



Research Article

## Hydration of silica and its role in the formation of quartz veins - Part 2

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**Abstract.** The aqueous chemistry of silica and the formation of abundant polymeric silica species in natural sediment accumulations is set out in Part 1. Part 2 continues to describe the amorphous silica in sediments and presents more evidence for the formation of quartz veins from silica gels. The physical chemistry for the formation of oolites in quartz veins, pygmatic folding of quartz veins, the enhanced growth of crystals in quartz veins, the precipitation of gold in quartz and the mechanism for replacement or metasomatism by quartz (silicification) are detailed. Current physical chemistry applies not only to precursor silica gel but also to the hydrous precursors of other crystalline rock minerals such as clays, mica, hydrous ferromagnesian minerals and mineral deposits. “The Origin of Rocks and Mineral Deposits - using current physical chemistry of small particle systems” provides a new basis for understanding geological phenomena. This has now been published in Elliston<sup>1</sup> 2017 (Connor Court, Brisbane, ISBN 978-1-925501-36-0).

Part 2 continues the illustrations and diagrams numbered in sequence from Part 1 and the conclusions relate to both parts of this article.

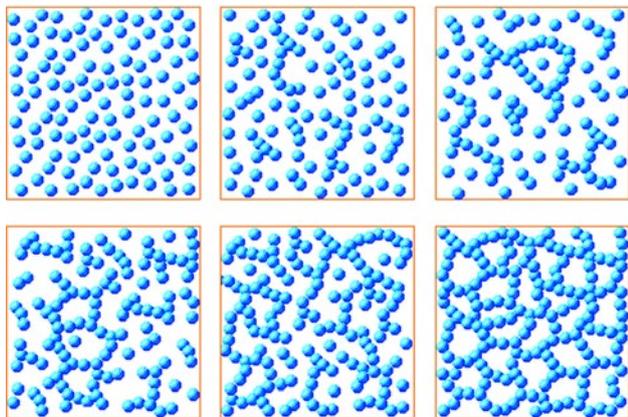
**Keywords.** Accretion, concretion, charged particle, pygmatic folds, precursor mineral, enhanced crystal growth, metasomatism, porphyroid, granite.

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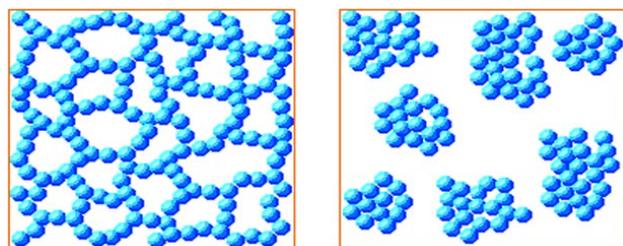
### THE NATURE OF SILICA IN VEINS

Dispersions of monomer are at first stable but as polymer formation develops the monomer is more rapidly consumed. The movement of monomeric silica dispersion tends, over time, to transfer significant quantities of quartz. The old concept of quartz “sweating out of” the host granites or sediments finds a complete explanation in what is now known of the properties and behaviour of polymeric silicic acids.

The dispersions or gels (accumulating in the precursor quartz veins) of poly silicic acids are unstable in the sense that the particles grow in size and aggregate into denser precipitate, or gels (Figure 48). It should be noted that, when substantial salt concentrations and alkaline conditions prevail, the gelling process does not produce a homogeneous gel. The silica usually appears



**Figure 48.** The gelling process involves formation of an increasing amount of the sol being converted to microgel with increasing viscosity until it solidifies. This “solidification” in the first instance is achieved when there is sufficient three-dimensional cross linking to entrap the solvent in pockets. Initially it is a wet weak watery gel which becomes essentially a dispersion of solvent in “spongy” solid. A gel is by definition a visco-elastic solid with all linked parts of the meshwork immobilised in relation to all other linked parts. It is “sensitive” to disruption by shock or shear (thixotropic). [From Iler, 1979, p. 232]

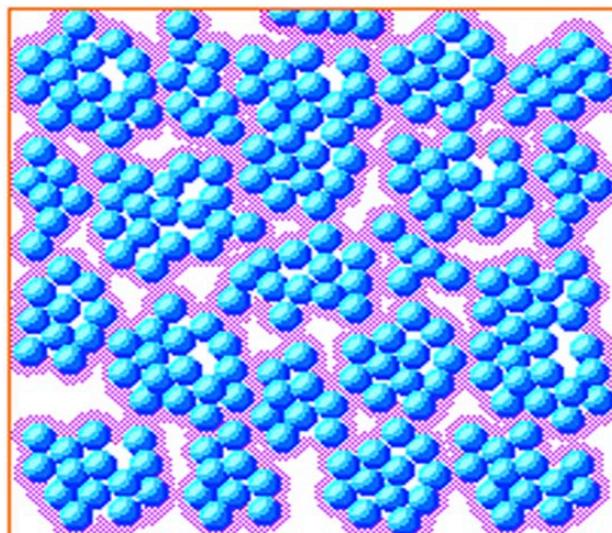


**Figure 49.** This diagram is a two-dimensional representation of the difference between a three-dimensional gel meshwork with its cross-linked chains of silica spheres and a precipitate of three-dimensional clusters of colloidal silica globules.

as a white precipitate or a white opaque gel, owing to partial precipitation before gel formation.

Figure 49 indicates the difference between gel and precipitate of the primary particles which are about 3 to 6 nm in natural silica gels. Due to the presence of salt and higher pH (most pore fluids have a pH about 7.5 to 8.2) the white silica gels of the quartz vein precursors are thought to be partly precipitated to aggregates of around 30 nm which “gel” to form chains of these spheres.

Maximum thixotropic sensitivity occurs when such small three-dimensional aggregates link together into a larger network extending through the liquid medium (Figure 50). Aggregates link together through hydrophobic bonding and such linkages are readily broken by



**Figure 50.** Maximum thickening effect and thixotropy are produced by small aggregates linking together into an extensive three-dimensional gel network throughout the liquid medium. Natural silica gel occurring as the precursor to vein quartz is thought to be partly precipitated (white colour), thixotropic, and dense enough to support mineral and wall rock fragments. In most cases it is probably of this type. [From Iler, 1979, p. 591]

shearing forces and readily re-established when the mass is at rest. This would apply to the precursor gel stage of quartz vein development where the vein material is highly thixotropic.

#### *The amorphous silica in sediments*

The gel structure of amorphous silica in sediments is rather uncertain. Under the conditions of most newly deposited marine sediments where pH is around 7.8 to 8.2 with salts present, chaining of silica spheres would probably involve particles about 1 nm in size. While these conditions would favour stable polymeric silica, the chained particles are too small to be seen with an electron microscope.

It is also not clear how the small spherical silica particles would interact, or have their normal ‘chained meshwork’ structure modified by the presence of other charged sediment particles. Just as the behaviour of ionic species in the pores of a mud are severely modified by their interaction with charged surfaces, so also is the behaviour of charged particles.

Silica spheres under natural conditions are negatively charged and at about 1 nm in size they would be expected to interact with the positively charged edges of clay platelets. For montmorillonite these platelets are

about 30 to 50 nm in size but for illites the platelets can be 1000 to 1500 nm.

The 'gel structure' of silica in natural muds cannot be considered as separate from that of the sediment particles as a whole unless the sediment is essentially silica such as chert, jasper, or one of the deep marine siliceous oozes. A further complication is the fact that much of the hydrated silica in sediments is derived from the hydrolytic degradation of clays. Progression of the 'zip fastener' reaction to complete hydrolysis yields sheet-like networks of silica gel, residual tetrahedral layers or fragments of them, from the hydrolysis of clays, ferromagnesian silicates and quartz (in slightly alkaline sea water).

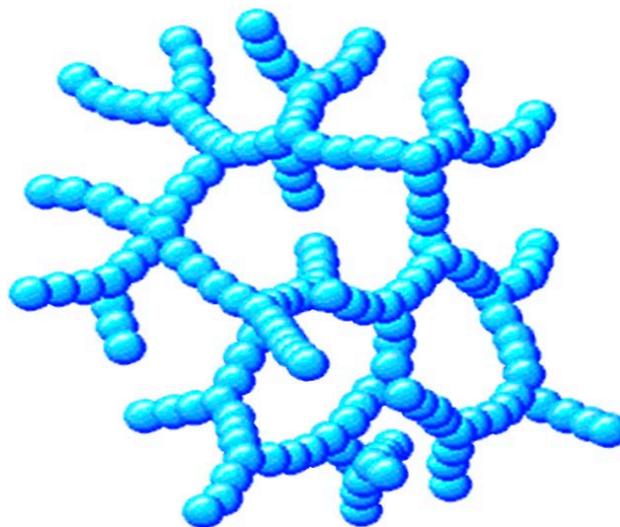
These are surfactants and as polyelectrolytes, that is polymers whose repeating units are ionised or ionisable in water, they are strongly surface active. This polymeric form of silica usually adsorbs on oppositely charged surfaces but it may also adsorb on neutral or negatively charged surfaces. An entropy driving force can enable one adsorbing polymer to free to solution many previously bound water-molecules. This yields a net increase in the number of kinetic units in the system. Much of the amorphous silica in natural muds can therefore be regarded as 'coating' the other particles.

#### *The chemical equilibria of silica in sediments*

Silica is also in chemical equilibrium with the other constituents of the sediment. The hydrolysis of clays, the 'zip fastener' reaction, is reversible and depends on the concentration of one of the reactants, namely water. If water is in excess, under most diagenetic conditions the clays will continue to slowly hydrolyse. Without shear, when water is removed from the system, the tetrahedral and octahedral sheets of hydrolysed clay platelets re-combine to restore the original clay structure. Iler<sup>2</sup> (1979, p.193) points out that over a long period of time monomeric silica,  $\text{Si}(\text{OH})_4$ , reacts with  $\text{Al}^{3+}$  ions at 25°C to form colloidal aluminium silicate of halloysite composition:



There is no question that where the amorphous silica constitutes all or most of the sediment such as in a chert bed, quartzite, or siliceous ooze, the gel structure is a chained meshwork of spherical particles. Figure 51 from Iler<sup>2</sup> (1979, p. 235) indicates the type of meshwork packing of spheres when they are large enough to be observed by electron microscopy. In a sediment they are probably more like those illustrated in Part 1 that show the way they aggregate through micro-accretions



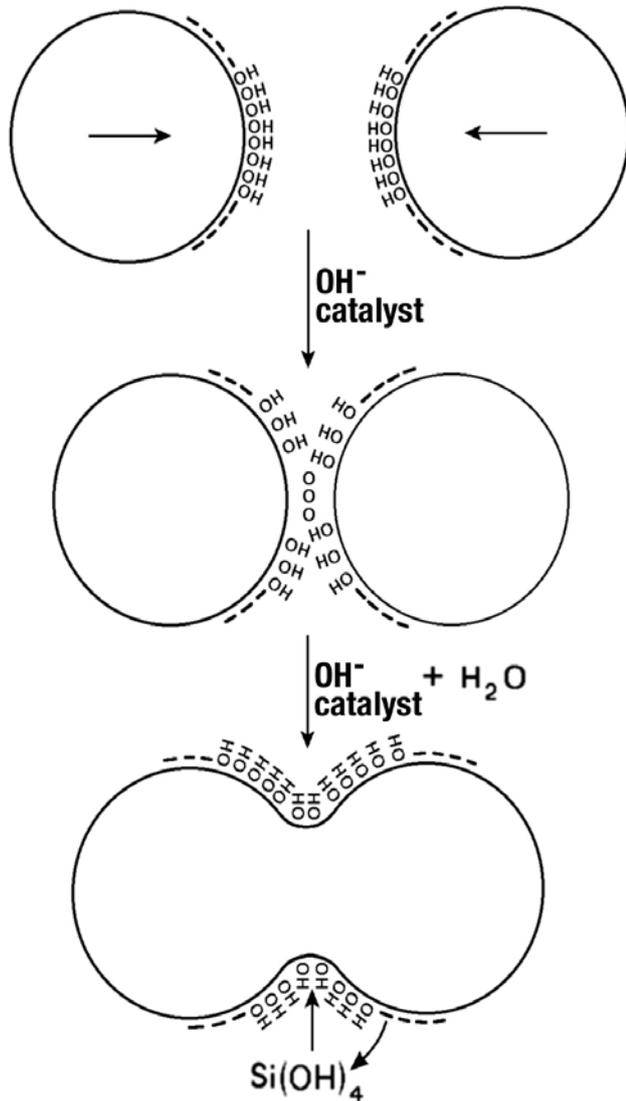
**Figure 51.** In natural silica gels the density and structure vary by a number of different kinds of packing in the meshwork arrangement of the particle chains. In a more open regular meshwork such as that illustrated here, the number of particles linked to a given particle can vary. In this example each joining sphere is touched by 3 or 4 surrounding spheres but denser linking arrangements are common.

to more stable 'close-packed' macro-aggregates when the sediment is re-liquefied and involved in flow. The extremely small size of the ultimate particles in this form of silica must be kept in mind.

