a gel condition in a flowing colloidal dispersion subjected to shear by laminar flow of a thick paste. Thixotropic liquids may rapidly revert to a higher viscosity condition when linkages establishing between particles throughout the flowing mass overcome the momentum of the moving mass. This “instant re-freezing” preserves flow foliation, the shape and form of intrusions, suspends fragments, etc.

Silica: Ordinary sand or crystalline quartz (SiO_2).

Silica Polymers, where do all the natural silica polymers come from? Quartz is not soluble in water including normal ground water and stream water in the cycle of erosion. It is transported by the streams and rivers as gravel and sand grains and generated by coastal erosion 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 conditions (seawater pH 7.9 to 8.3) by a process called “proton promoted dissolution” (Iler², 1979, fig. 1.11.) This is shown diagrammatically as: -

Molecular dispersion from crystalline silica in water as $\text{Si}(\text{OH})_4$ 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 $\text{Si}(\text{OH})_4$ molecules polymerise to short chain polymeric silicic acids called “oligomers”.

Silicic Acid: See Figures 1 and 2 and captions.

Where do all the natural silica polymers come from? The answer to this is that there are immense quantities of sand and silicates soaking for thousands of

years in even greater quantities of slightly alkaline sea water. Reversible chemical reactions are driven by the quantities of reacting substances. In the late stages of diagenesis when natural sediments are losing water, the hydration reactions reverse and siloxane linkages predominate.

Silanol: Is a fully hydrated form of silicic acid that can condense to a direct chemical silicon-oxygen-silicon linkage by loss of a water molecule.



Siloxane: the direct silicon-oxygen-silicon chemical linkage is called siloxane.

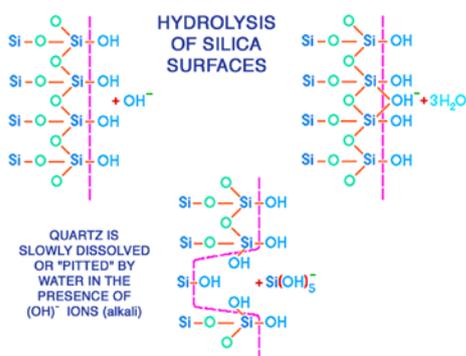
Sol: is a homogeneous suspension or dispersion of colloidal particles in a liquid or gas. In the glossary of geology, a sol is also defined as a completely mobile mud that is in a more fluid form than a gel.

Small particle systems: are materials or substances made up of small particles. They are independent of the chemical composition of the particles but the very small size of the component particles means that the surface charge enables their interaction with other charged particles and ions in the pore fluids surrounding them. Mud is “sticky” because the particles cling to each other and to surfaces they come in contact with. Examples of small particle systems are mud, clay, silica gel, thick paints, food colloids (like yoghurt, cream, soup, etc.).

Surface charge: See Figures 3 and 4 and captions and description in associated text.

Surface chemistry: is the study of the special chemistry that is related to the solid-water interface. Surface chemistry and colloid chemistry are closely interrelated because the behaviour of colloidal particles is dependent on the properties of the very large surfaces they present to the solvent in relation to their very small volume. The solvent, ions, complexes, and other charged particles interact with all surfaces but are especially important in their interactions with colloidal particles.

Surface energy: is the difference in energy per unit area between the surface of a given crystal lattice or substance and the energy of the same number of atoms (comprising the unit area) situated within the bulk of the crystal or substance. Surface energy is clearly dependent on the atomic geometry of the atoms exposed within the unit area of surface. The atoms exposed at the surface are able to interact with particles, ions, solvent, or other substances. They have ‘dangling bonds’ or charge that can compensate each other, hydrate, adsorb surface species, or form new chemical compounds. Bonds or linkages of atoms comprising a comparable



area within the crystal or substance are in equilibrium with those surrounding them.

Syneresis: is the spontaneous aging or contraction of a gel meshwork within itself by the establishment of a greater density of cross-linkages and elimination of water. The particles or particle-chains achieve greater co-ordination. The total surface energy is lowered, and the internal surface and adsorptive capacity are reduced. The contraction and greater gel density causes shrinkage cracks or a pattern of holes or channels (like those in cheese) which is independent of whether or not the gel is immersed in water. In syneresis the particles move closer together under the influence of van der Waal's attractive forces so that the less dense, sparse, weak "watery" gels tend to be less or non-synerectic. The crystalline state is the low energy state of matter.

Thixotropy: is the isothermal reversible re-liquefaction of a gel or coagulated sol. Thixotropy is due to mechanical shock or shear which disrupts the gel particle linkages allowing the colloids of the system to revert to a dispersed sol or more fluid gel at the same fluid content. This isothermal gel to sol or to more-fluid-gel transformation is reversible and repeatable. Thixotropy is mainly induced by shock. A short sharp oscillation throughout the gelatinous mass is more effective in destroying all, or sufficient of, the interparticle linkages at the one time so that the meshwork structure will collapse and the material revert to a fluid. Differential liquefaction depending on hydration (differing Bingham yield points) of different colloidal components allows separation of more mobile hydrous materials which can then simply flow out of the disturbed mixture.

Rheopexy: is the accelerated resetting to a gel condition in a flowing colloidal dispersion subjected to shear by laminar flow of a thick paste. Thixotropic liquids may rapidly revert to a higher viscosity condition when linkages establishing between particles throughout the flowing mass overcome the momentum of the moving mass. This "instant re-freezing" preserves flow foliation, the shape and form of intrusions, suspends fragments, etc.

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