#### *The 'aging' of silica gels in sediments*

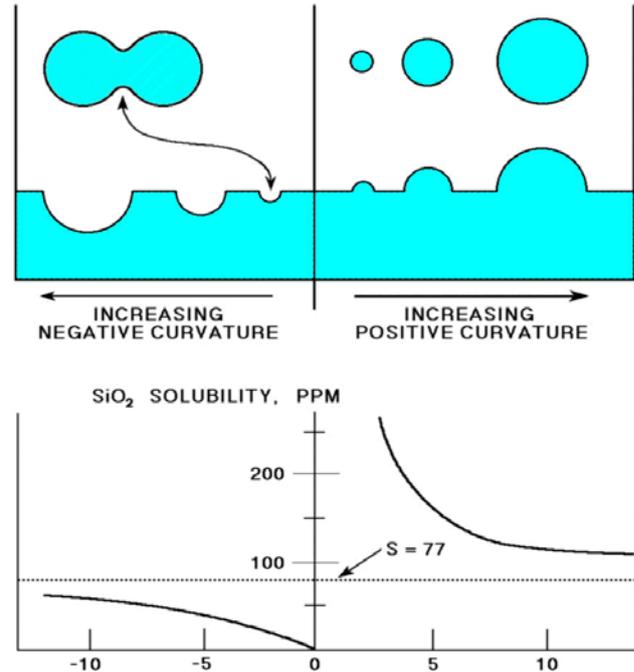
Iler<sup>2</sup> (1979, pp. 224-230) points out that the silicic acid "balls" or particles chaining together to form a gel can be linked by inter-particle siloxane bonds when catalysed by a base (Figure 52). Also, the laws of solubility apply, whereby according to the Ostwald-Freundlich equation, solubility at the negative radius of curvature (Figure 53), in the neck between contacting spheres, is less than elsewhere on the spheres. At equilibrium conditions with the monomer, and as the gel ages, the polymerisation tends to increase in the crevice at the point of contact between the spheres while solution would occur from the protuberant portions of the sphere as in Figure 54. Electron microscope studies of the fine porous silica gel (Sugar and Guba<sup>3</sup>, 1954) have shown that the structure is indeed made up of a thread-like fibre network, but the fibres were made up of chains of spheres as in Figure 55.

The "chaining" arises because new charged particles from dispersion are added to a doublet in alignment or to the end of a chain. When added in this position a new



**Figure 52.** When there is little or no charge repulsion between silica particles such that they can come together to form chains (linked by van der Waals' attraction), chemical siloxane bonds, catalysed by the presence of hydroxyl ions, also develop as indicated. Once bonded the particles grow together by diffusion and condensation of additional  $\text{Si}(\text{OH})_4$ . The resilience and strength of some silica gels is greatly increased when the chains of silica spheres are also chemically linked. [From Iler<sup>2</sup>, 1979, p. 224]

particle has only to overcome the repulsive force due to one of the particles it is joining. If it approaches from the side position, the other similarly charged particle or particles would contribute to the repulsion. It is therefore at the end position that the joining particle can first approach close enough for van der Waals attraction to exceed the coulombic repulsion.



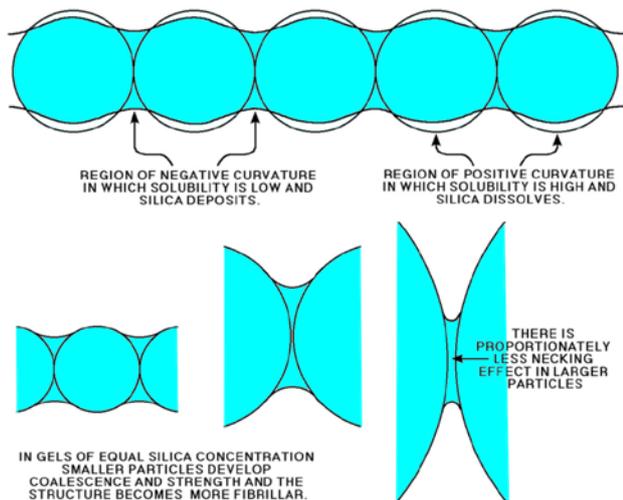
**Figure 53.** The solubility of silica varies inversely with the radius of curvature of the surface according to the Ostwald-Freundlich equation. The positive radii of curvature are shown as cross-sections of particles and as projections from a silica surface. Negative curvatures are shown as depressions or holes in a silica surface or in the crevice between two adhering particles. The solubility in ppm is indicated in the lower diagram. Two important practical effects are: (a) When very small particles are brought into the same suspension as larger ones, especially at high pH where  $\text{OH}^-$  ions catalyse solution and deposition, small particles dissolve and larger ones grow. (b) At the point of contact between two flocculated colloidal silica particles in a chain where the radius of curvature is negative and small, the solubility is low and silica dissolves from the particle surfaces to be deposited at the point of contact. (From Iler<sup>2</sup>, 1979, p50)

#### MORE EVIDENCE FOR QUARTZ VEINS FORMING FROM SILICA GELS

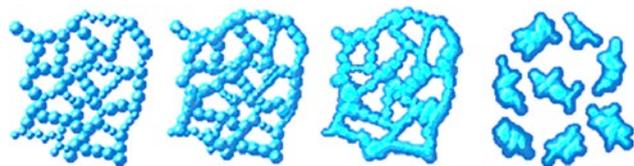
##### *Orbicular structures and oolites in quartz veins*

The wetter parts of jaspoidal lodes, quartz magnetite bodies, and quartz veins which crystallise from gelatinous precursors, may develop oolitic concretions during their gel stage. Spherical and globular structures are not very commonly found in quartz veins and siliceous lodes because, like colloform banding, injection or episodic re-mobilisation of the precursor lode materials usually destroy primary precipitation structures.

However, when siliceous oolites and orbicular structures are found in vein or mineral lode material they constitute an unequivocal indication of their development in a gelatinous medium by diffusion of hydrous



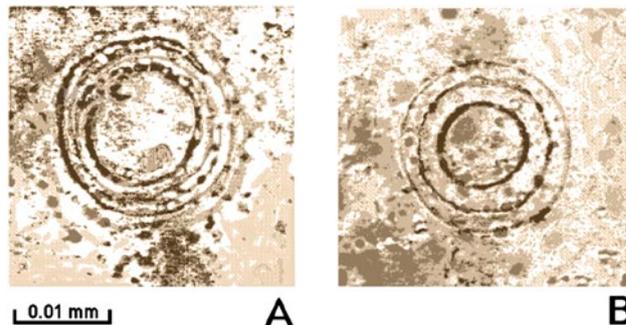
**Figure 54.** A chain of small particles is converted to a fibre or rod by the laws of solubility. Solubility at the negative radius of curvature of the neck between the spheres is less than elsewhere on the spheres so that, as the system tends to equilibrium, silica builds up in the region of the contacting spheres and "rounds off" protuberances. The effect is greater for smaller particle chains. [Adapted from Iler<sup>2</sup>, 1979, p. 230]



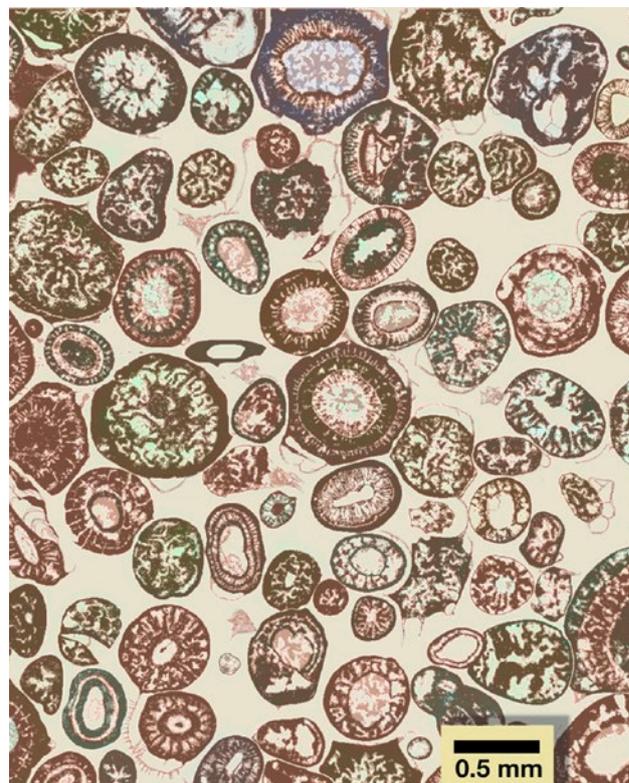
**Figure 55.** Stages in the aging of a gel are illustrated from the chaining of spheres and their greater coalescence, to the coarsened structure which results from drying or heating where the structure disintegrates to irregular rounded particles. [Adapted from Iler<sup>2</sup>, 1979, p. 530]

polymeric silica particles. The diffusion processes which give rise to oolites depend on the structure of precursor stage silica gel in the veins and diffusion of mobile particulate species within them. Having regard to the nature of the vein gels an occasional occurrence of oolites resulting from these simple diffusion processes would certainly be expected.

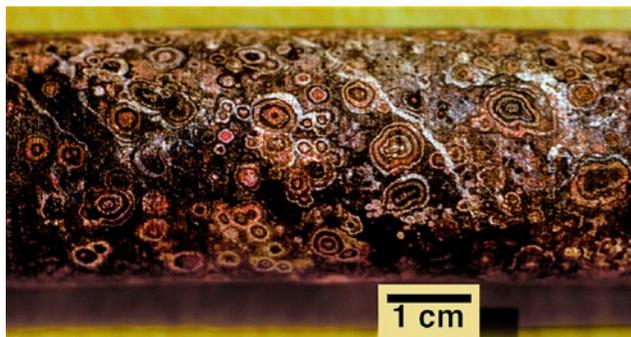
The precursor vein host and mobile species may be identical chemically yet quite different structurally (eg.  $\text{Si}(\text{OH})_4$  and silicic acid polymers). This is why it is quite possible to develop silica concretions in silica gel (as Lougheed's<sup>4</sup> microspheres in Figure 56), ferric hydroxide concretions or oolites in ferric hydroxide matrix (Lindgren<sup>5</sup>, 1933, p. 277; Carozzi<sup>6</sup>, 1960, p. 352), or calcite oolites in limestone or an essentially calcitic matrix as in Figure 57 of Lindgren's Short Creek oolites.



**Figure 56.** Examples of silica microspheres or concretions of silica in chert from the siderite-chert facies of the Gunflint Iron Formation, Kakabeka Falls, Ontario. These silica in silica concretions illustrated by Lougheed<sup>4</sup> (1983, p. 327) may be coated sparsely with micron-sized carbonate crystals (white) and carbon flecks (spots and dusting).



**Figure 57.** Calcite oolites in a calcitic matrix further emphasise the point that gelatinous oolite precursors do not have to be different in composition from the gelatinous lime muds in which they form. They differ in precursor gel structure in that the oolitic nuclei must be 'close packed' and synergetic while the host mud is an open-meshwork porous gel through which very small particles can diffuse. These oolites from Short Creek, Missouri, (Lindgren<sup>5</sup>, 1933, p. 267) show the evidence of their soft gelatinous precursors in the mutual indentation and distortion, fracture fragments, composites, overgrowths, and syneresis shrinkage patterns.



**Figure 58.** Orbicular quartz-magnetite from drill core through the lower part of the Peko diapiric ore pipe, Tennant Creek. The oolitic texture indicates that precipitation of precursor lepidocrocite and polymeric silica round synerectic nuclei is a sol-gel transition rather than a chemical reaction or from supersaturated solution. Clearer quartz veins which cut the oolites reflect the soft particulate nature of the precursors.

Similarly, because the ‘colloidal processes’ by which concretions develop are not dependent on the chemistry, mixed oolites with successive rims of different substances are commonly developed as in Figure 58.

#### *Some examples of siliceous oolites in veins and lodes*

The concretions of silica in chert illustrated by Loughheed<sup>4</sup> in Figure 56 are significant in showing that the development of the concentric spheres is a physical or structural change in the polymeric precursor particles and not chemical. The hydrous silica particles (“little balls”) do not initially react with each other chemically but they deposit and build up round a synerectic nucleus from very small sol particles dispersed in the surrounding chert precursor to the ‘close packed’ dense gel of the concretion. It is a sol to gel transition at the precursor stage whereas the chemical reaction is the subsequent loss of water on crystallisation.

After condensation and lithification of the whole formation, these concretions could not be seen at all if it were not for the small carbonate crystals and carbon flecks which coated the former surfaces of these denser globules within the gel.

Radiating quartz crystals have grown radially round dawsonite needles in a large impure quartz vein at Mt. Gee in the Flinders Ranges in South Australia as shown in Figure 59. The dawsonite  $[\text{Na}_3\text{Al}(\text{CO}_3)_3 \cdot 2\text{Al}(\text{OH})_3]$  apparently grew as slender needles supported in the soft precursor silica gel of the vein so that subsequent quartz crystallisation was nucleated from their rod-like surfaces. Concentric banding or tubular zones equidistant from dawsonite needles (Figure 60) reflect the concre-

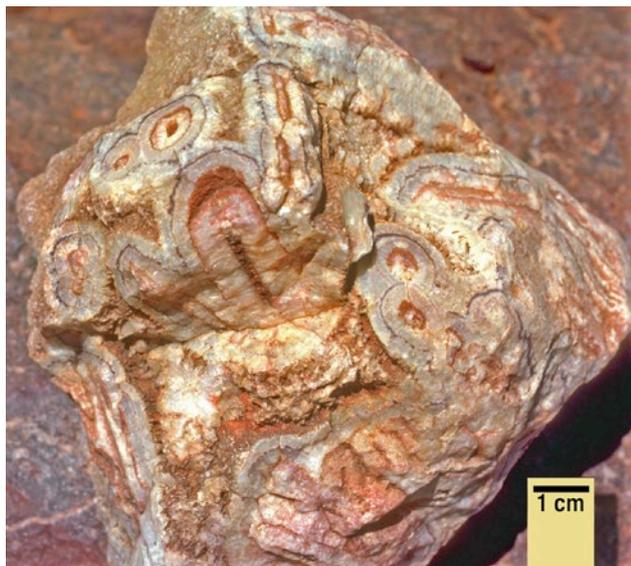


**Figure 59.** At the precursor stage, denser concretionary polymeric silica precipitated around dawsonite needles grown in the pre-crystalline silica gel. The denser concretionary silica subsequently crystallised to form a radiating spherulitic pattern of crystallisation which now forms tubular shaped clusters of radiating fine crystals round the nucleating dawsonite needles. The concentric banding or zones probably represent concretionary desorption of impurities (Liesegang-type) prior to crystallisation. The outcrop is at Mt. Gee in the Flinders Ranges, SA.

tionary banding similar to the carbon dusted zones in Figure 56 or the chlorite bands in Part 1, Figure 45.

Much of the large pyritic gold-copper lode at Mt. Morgan in Queensland was highly siliceous. Some of this silica was ordinary white vein quartz but most of it was a dull grey earthy quartzite-looking silica. Apart from the abundant sulphides it was discoloured with traces of impurities such as kaolinite, sericite, chlorite, or haematite.

One of the early phases of this mineralisation in the lode system is a massive injection of rather impure cherty grey silica. This early emplacement of siliceous material could be regarded as a “dirty early” quartz vein although,

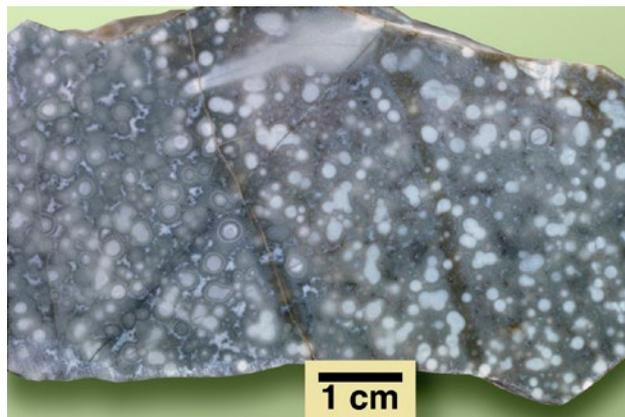


**Figure 60.** Concretionary polymeric silica at the precursor stage has formed round dawsonite needles grown in silica gel. It has subsequently crystallised in a radiating spherulite-like pattern to form interfering coarse tube-like clusters of fine radiating quartz crystals along the slender dawsonite ‘needles’ from which they nucleated. This vein quartz is from Mt. Gee in the Flinders Ranges, SA.

like many such early emplacements in highly hydrous lode systems, it is rather bulbous and irregular in form and it is re-invaded by several phases of later mineralisation and later vein networks. However, the early impure grey silica intrusion clearly had a silica gel precursor because it is oolitic (Figure 61). The overlapping and merging concretions which are abundantly developed, resulted in the nickname “bird’s eye” porphyry.

Its concretionary texture reflects the fact that this impure silica gel precursor was re-mobilised into the vein or body in which it is found. The flow of the liquefied precursor generated small denser random nuclei. In the subsequent ‘static’ stage, when the permeable gelatinous matrix material had again ‘gelled’, these synerectic close-packed micro-accretions form the nuclei for concretionary overgrowth. Concretion is by diffusion of particles individually to the surface of the nuclei where they precipitate to become part of each close-packed concretionary mass. Similar ‘dirty’ grey quartz to this concretionary ‘elvan’ is also illustrated as the matrix of the chloritic fragment breccia in Part 1, Figure 37.

In another more jaspoidal variety of this early mobilised silica gel at Mount Morgan, the oolites are rather larger and some of the concentric banding where it was outgrown in a scalloped pattern, was called locally



**Figure 61.** An irregular bulbous intrusion of impure cherty grey silica is part of the Mt. Morgan Mine lode system in Queensland. It has an “orbicular” or oolitic texture formed by concretion round small accretionary (denser synerectic) nuclei which were developed during intrusion and flow of the precursor polymeric silica. The texture positively indicates the silica gel precursor of this siliceous lode or ‘elvan’.

“hurgledurgelite” (because at the mine there was some uncertainty as to its origin).

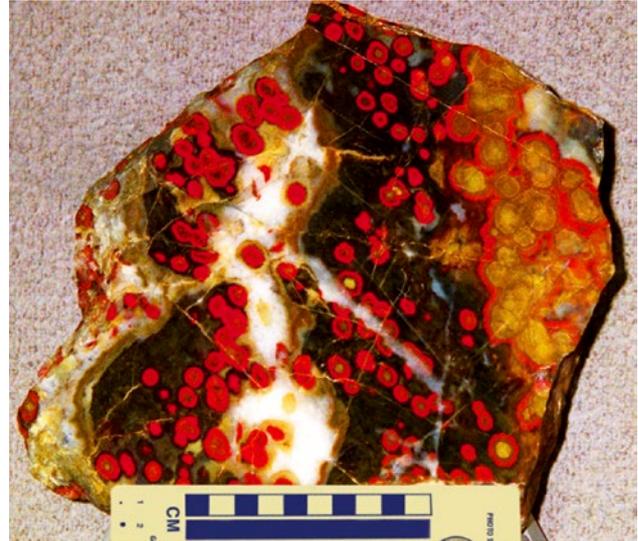
Some of the larger concretions in this marginal jaspoidal chert body (Figure 62) have grown over and incorporated smaller ones. This is common in colloidal gels where the concretion is essentially the same composition as the less dense gel in which it is developing. These large round ‘blobs’ of synerectic silica show little or no concentric internal banding indicating that their growth involved a degree of infill or incorporation of their silica gel matrix rather than its displacement. Displacive concretion occurs when the growing ‘close-packed’ gel mass is stronger than its enclosing less dense matrix and this is usually the case for mixed layer oolites or when other colloids are involved.

A siliceous lode cored in drilling at the Abra prospect at Jillawara, Western Australia, contains jasper concretions (Figure 63). Rather complex small oolites and their fracture fragments occur in early quartz-jasper vein material and are cut by later stylolitic quartz veinlets. These jasper oolites have all the features of full-scale larger concretions which show successive rims, mutual indentation, complex cores, plastic and fractured ovoids, regrowth on fragments, folding and unconformities in the rim patterns, etc. Their development clearly indicates that the matrix vein material was originally a particulate polymeric silica gel precursor.

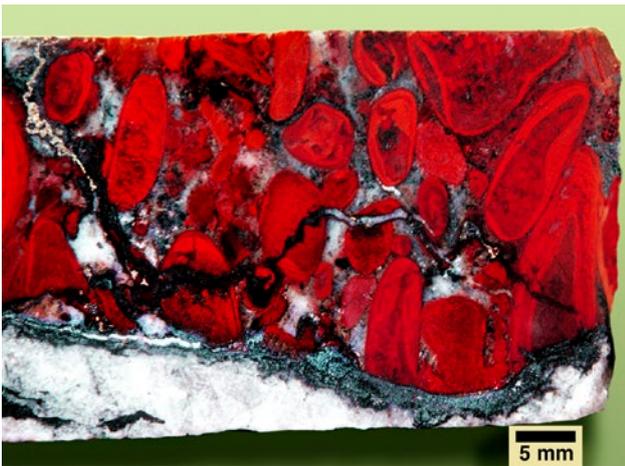
The Smithsonian Institute displays a piece of a massive dark siliceous lode from near Gilroy in California which contains abundant jasper oolites (Figure 64). The highly hydrated lode in which the oolites developed has



**Figure 62.** Some of the larger concretions in the Mt. Morgan siliceous 'elvan' grow over and incorporate smaller ones. Where the concretion has essentially the same composition as the less dense gel medium in which it is developing, the growth of the 'close-packed' nodule is often as much by infill and incorporation of the host silica gel matrix rather than by its displacement (like bedding preserved through concretions in sediments). Syneresis exudes impurities to the rims.



**Figure 64.** Later diagenetic colloidal silica branching into veinlets, fills syneresis cavities in an oolitic jasper lode. Earlier khaki chert rims the syneresis cavities in a similar manner to its occurrence in geodes and it fills veinlets which cut the soft precursor oolites. The jaspers, the chert, and the oolites undeniably indicate precursor silica gel. This Smithsonian Institute specimen is from near Gilroy, California, USA.



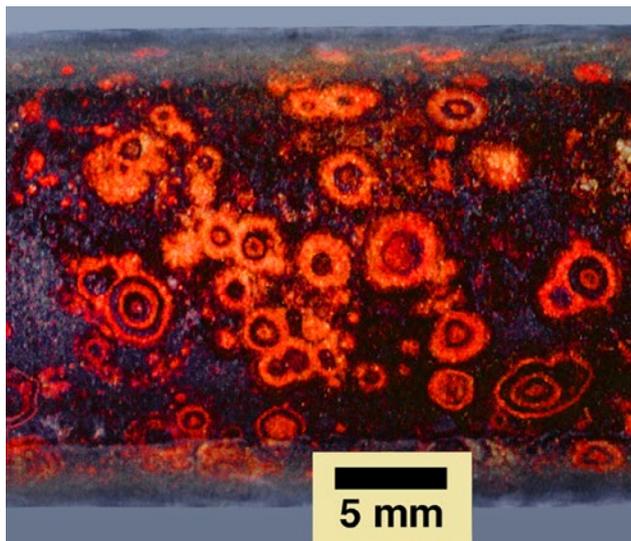
**Figure 63.** Brilliant jasper oolites occur in core through a quartz lode at the Abra Prospect, Jilawarra, W.A. Jasper is metacoloidal and a soft precursor stage of these overgrowths on accretionary siliceous nuclei is indicated by their plastic deformation, mutual indentation, and fragmentation. They are cut by later stylolitic quartz veinlets which meandered through the soft gelatinous silica precursors.

subsequently contracted and further white polymeric silica partly fills the syneresis cavities. Earlier khaki chert rims these cavities and some of it fills veinlets which cut the soft precursor oolites.

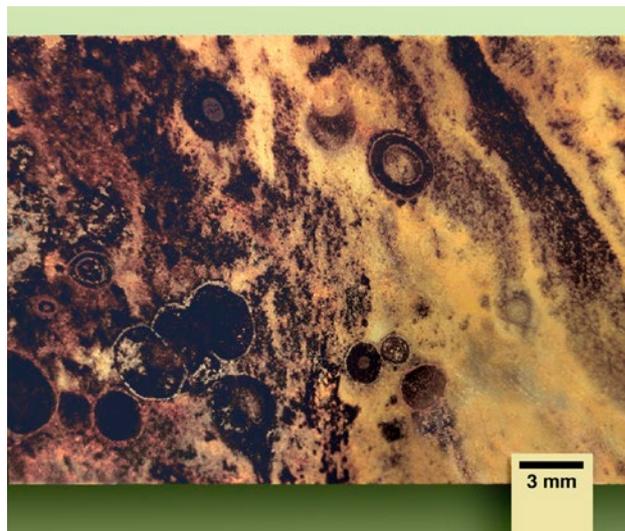
Studies of the Peko diapiric quartz-magnetite ore pipe some fifty years ago established conclusively that the quartz and magnetite of the main breccia body could not have been deposited from solution. The quartz magnetite is an intrusive, brecciated, and flow sheared mass which incorporates many fragments of the greywacke-shale wall rocks into which it intrudes. Some of these are several metres in size, rotated and unaltered with bedding still preserved. The massive quartz-magnetite must have been fluid at some stage in order to allow the blocks of included sediments to rotate and yet it had to 'set' quickly in order to suspend these blocks and the pieces of magnetite it contains like those in the Warrego ore pipe (Part 1, Figure 38) or the magnetite breccia pieces in the quartz lode at New Cobar Mine (Part 1, Figure 39).

The intrusive quartz-magnetite body with its central core of rich sulphide and gold mineralisation is itself auto-brecciated. It is too heavy (density 4.5) to have intruded as actual quartz-magnetite into the greywacke-shale sequence (density 2.7) and if the silica and iron had in fact been in hydrothermal solution together to form this deposit it should have contained or consisted of iron silicates rather than the respective oxides.

Evidence for colloidal precursors of the precipitated quartz, magnetite, and ore sulphides came from textures preserved in some of the auto-brecciated blocks and



**Figure 65.** Red jasper-magnetite oolites are found in the lower parts of the Peko diapiric quartz-magnetite ore breccia pipe at Tennant Creek, N.T. Composite oolites and some disruption of the rims reflect the soft nature of the precursor magnetite (lepidocrocite) and particulate colloidal silica. The texture and the metacoloidal jasper leave no doubt that this lode was emplaced as a precursor colloidal mass.



**Figure 66.** Jaspoidal chert-magnetite oolites are preserved in part of the Peko Mine main lode at Tennant Creek, NT. This section of the ore breccia pipe has not been disrupted by later re-mobilisation. Original colloform textures are often preserved in large rafts, or near the lode wall where later thixotropic re-liquefaction and intrusion of the ore pipe slurry has not affected the whole semi-consolidated mineral mass.

zones which had been less disturbed in positions deeper and peripheral to the main ore zone.

These blocks and lower zones in the Peko ore pipe contain quartz-magnetite oolites (Figure 58), quartz-chlorite oolites (Part 1, Figure 36), jasper-magnetite oolites (Figure 65), and jaspoidal chert-magnetite oolites (Figure 66). There are other concretionary overgrowths and colloform banded structures in the ore sulphides and gangue minerals in this pipe but the siliceous oolites are clear evidence of the gelatinous nature of the silica in the lode at the precursor stage and the ability of smaller polymeric silica particles to diffuse within it.

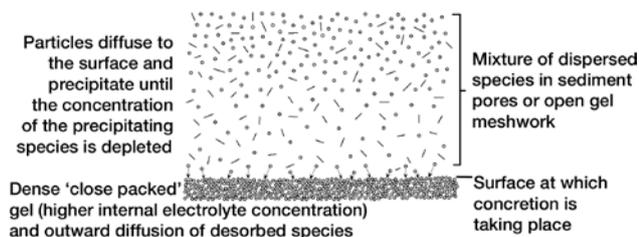
#### *Particle interactions involved in the formation of oolites*

The mechanism of oolite formation requires the specific adsorptive, synergetic, and concretionary properties of the parent gel system to the extent that any alternative genesis is precluded.

A poor understanding of the 'colloidal processes' which give rise to concretions is reflected in the geological literature. This is sometimes acknowledged (eg. Heinrichs<sup>7</sup>, 1984, p. 239) and therefore the main steps in the auto-precipitation of metastable colloidal suspensions in sediment pore fluids or within a gel meshwork are summarised as follows.

The process of concretion within a small particle system such as a fine-grained sediment, is characterised by the diffusion of macromolecules or colloidal particles from the surrounding disperse phase, particle by particle, to accumulate about a central nucleus. Such concretion produces spherically or elliptically symmetric accumulations of higher particle density and compaction than the medium from which it is diffusing. The process is 'static' during diffusion and the two gel phases are not liquid or the gel meshwork of either disrupted. It is usual for the main matrix to be thixotropic and have been mobilised to form denser accretions that then form synergetic nuclei for the concretionary overgrowth.

In most systems the disperse particles diffuse down a concentration gradient in the interstices of the surrounding matrix gel of the system. This gradient is created by the removal of particles from dispersion as they precipitate at the nucleus or internal surface on which the concretion is developing. The nuclei constitute a macroscopic aggregate of particles or an internal 'surface' which is the boundary of the much denser gel within the more permeable and 'open framework' gel of the surrounding matrix (Figure 67). When Brownian motion moves the charged particles in the direction of the precipitating surface, they "see" the deficiency or absence of similar charge and are thus less repelled in this direction. Diffusion acts to keep the concentra-



**Figure 67.** Diagram of the surface of a synergetic nucleus to which colloidal particles are diffusing to build up a concretionary overgrowth. This internal surface within a sediment such as a mud, ooze, or slime is merely a denser 'close packed' gel. The active concretionary nucleus is synergetic, condensing under van der Waals' attractive forces such that surface energy, internal surfaces, and adsorptive capacity are reduced. Synergetic liberation of sorbed electrolytes within the nucleus and the new overgrowth. This perpetuates the precipitation of new species.

tion constant and thus is established the gradient along which a continuing supply of particles move to the precipitating surface.

The mechanism of precipitation at the surface of the developing concretion is generally dependent on the nature of this surface and its charge but in all cases, it results in a reduction of the total surface and of surface energy.

The formation of oolites or any form of concretion depends on a nucleus or internal surface at which there is a change in physical conditions. The precipitation is not a purely chemical reaction but more usually a change in the parameters which determine the nature of the surface charge on the colloidal particles. As pointed out (Part 1 pages 47 to 50) substances with points of zero charge (pzc) near the middle of the pH range (like  $\text{FeO}\cdot\text{OH}$ , 6.8;  $\text{Fe}_2\text{O}_3$ , 4.8-8.6;  $\text{AlO}\cdot\text{OH}$ , 7.8-8.8) show marked variation in their surface charge dependent properties as a consequence of relatively minor variations in parameters such as pH, electrolyte concentration, etc.

Thermodynamically, the most stable state for the total system is that of minimum free energy. Since there is free energy associated with the particle surfaces, in proportion to their area, stability requires that the total surface area be minimised, which can only be achieved by their coagulation into larger particles. This process is favoured by interparticle attractive forces (van der Waals), but opposed by the electrostatic repulsion of similarly-charged particles. Therefore, a colloidal suspension, or sol, can exist in metastable condition, with no observed tendency to coagulate, as long as the electrostatic repulsion effect predominates. However, coagulation of a stable sol can be induced by changing the system in any of several ways. These include:

- (a) Changing parameters, such as temperature or pH, that determine the nature of the surface charge on the dispersed particles.
- (b) Addition of oppositely-charged particles (eg. electrolyte ions, or particles of another colloidal system with different pzc) to the system, to neutralise the residual surface charge.
- (c) Reduction of the mean interparticle distance to the point where attractive van der Waals forces predominate over the electrostatic repulsive forces. van der Waals attractive forces vary approximately proportionately as the inverse of the cube of the interparticle distance and therefore strengthen rapidly as the interparticle distance diminishes. Electrostatic repulsive forces vary inversely as the square of the interparticle distance, and therefore strengthen less rapidly at decreasing interparticle distances. Reduction of the interparticle distance can be a consequence of various processes such as load compression, removal of interparticle fluid, increased kinetic motion at increasing temperatures, etc.
- (d) Addition of "bridging" particles, such as long-chain polymers, which suffer no electrostatic repulsion and can link the sol particles into loosely bound flocs, which then become large enough to settle into more compact aggregates.

The main physical condition which changes at the surfaces of the nuclei on which oolites develop, is the concentration of the electrolyte. The 'close packed' nuclei where the particles of the denser gel are more cohesive, semi-ordered, and spontaneously drawing together (synergetic) under the influence of van der Waals strong forces of attraction (Part 1, Figure 6) are, as a cluster, reducing internal surfaces, surface energy and thereby reducing adsorptive capacity.

This means that the electrolytes adsorbed on the particle surfaces within the nucleating cluster are desorbed into the residual interparticle fluid within the cluster. This fluid at the higher electrolyte concentration is exuding to the surface of the cluster as the denser gel condenses and ages. Mielenz and King<sup>8</sup>, in their 1953 paper on the physical-chemical properties and engineering performance of clays, discussed syneresis and recognised that (p. 237) in more concentrated systems van der Waals attractive forces operate to draw the clay particle clusters together in spite of the repulsion due to their diffuse cationic hulls. They say (p. 238) that in the more rigid gel that may thus form, syneresis will cause a contraction of the diffuse cationic layer of each particle which can only be accomplished by expulsion of water with a different electrolyte content to that of the original suspension.

Any dispersed particle in the surrounding medium which approaches or contacts the internal surface therefore encounters a higher electrolyte concentration which reduces the thickness of its Helmholtz double layer thereby reducing the force of repulsion between particle and surface or particle and other similarly charged dispersed particles.

Particles therefore precipitate at the surface of the synerectic nucleus and having passed through this transition from the metastable dispersed phase to become part of the 'close packed' dense gel nucleus, they also condense or 'age' under the influence of van der Waals strong attractive forces further reducing surface energy and internal surfaces. As part of the synerectic nucleus, the particles accumulating on the perimeter in turn desorb their adsorbed electrolyte species which they brought to the surface by diffusion as particles. This then exudes to the new surface perpetuating the growth of the concretion (Figure 68).

Some concretions can therefore grow to enormous size because the growth is only limited by maintenance of an open water-rich gel meshwork through which a continuing supply of particulate species can diffuse (Figure 69, Moeraki boulder).

These non-chemical sol-gel transitions, the diffusion of ions and small charged particles within fine grained sediments or open meshwork gels can be confusing for geologists if the essential nature of these particulate systems is not kept in mind. The colloidal size range spans three orders of magnitude from 1 to 1000 nanometres and there is no precise "cut-off" at these limits. Both smaller and larger particles retain certain colloidal properties, the smaller ones behaving increasingly like molecules and ions whereas the larger ones behave increasingly like ultra-fine granular material. Within the colloidal size range the material is semi-solid (visco-elastic with a Bingham yield point) with an almost infinite variety of structures, flocs, packing arrangements, particle clusters and 'chains', etc.

These 'colloidal processes' which develop concretions are not dependent on chemistry. They require a diffusive gradient in a 'weak wet' open meshwork gel in which there are pre-existing small clusters or larger nuclei of 'close packed' particles where van der Waals attractive forces are drawing them strongly together (syneresis) so that the mass exudes electrolyte which will precipitate additional diffusing particles at their surface.

The conclusion is that the concretionary process can only occur in aqueous particle systems.

## PTYGMATIC QUARTZ VEINS

### *Examples of ptygmatic quartz veins*

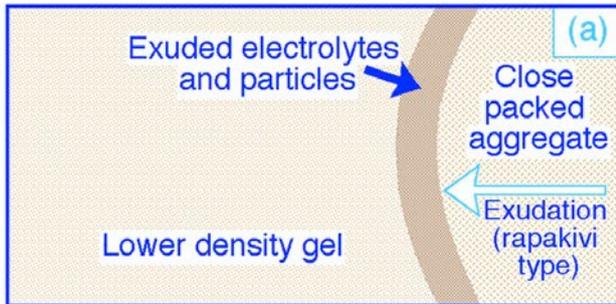
One of the clearest indications that the formation of ptygmatic veins involves colloidal precursors and a soft yielding host material is the occurrence of ptygmatic chert micro-veins in a laminated chert matrix as shown in Figure 70. This structure is due to physical differences (like viscosity) between the vein precursors and that of its matrix which is almost identical chemically. Both the ptygmatic micro-veins and their host chert are metacoloidal and have obviously been derived by the dehydration and crystallisation of sedimentary polymeric silicic acids.

The 'loopy' nature of the several successive injections of vein chert into its laminated or bedded host precursor ooze, is due to an inherent property of colloidal silicic acid. This has a viscosity dependant on the rate of flow during its remobilisation and injection into the veins. The successive thixotropic liquefactions and rapid re-gelling to preserve the 'loops', which is indicated by later ptygmatic veins cutting several earlier generations, are also a characteristic of colloidal systems.

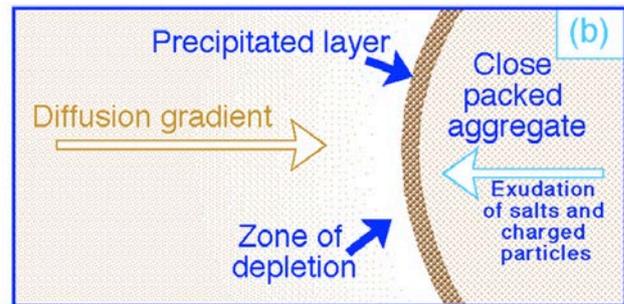
Figure 71 shows a ptygmatic quartz vein in drill core from the New Cobar Mine at Cobar, N.S.W. This vein cuts across the cleavage in its host shale yet in some places it has been offset by further movement on the cleavage planes. The precursor polymeric silica in the ptygmatic vein appears to have been still mobile at the stage of this later minor movement as small 'spurs' and offshoots from it project into cleavage planes similar to those in Figure 72. However, shrinkage cracks or breaks in the internal quartz of this ptygmatic vein itself show no relation to the cleavage in its host shale.

A soft shale host is indicated by the double ptygmatic quartz vein intersected in the drilling at Orlando Mine, Tennant Creek, NT. These veins are not in parallel straight fissures subsequently folded because the 'loops' in the folding are quite discordant and the thickness of the shale material between these adjacent veins is quite variable. The veins also contain abundant fragments of their chloritic host sediment and at the time of intrusion they were clearly able to flow into the soft precursor paste in any direction. The whole system appears to have been under hydraulic pressure which was carrying the load as a water-rich diagenetic gel and it is inferred that only a small differential pressure was required to intrude these veins (Figure 73, Orlando).

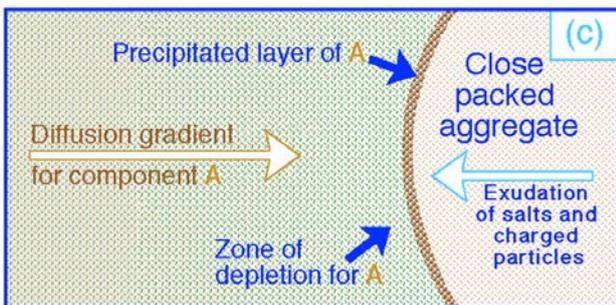
The detail of most ptygmatic quartz veins shows that they are post-cleavage as in Figure 71 and have micro-veinlets or apophyses which extend out into the fabric of their soft precursor host rocks. The bedding planes



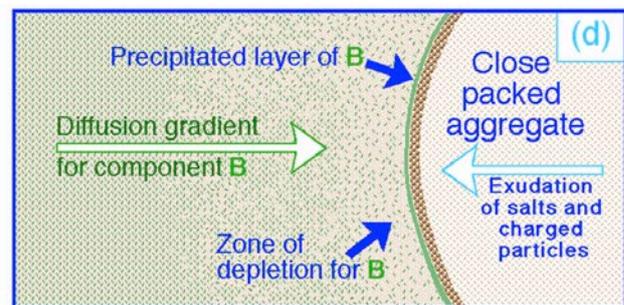
Synerectic condensation in denser accretions or nuclei desorbs electrolytes which also displace coating particles at higher concentrations.



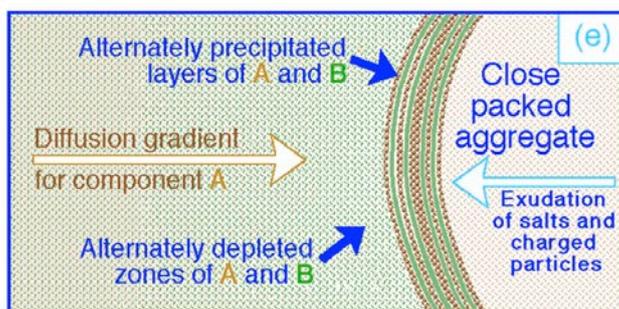
A single dispersed phase in less dense gel surrounding the synerectic nucleus is precipitated at its margin by exuding electrolyte.



When two or more components are dispersed in the surrounding less dense matrix, a precipitating component is depleted near the concretionary nucleus while diffusion increases concentration of the alternate component.



The alternate component is then precipitated until it too is depleted while the concentration of the first component is replenished by diffusion.



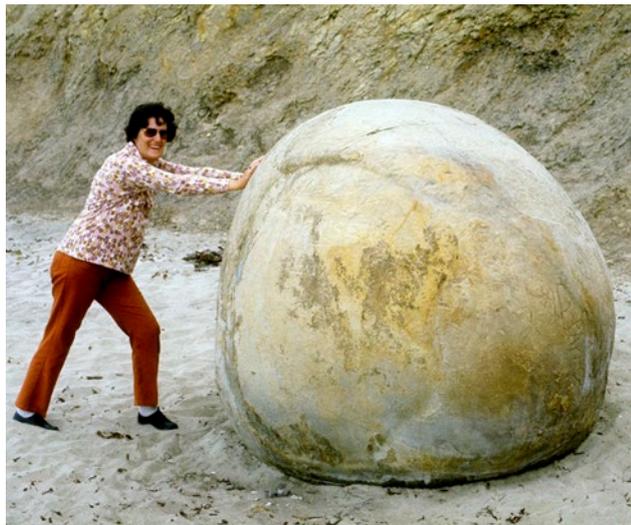
Rhythmic layers reflect the successive depletion and increase in concentration of the components where the thickness of layers is controlled by the diffusion rates for the respective dispersed particles.

**Figure 68.** A schematic diagram indicates the exudation from synerectic nuclei of desorbed electrolyte and 'surface coating' charged particles which precipitate concretionary overgrowths or rimming bands. The principal stages in the saturation - precipitation - depletion - diffusion and re-saturation cycle that gives rise to rhythmic layering are indicated. Essentially the mechanism by which the diffusing particles are precipitated at the surface of the growing nucleus, is by coagulation. They encounter an increase in the concentration of electrolyte diffusing outward from the nucleus. This reduces the thickness of the Helmholtz double layer so that they can 'plate out' on the surface.

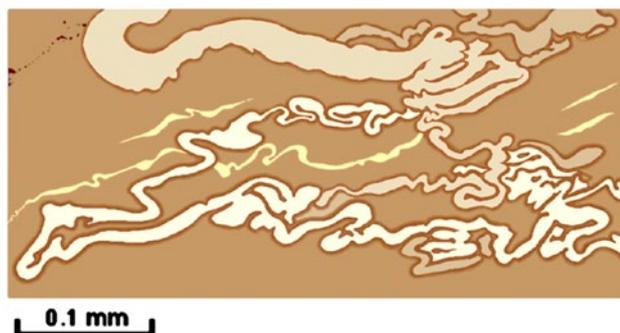
in this shaly dololomite from drill core at Woodcutters Mine, NT., are 'wavy' having responded to the soft diagenetic deformation at the time the ptygmatic quartz

vein was intruded.

Slobodskoy<sup>9</sup> (1970, p. 449) describes monomineralic ptygmatic quartz veins which merge along their strike



**Figure 69.** A very large calcareous concretion has weathered out of soft shales. It is at Moeraki, south of Timaru, New Zealand. Rapid shoreline erosion of the bank of soft shale is exposing a number of these concretions which are left on the beach as the “Moeraki Boulders”. The size of the concretion indicates that the process is self-perpetuating and can continue as long as hydroxy-carbonate particles can diffuse to its surface.

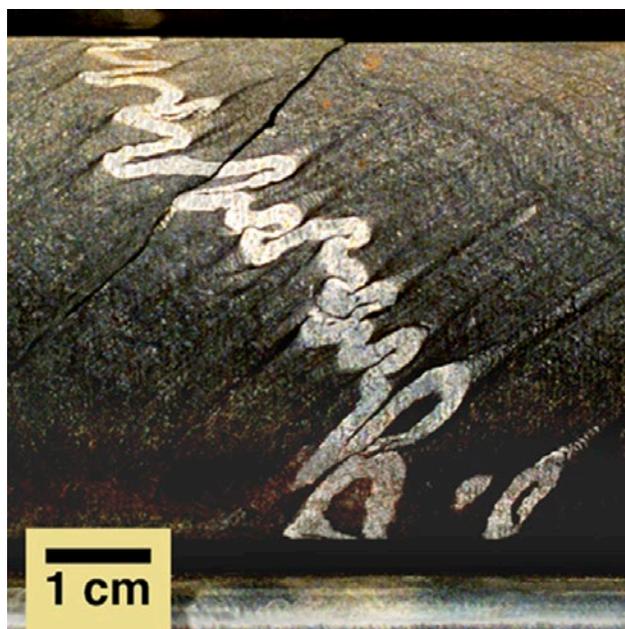


**Figure 70.** Ptygmatic micro-chert veins in a laminated matrix chert show the ‘loopy’ nature of the fluid precursor silica gel injected into a precursor ooze. Both matrix and ptygmatic veinlets are metacolloidal chert so the difference at the time the precursor was injected is in the gel structure or consistency - plastic gel and non-Newtonian fluid. The shear thinning property of the fluid silica polymer causes the looping and bulging. This specimen from Richie Lake<sup>17</sup>, Sokoman Iron-formation is illustrated by Dimroth and Chauvel (1973, p. 122).

into ptygmatic quartz-oligoclase aplitic veins. He points out that crossing veins do not necessarily displace each other, and that the folding is such that the walls would not fit back together if the vein material were removed. The host rock has had to yield.



**Figure 71.** The detail of a ptygmatic quartz vein in the core of the New Cobar Mine at Cobar NSW, shows that it cuts across the cleavage yet it has been offset in places by further movement on the cleavage planes. Precursor polymeric vein silica also appears to have been mobile at this stage as small ‘spurs’ and offshoots of it project along the cleavage planes.

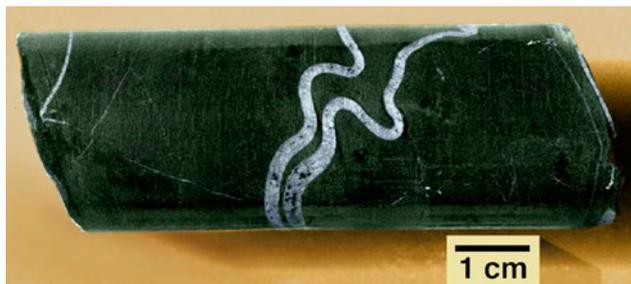


**Figure 72.** A ptygmatic quartz vein intrudes approximately parallel to the bedding in soft mobile dololomite. The ptygmatic loops have diffuse “tails” of quartz extending from them into the de-watering cleavage indicating that the vein was emplaced in the soft sediment before compaction and de-watering was completed. Woodcutters Mine, east of Batchelor, Northern Territory.

#### *The rheology of ptygmatic vein material*

This rheology, that is thixotropy, rheopexy, and viscosity dependant on the rate of flow, is quite specific to particle systems which have a Bingham yield point and where their cohesion depends on glue-like particles “sticking” together (interparticle attraction without chemical linkages).

The ‘loopy’ discordant folding itself arises where flow round the outside of the loops or through the

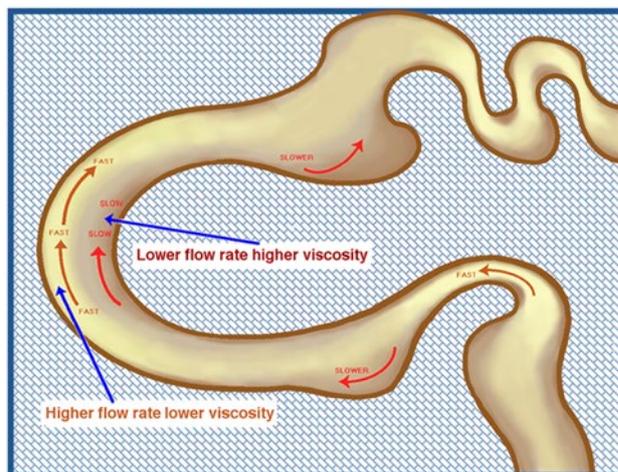


**Figure 73.** These two diverging and 'wandering' pygmatic quartz veins in chloritic shales were intersected in drilling at Orlando Mine Tennant Creek, NT. The veinlets were apparently intruded when the diagenetic sediment was water-rich, soft and carrying at least some of the overburden load by hydraulic pressure. Small differential pressures appear sufficient to intrude the fluid precursor silica gel.

'necks' or constricted parts of the vein is more rapid and therefore more fluid (lower viscosity) than on the inside of the loops or in wider parts of the vein.

Such thixotropic particle systems re-liquefy as non-Newtonian fluids which have a viscosity dependant on the rate of shear (Mysels<sup>10</sup>, 1959, p. 269; Van Olphen<sup>11</sup>, 1963, p. 131; Yariv and Cross<sup>12</sup>, 1979, p. 388). That is the viscosity diminishes as the shear or flow rate increases. This is subject to hysteresis which is the time taken for the viscosity to reach equilibrium at a particular rate of shear, but the overall effect during pasty flow is one of shear thinning behaviour. The paste is more fluid and mobile wherever it is moving faster. This is the reason for the in-welling and bulbous pod-like intrusions. Once re-mobilised, the precursor material pours in until it is slowed by equalisation of the small pressure differentials. When flow rates decline to the critical rate at which rheopectic re-setting re-establishes the gel condition, flow stops abruptly and the whole structure is preserved for eventual lithification.

The intrusion of a vein or a paste of polymeric silica particles as a fluid into a homogeneous plastic yielding host is indicated in Figure 74. It is the variable viscosity across the intruding sheet as it flows round a curve which causes it to loop sinuously back and forth down the slight pressure gradient. The amplitude of the loops is related to the thickness of the pasty sheet intruding and the differential viscosity which varies with the rate of flow causes the vein to 'loop' or zig-zag continuously as it is injected into a uniform soft medium. It behaves in the same way as a thin stream of cream does as it is poured slowly from a jug. For non-Newtonian fluids the phenomenon is called 'shear thinning'.



**Figure 74.** Diagram of an intrusive pygmatic vein comprising a pasty mixture of particulate sediment components like clay, polymeric silica, chlorite, etc. More hydrous and lower viscosity components tend to separate from the mixtures when they are mobilised. At higher rates of flow these more fluid materials are even less viscous. This causes their intruding veins to bend tortuously as they flow along pressure gradients, "jet" through thin connecting necks, well into bulbous forms, or diffuse in cloud-like masses into the plastic host rocks. The viscosity is dependent on the rate of flow.

#### *The stress fields indicated by pygmatic folding*

The pygmatic structures exhibit highly disharmonic, extremely tortuous folds which are distinguished from shear folds by the fact that no relation exists between the thickness of the folded material with respect to crest and limb of the folds. Their limbs can be thickened and the crests thinned whereas the reverse is true of shear folds. There are also indications of blastic crystal growth where the borders of pygmatic veins are blurred by subsequent crystal growth across their margins.

Where two or more pygmatic veins cross each other, they do so without any tectonic interdependence; that is, forces which might have been responsible for the intense fold pattern in one vein, are inconsistent with those needed to fold the next crossing pygmatic vein. These in turn are not consistent with the folding in the third, or fourth, etc. (Figure 70). In this type of random discordant folding any analysis of the stress fields which may have caused the folds can only be interpreted by isotropic or fluid deformation because it is not possible to establish solid phase transmission patterns of mechanical vectors. Any deformation pattern in a solid phase must be anisotropic. The deformation in this case arises within the pasty semi-solid vein material itself as it is injected into its soft and yielding host.



**Figure 75.** A ptygmatic sediment dike invades and transects the Greta coal seam apparently prior to its consolidation. The material of the dike is sandy with abundant clay, and close examination has shown that much of the rounded granular fine quartz is accretionary. Wet sediments trapped under gelatinous semi-consolidated coal apparently gave rise to this ptygmatic dike. Pelton Colliery, Newcastle, New South Wales.

These observations, and the fact that many tightly folded ptygmatic veins “go straight” for a segment (Figure 75), or have each branch folded independently when they fork into two or more branches, make it difficult to accept any hypothesis that the veins were injected as straight veins and then heaped into the highly tortuous fold pattern as the host rock and vein collapsed together.

Many others, such as Sederholm<sup>13</sup>, 1907, p.89; Holmquist<sup>14</sup>, 1920, p.212; Niggli<sup>15</sup>, 1925, p.14, have suggested the veins were folded during their “injection”, that is, in a liquid state through flow movements relative to a plastic host rock. In this view the veins were never straight and their curved rather meandering structure resulted from the tendency of the fluid phase to follow the paths of least resistance within the soft and yielding host rock. They often show complex over-folded structures which could never be formed by the opening of fissures. It is also observed that thick layers produce folds of larger amplitude than thin ones and it has been pointed out that during re-mobilisation a mass transport of material from the host rock into the ptygmatic veins is indicated.

In reality there is no question of the random isotropic nature of ptygmatic folds, Part 1 Figure 30, Figure 70, and Figure 76. The pasty vein material is “heaped in” on top of, and transecting or adding to, earlier vein material. Completely random folding of the type described by renowned Australian professor S. W. Carey as “chicken guts” folding can be developed. There is very clear evidence that the previously injected ptygmatic vein retained the same plastic character as its host material. It responds similarly when re-injected by a lat-



**Figure 76.** A ptygmatic-type clastic mud dyke or “dirty early quartz vein” has been intruded into soft diagenetic 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. Explorer 8 drill core, Tennant Creek.

er ptygmatic vein as in Figure 70. This is a conspicuous example of ptygmatic injection of chert veins into a soft laminated chert host.

*Ptygmatic veins develop in soft pliable pre-crystalline materials as their hosts*

In many cases there is clear evidence that ptygmatic veins have been injected into soft precursor host materials. Most of them are into sediments at the diagenetic stage (syn-diagenetic) or they intrude into soft walls of newly deposited mineral matter associated with hydrothermal zones. In some cases, there is quite definite evidence that the host materials were at the soft precursor stage when the veins were injected.

Figure 75 is a ptygmatic clay-rich sediment dyke in the Greta coal seam photographed in the workings of the Pelton Colliery at Cessnock. The coal was obviously soft and unconsolidated at the time of its intrusion. There is no question that ptygmatic veins occur in soft sediments. This is shown by the intrusion of mud dykes and ‘muddy’ quartz veins through haematite shales near Juno Mine in Tennant Creek, Part 1, Figures 30, and Figure 76.

A ptygmatic chlorite vein meandering across slate cleavage and merging with chlorite in its host Appalachian shale-slates is illustrated by Weaver<sup>16</sup>, 1984, p. 49. It is reproduced here as Figure 77.

In Figure 78, Dimroth and Chauvel<sup>17</sup> (1973, p. 122 record a small ptygmatic chert vein injected into greenalite in the Sokoman Iron Formation at Lac Helluva, Labrador. Needle-like minnesotaite crystals have nucleated on the vein margins and developed by growth of the greenalite out into its surrounding host. These spiky crystals clearly developed in the soft host after the ptyg-



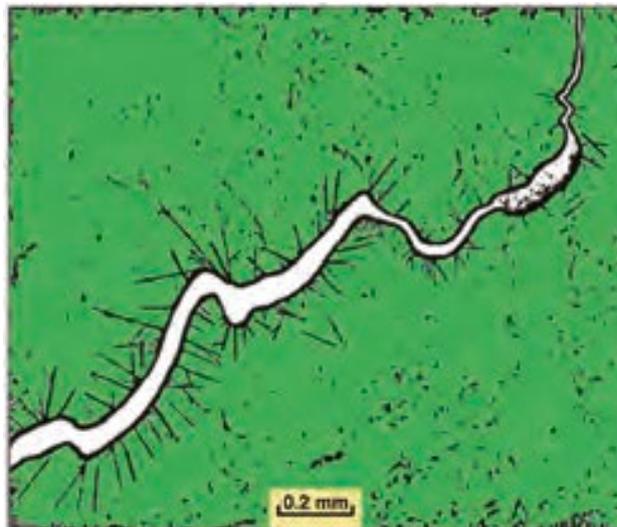
**Figure 77.** During diagenesis the highly fluid pale green chlorite content of the Conasauga shales was able to flow under a small differential pressure into a ptygmatic veinlet as illustrated by Weaver (1984, fig. 38). Chlorite in the veinlet, possibly only a little 'cleaner', is the same as that in the fabric of the diagenetic mud from which it merges and oozes out into the vein from a series of interlayer off-shoots.

ment with model substances, but in the case of natural sediments (Part 1, Figure 30) it is water rich mud trapped under the gelatinous ferruginous shale that is light enough to well upward into the plastic host materials under a very low-pressure differential.

These enigmatic ptygmatic veins are not an enigma if the material of the vein is intruded into soft host material as a thixotropic paste.

#### *Ptygmatic veins of other metal oxides*

The ptygmatic vein form is entirely dependent on the rheology of the intruding material and its soft precursor host. Similar ptygmatic veins and vein hosts

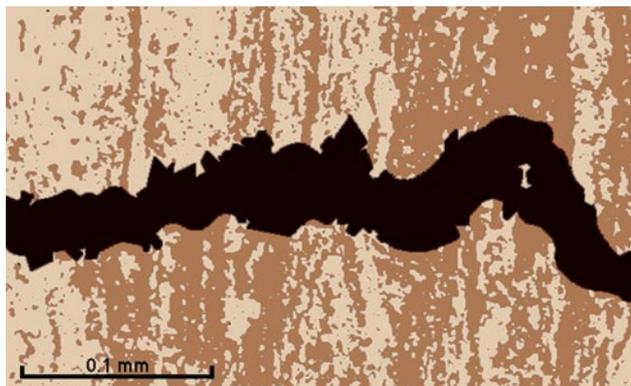


**Figure 78.** Round a stylolitic quartz vein from the Sokoman Iron Formation, Lac Helluva, Labrador, Dimroth and Chauvel<sup>17</sup> (1973, p. 122) show minnesotaite needles nucleated at right angles to the sinuous convolutions of the vein. The vein, by facilitating water release, has nucleated the crystallisation and it was clearly emplaced prior to the time the minnesotaite crystallised from its surrounding hydrous ferromagnesian precursor.

include mica-schists (Figure 77), slates (Figure 73), cherts (Figure 70), banded iron formations (Figure 79), coal seams (Figure 75), and haematite shales (Figure 76). Ptygmatic veins of single minerals or where it appears that involved eutectics could not be invoked to lower 'melting points', include quartz veins (Figure 72), calcite veins, chlorite veins (Figure 77) haematite veins (Figure 80), magnetite veins (Figures 79 and 81), and mud (Part 1, Figure 30).

In Figure 80 a highly sinuous and 'loopy' vein of haematite is illustrated where its precursor ferric hydroxide has injected into previously soft chlorite near the margin of the One-Oh-One lode near the Orlando Mine at Tennant Creek. This vein is also complexly branched, thickened, and apparently remobilised several times. The bladed haematite crystals are in random clusters which have no relation to vein walls, its flow during intrusion, or any regional stress field.

Micro stylolite-like ptygmatic veinlets of magnetite (Figures 79 and 81) occur in the Mary Ellen Mine in the Biwabik Iron Formation, Mesabi District, of the Lake Superior iron ore province (van Hise and Leith<sup>19</sup>, 1911). The ptygmatic magnetite veinlet in Figure 81 occurs among haematite oolites in cherts which clearly indicate a very soft diagenetic environment because the ptygmatic magnetite veinlet cuts their margins. Some precursor internal amorphous silica has also been re-mobilised



**Figure 79.** A ptygmatic micro-veinlet of magnetite (black) cutting chert (white) and hematite (grey) bands is from the Mary Ellen Mine, Biwabik, Minnesota. The magnetite octahedra projecting across the veinlet boundary clearly indicate that crystallization is later and that the magnetite had an intrusive non-crystalline precursor with shear thinning properties as indicated by the ptygmatic folding. A thixotropic ferric hydroxide vein precursor is unmistakably indicated. (From Lougheed<sup>4</sup>, 1983, p. 339.)

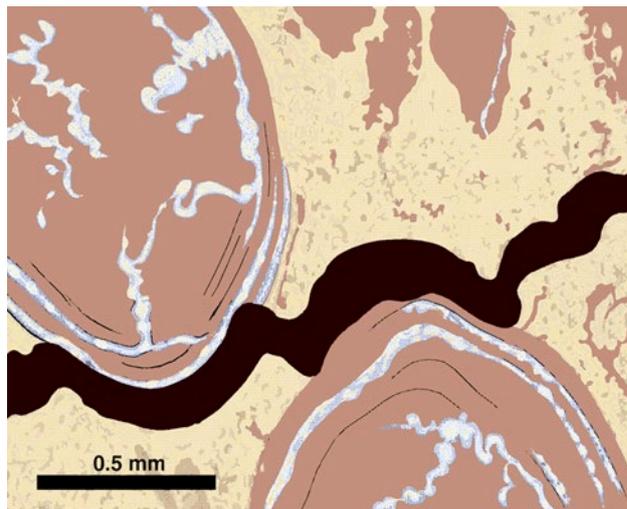


**Figure 80.** A complex ptygmatic haematite vein system has intruded into the marginal chloritic sediment at the One-Oh-One prospect near the Orlando Mine, Tennant Creek. The massive crystalline specularite contains slivers of chlorite wall-rock and the ptygmatic folding indicates that the precursor ferric-hydroxide was colloidal at the time it was intruded (viscosity dependant on the rate of flow).

within them, probably in syneresis shrinkage cracks, and this intrusive infilling silica itself has assumed a slightly ptygmatic form.

The obviously once fluid micro-veinlet of magnetite in Figure 79 also cuts banded chert - haematite unit from a banded iron formation at the same location. These occurrences indicate clearly that the mobile iron hydroxide precursors do not react chemically with their polymeric silica (chert) hosts.

As Lougheed<sup>4</sup> (1983, p. 339) claims, they are evidence for the mobility of the iron oxide now crystallised as magnetite. It could not be suggested that the ptyg-



**Figure 81.** A stylolitic veinlet of magnetite cuts the margins of hematite oolites in a chert matrix at the Mary Ellen Mine, Biwabik, Lake Superior province. These hematite oolites have well developed syneresis shrinkage cracks filled with quartz which also extends into 'saddle reefs' or layers within the rim zones. The remobilised silica gel precursor has been intruded (ptygmatically in places). A ptygmatic magnetite veinlet cutting soft precursor chert and hematite oolites is very clear evidence for viscosity dependent on the rate of shear (flow). Recorded by Lougheed<sup>4</sup> (1983, p. 339).

matic micro-veinlet amongst the oolites or crossing the chert laminae was injected as fluid molten magnetite, as a precipitate from meteoric weathering, or as magnetite in some solid crystalline state. The magnetite crystal growth across the margin of the veinlet in Figure 79 indicates that the crystallisation is later. What then are the alternatives? Clearly the rheology and shear-thinning properties of the ferric hydroxide precursor gels are needed to interpret these observations of vein development and to account for the diagenetic mobility of the magnetite precursors.

#### THE ENHANCED GROWTH OF CRYSTALS IN PRE-CRYSTALLINE VEINS

*The crystallisation of vein minerals is after vein emplacement*

It has always been held that the crystalline minerals observed in veins were formed after the vein had been emplaced and established as a hydraulic fracture or opening in the rock. The clear evidence for this, particularly in sinuous veins, is that the crystal growth is often nucleated on the vein walls and the orientation of the crystals follow round the sinuous curvature of the vein wall always projecting towards its centre. The vein walls

were there and the vein opening established before the crystals grew inward from them as in Part 1, Figure 47.

Whatever mechanism of vein emplacement could be envisaged, this unequivocally implies that the vein was filled with some precursor fluid or substance from which the crystals subsequently grew. The crystal growth was sometimes insufficient to fill the vein space leaving vughs or chains of crystal cavities in the centre of the vein. These crystal cavities are like those in condensing and crystallising chert geodes as illustrated in Part 1, Figure 26.

The evidence for the growth of crystals inward from condensing colloidal precursors as in geodes, is also often seen in veins as in Part 1, Figure 43 where the crystals grow inward from banded colloform silica near the margin of the vein. Occasionally colloform silica fills the whole vein space as in Part 1, Figure 46.

#### *Enhanced crystal growth in precursor vein gels*

The colloidal nature of vein precursors is further indicated by enhanced or surface catalysed crystal growth. Crystals growing in gelatinous media, such as soft vein precursors like polymeric silica gels, are supported within this soft material. Crystals can develop directly within the material itself or by diffusion of soluble ions or small particles through the media to the growing crystal face. For example, quartz crystals grow within vein precursor silica gels by diffusion of the very small and mobile  $\text{Si}(\text{OH})_4$  species to 'infill' the condensing gel meshwork by the simple exothermic chemical reaction:



Frequently the gel coating on a particular crystal face of a growing crystal will catalyse growth on that face to the detriment of other crystal faces of differing crystallographic orientation. When this occurs on very small newly nucleated 'seed crystals', it can result in spectacular needle-like crystals as one of the very small faces grows to the exclusion of all others. Fine acicular rutile needles which are often found in clear vein quartz are a good example (Part 1, Figure 27). Fine needle like or bladed crystals of dawsonite, chlorite, haematite, or magnetite also commonly reflect the enhanced crystal growth of the included mineral in the gel of the vein precursor. Chlorite crystals grown from wall rock material included in vein quartz from the Wagga Tank Prospect drill core are illustrated in Part 1, Figure 42.

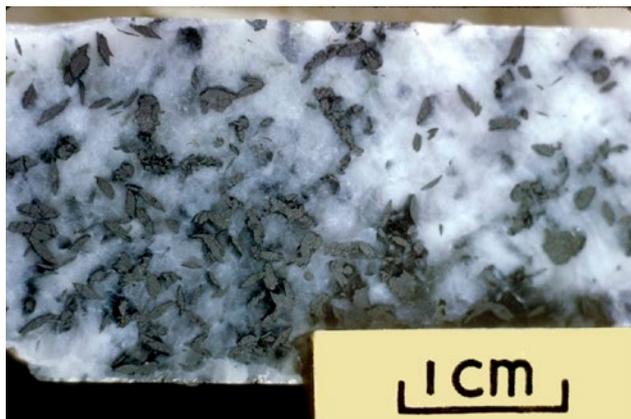


**Figure 82.** Radiating acicular hematite needles have grown out like spikes into a gelatinous dolomite precursor of the lode at Juno Mine, Tennant Creek. This 'wild growth' from a central nucleation point is typical of bladed and spherulitic crystal patterns developed in gelatinous media where enhanced (catalytic) crystal growth on one of the small seed crystal faces proceeds almost to the exclusion of growth on other faces.

Where many crystals are nucleated together such as on the surface of a small synergetic 'gel ball' like an accretion, framboid, or oolite set within gelatinous media, spherulitic growth (Part 1, Figure 45), 'wheat sheaf' structures, or axiolytic outgrowths can develop. A good example of this type of enhanced crystal growth in gels producing a radiating acicular texture is the slender haematite needles developed in the gelatinous dolomite precursor of the Juno Mine lode at Tennant Creek (Figure 82).

Because of the catalysis on a single specific face of the 'seed crystal', needle-like crystals of many different minerals and chemical compounds have been grown experimentally in polymeric silica and other gels to demonstrate this phenomenon (Henisch<sup>20</sup>, 1970).

Sometimes the catalytic crystal growth enhancement induced by the host gel for the developing crystal occurs on two of the 'seed crystal' faces. In this case bladed or platy crystals develop. Bladed magnetite crystals in quartz from Peko Mine are shown in Figure 83.



**Figure 83.** Catalytic crystal growth enhancement sometimes occurs on two faces of the original seed crystal resulting in growth of a bladed or platy crystal form. This magnetite in quartz from Peko Mine in Tennant Creek has probably grown from dispersed lepidocrocite to developed this bladed form instead of the more usual compact octahedra.

These crystals most probably grew from a dispersion of fine iron hydroxide or hydroxy oxide particles like lepidocrocite [ $\text{FeO}(\text{OH})\cdot\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ ].

The silica host for the bladed magnetite must have been a polymeric gel in order to support the heavy magnetite crystals and to provide the catalytic coating which favoured crystal growth on two faces of the magnetite crystals. These are normally compact octahedra.

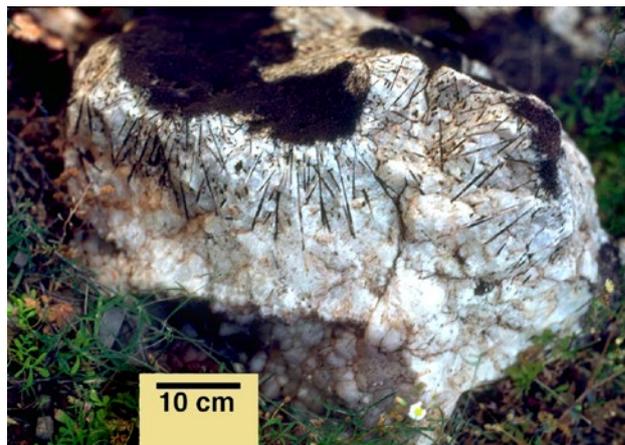
Magnetite and quartz rimmed oolites (Figure 58) occur in this same Peko main lode. These definitely indicate the dispersion of particulate hydrated iron oxide species.

Crystal growth in the gelatinous medium of the early vein material is enhanced because the gel allows diffusion of the crystallising species to the growing crystal face; it acts as a crystallising catalyst to the face it is coating; and the gel yields to support the delicate needle like crystal as it grows.

Figure 59 illustrates vein quartz from Mt. Gee, Flinders Ranges, South Australia, with scalloped crustiform and subspherical colloform concretionary textures see also Figure 60 and Figure 84. Here the same polymeric silica precursor gel has supported the delicate acicular dawsonite needle growth.

#### *Precipitation of gold in quartz*

The catalytic surface coating which enhances crystal growth in gels and facilitates the growth and development of well faceted crystals in gelatinous media directly from dispersed particulate species is quite significant. The phenomenon has been recognised for many years following the experiments of Hatschek and Simon<sup>21</sup> (1912) and Boydell<sup>22</sup> (1925) who demonstrated that gold



**Figure 84.** Colloform vein quartz from Mt. Gee, Flinders Ranges, South Australia, contains delicate acicular dawsonite needles. A precursor gel stage of the quartz is indicated by the enhanced growth of these needle-like crystals. They were supported in a yielding medium through which material for crystal growth could diffuse. Subsequent quartz crystallisation nucleates at, and radiates from, the pre-existing dawsonite needles.

sols diffused into silica gel would crystallise directly to metallic gold. In fact, silica gel appears to be a 'scavenger' for insoluble gold particles dispersed in aqueous fluid. The irregular and sometimes high concentrations of metallic gold in quartz veins is thought to be due to the 'quality', that is the gel structure and degree of hydration, of the polymeric precursor silica in the vein and to its maintenance for a long period during hydrothermal fluid seepage so that very low trace levels of gold particles are concentrated.

Hatschek and Simon's<sup>21</sup> experiments have since been repeated and further investigated by Henisch<sup>20</sup> (1970, p. 19). Henisch points out that the gel structure has some degree of long-range ordering which is why crystal faces of different orientations and having a different relationship to this ordering, are "catalysed" to different extents. Stumm<sup>23</sup> (1992, p. 218) confirms that a surface catalytic effect is observed when the surface of the substrate or gel coating "matches well" with the crystal to be formed.

#### *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. Henisch<sup>20</sup> (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.

Since enhanced crystal growth occurs in a number of different types of gelatinous materials and involves many different particulate and ionic dispersed species, it is very doubtful that the actual catalytic action is fully understood. Healy<sup>24</sup> (1969) grew galena crystals from PbS sols in silica gel and from these experiments he was able to discern that in many cases small acicular tubules, not necessarily of PbS, first developed and that along the surfaces of these minute hollow rod-like structures, small perfect cubes of PbS developed. This type of surface nucleation and growth of the crystals in gels appears to be similar to the radiating quartz spherulites developed round dawsonite needles at Mt. Gee in South Australia.

Any substance precipitating from solution must first form molecular species which must then come together with other molecules to develop a crystallite nucleus. Stumm<sup>23</sup> (1992, p. 217) points out that if this nucleus is smaller than a single unit cell, the growing crystallites are most likely to be amorphous. This is because these nascent or part formed lattice units of a crystal must have 'broken' or 'unsatisfied' lattice bonds. Such a cluster of crystalline molecules less than a unit cell in size has enormous surface energy and is highly charged by virtue of its unsatisfied lattice points. Such exceedingly small charged particles in an aqueous system are immediately hydrated with dissociated water or "coated" with polar water as an adsorbed water monolayer. It is this water of hydration, and any adsorbed water monolayer which creates the metastable 'gel' condition of the material.

The very small particles if they are formed slowly enough or at very dilute concentration form a metastable hydrate (critical cluster) which then impedes further crystallisation until the particles aggregate into syncretic clusters which can spontaneously desorb water by drawing together under van der Waals strong interparticle forces of attraction.

Silica differs from the other metal oxides, hydroxides, sulphides, etc. in that in its dispersed or 'soluble' form the neutral monomeric  $\text{Si}(\text{OH})_4$  species predominates. Because the ionisation constants of the polymers are greater than that of the monomer it reacts more rapidly with the dimers and higher polymers than with another monomer. Quartz crystal growth within precursor silica gels in quartz veins is therefore by diffusion of the monomer to react at the face of the growing crystal with surrounding polymer so that siloxane linkages then form the developing lattice.

## REPLACEMENT

### *Replacement criteria*

'Replacement' or 'metasomatism' are often routinely used with little regard to the physico-chemical process by which the 'replacement' of one mineral with another is actually accomplished.

To accomplish such a 'replacement', certain requirements are obvious. New matter in the form of ions, radicals, molecules, or very small particles must be moved in to the replacement site. There must be a mechanism for the exchange of material at this site with the new material arriving and the 'replaced' matter must be moved out.

One of the first papers to logically address these requirements and to consider processes involved in effecting 'replacement' was Holser<sup>25</sup> (1947). He points out that the replacing substance must have access to all parts of the material being replaced and says that most replacement must therefore be accomplished in openings of the very smallest size if it is to be complete. The types of openings he considers are:

- 1) Supercapillary - that is cracks, fissures, openings, intergranular pores, etc. in which fluids can flow and effect transport of dissolved or suspended matter over relatively long distances.
- 2) Capillary - (a) Open highly hydrated gel meshwork with particles in 'loose' or open structures such that fluid flow is restricted and solutes and sols move by diffusion.  
(b) Dense strongly crosslinked gel meshwork in which fluid movement is mainly by diffusion and movement of sols and solutes is restricted to vary markedly according to particle size, shape, and charge (gel chromatography).
- 3) Grain boundaries, hydrated crystallites, or incomplete lattices where some diffusion of fluids is possible and fluids and ions can be transferred by reversible "shuffling" reactions like adsorption-desorption reactions.
- 4) Intra lattice spacings where very limited movement of ions occurs within the lattice itself such as the slow migration of entrapped silanol terminations within a strained natural quartz lattice (White<sup>26</sup>, 1971).

No substantive 'replacement' would be possible within a crystal lattice because of the inability to diffuse many larger ions or particles either in or out. Therefore, if observations suggest replacement of a whole mineral or rock volume it must have been porous and gel-like so that the replacing ions, molecules, or particles could gain access to all parts of it. Similarly, when replacement occurs, the material substituted must remain gel-like at least for some time so that the replaced ions, molecules,

or particles can continue to get out.

Considering the various aggregates, flocs, tactoids, or curd-like particle associations and the three orders of magnitude in the size range of colloidal particles themselves, the size of pore spaces probably extends over four orders of magnitude or more. There is clearly a gradient from open highly hydrated sediment gel meshwork to dense strongly crosslinked and semi-ordered 'close packed' particle aggregates. Openings the size of those in densely crosslinked gels would severely limit or preclude fluid flow and therefore restrict fluid transport of any sort. As Liesegang phenomena so clearly indicate, ion or small particle migration in such aging or compact gels is controlled by diffusion.

Holser<sup>25</sup> (1947) points out that matter may be transported in solution or suspension and that such fluids may hydrolyse, disperse, disaggregate, or mechanically disintegrate particles and particle clusters. The surfaces in turn may precipitate, adsorb, or settle material into the spaces left by these processes.

If the requirement of metasomatism is to "change the body" of the material being replaced, then the "openings of the smallest size" must give access to all parts of the body being replaced. It must be like a sponge with very small pores. Consequently, the replacement can only be achieved by ions, molecules, or very small particles. A gel or the gelatinous precursors of a wide range of ore and rock minerals which "soak" for very long periods of time in ore forming fluids, are indeed susceptible to 'replacement'.

Transport by fluids is both by stream flow or seepage and by diffusion. Ions and charged particles diffuse down a concentration gradient. Thus, if an ion or charged particle is precipitated or adsorbed from the fluid, further ions or particles will move along the gradient so created towards the place of precipitation. In the case where the diffusing ion or particle is exchanged for one then released by substitution, the concentration gradient in respect of these newly released ions or particles will be in the reverse direction and they will diffuse outwards. Diffusion is therefore particularly appropriate for replacement. It allows movement of ions or particles to the replacement site and removal of those displaced. This was recognised by Lindgren<sup>5</sup> (1933, p.177): -

*"The great importance of diffusion is probably in the mechanism of replacement. In the ultimate small spaces available for metasomatism, there is constant change of concentration; and diffusion attends to the moving up of the new molecules and the removal of the by-products of replacement. Diffusion acts easily in a gel."*

Chemical reactions affect the rate of diffusion and may stop or impede it (as in the case of Liesegang rings)

but Holser<sup>25</sup> (1947) concludes that diffusion is much more effective than fluid flow in metasomatism. Four types of replacement are recognised:

- 1) Filling the spaces occupied by fluid within the original pore space or gel meshwork.
- 2) Displacing or pushing aside the existing gel structure by the formation of a precipitated or denser structured gel as ions or charged particles diffuse to and expand the nucleus around which they are precipitating (like oolite growth, etc.).
- 3) Infilling the original gel meshwork by diffusion of a disperse phase to the surface of this "infilling volume" or replacement front (like the diffusion of monomeric or oligomeric silicic acid into its polymers to make denser gels).
- 4) Replacement of units in the original gel meshwork by a chemical reaction or by radicle or particle exchange which results in formation of a new gel.

These types of 'replacement' correspond to the normal behaviour of dispersed species within colloidal materials:

- a) Coagulation or auto-precipitation of the metastable sols in open spaces.
- b) Concretion.
- c) Infill concretion.
- d) Chemisorption.

In each case the particles of the system are interacting with ions, other particles, and surfaces, to condense, reduce surface energy, and to progress toward the lower energy crystalline state.

## EXAMPLES OF REPLACEMENT

### *Silicification*

Solutions or gels of polysilicic acids are somewhat unstable in that these molecules or particles grow in size and aggregate into denser precipitates or gels. They accumulate in precursor quartz veins, in the interparticle spaces in mineralising systems and stock-works, in the pores of sediment gels, or in natural openings like the syneresis cavities in the centres of geodes. A well-known example is the 'secondary' quartz surrounding sand grains and filling the pores of sandstones so that quartzites result from their eventual crystallisation.

Significant volumes of sediment near veins and mineral channels (elvans) are "silicified", that is, infilled with 'secondary' or polymeric silica which attracts more of the mobile monomeric and oligomeric species. It then becomes denser and hardens due to the crosslinking and 'infilling' of the readily diffusible neutral monomer [Si(OH)<sub>4</sub>].

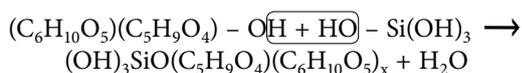
This silicification and infilling of expanded pore spaces, veins, geodic cavities, etc. is actually achieved largely by chemisorption. After the “little balls” of colloidal silica have established a meshwork, the mobile silicic acids or the monomer ‘add on’ to the pre-existing polymers or disordered solvated crystal surfaces by chemical condensation reactions. However, in many cases the silica infilling is first achieved simply by the physico-chemical sol-gel transition of the very small colloidal or “little ball” species of polymeric silica precipitating as ‘infill’ concretions or building up on surfaces.

#### *The example of silica replacing wood*

While it is easy to envisage the infilling and creation of progressively denser silica gels in existing fluid filled pores and hydraulically opened veins, lode systems, etc., actual ‘replacement’ or ‘metasomatism’ which has also been described as “molecule by molecule replacement”, requires the removal of the material being replaced.

The commonly observed silicification of wood with preservation of its complete cellular and structural detail is perhaps one of the simplest examples of this exchange as in Figure 85. Iler<sup>2</sup> (1979, pp. 88-91) in his discussion of the silicification of biogenetic materials points out that chemical degradation must occur before the resulting space can be filled by silica deposition. That is, the cellulose of the wood or log being petrified must decompose by hydrolysis (gelatinise or simply “rot”) before the replacing silica could diffuse to all parts of it. Only the short chained oligomeric or monomeric silicic acids can diffuse within the gelatinous hydrocellulose mass and larger colloidal silica polymers cannot pass through the cell walls. For this reason silicification for the most part involves the monomeric  $\text{Si}(\text{OH})_4$  which must precipitate as a gel to allow continuing diffusion within the specimen.

Cellulose or polycellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ , the main constituent of wood, is well suited to such replacement by the mobile silicic acids. The repeating basic sugar-like chain of six carbon atoms has a an oxygen atom forming a cyclic link between the first and fifth carbon in the chain and this repeating group contains four hydroxyls. It can hydrolyse or ‘decay’ to several intermediate acids like humic, tannic, talonic, idonic, mannoic acid, etc. and the simpler tartaric and acetic acids also probably occur among the breakdown products. The basic chemisorption or condensation reaction with silica is:



**Figure 85.** The trunk of a giant redwood tree felled and buried by the ash of a nuée ardente some 3.4 Ma ago is now completely replaced by silica and almost re-exposed by erosion (some excavation). Original cellular structures are largely preserved in this ‘petrified forest’ some 12 km due south of Mount St. Helena in the Napa valley of California.

The natural decay of cellulose also results in an efflux of  $\text{CO}_2$  as well as the various organic acids. Finally, the silica also displaces the carbon forming -Si-O-Si-O-Si- chains together with organic and hydroxyl radicals. However, as Iler<sup>2</sup> (1979, p. 89) points out the actual chemistry of this displacement of the complex organic radicals by chemisorption has not yet been properly determined. It appears to depend largely on their steric configuration and catalysis at the exchange sites. It is recognised that natural silicification of wood proceeds to various stages. In many cases the silicified wood contains unusual amounts of organic residues which can sometimes be demineralised, embedded, sectioned, and stained in a similar manner to living tissue.

Cellulose decomposes by hydrolysis and oxidation much faster than lignin and because of these differenc-

es in chemical stability, the cellulose can be replaced by the silica before the lignin is attacked. In all cases of this type of replacement by chemisorption, the removal of dispersed mobile silicic acid species is by its chemical bonding to the decayed wood structure. This lowers its concentration and creates a diffusion gradient towards the site at which it reacts. Similarly, the organic acids or radicals displaced increase their concentration within the petrifying wood. This creates diffusion gradients outwards for these organic species. There are many places where water coloured like tea with the tannic and humic acids can be seen seeping out from under sand-dunes containing buried logs and wooden debris.

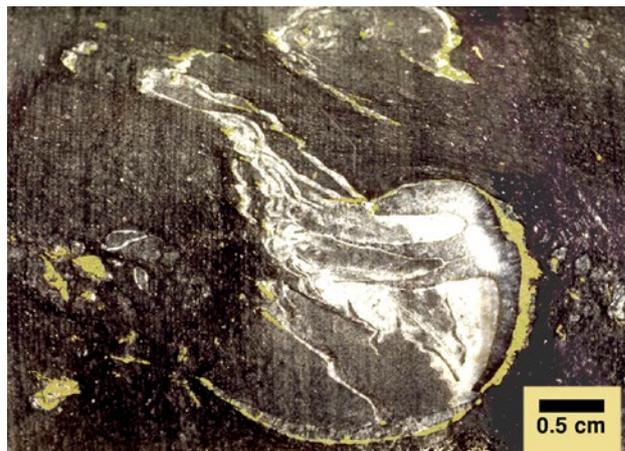
Fossilised wood has been produced reasonably successfully in the laboratory by Leo and Barghoorn<sup>27</sup> (1976). Wood specimens were boiled in water to free them of gas and then subjected to a succession of immersions for long periods in ethyl orthosilicate at 70°C. Silicified wood closely resembling natural petrification of a geologically young age was produced. After treatment, residual organic matter in the silica filled specimens was removed with oxidising acid and the silica lithomorph was found to faithfully reproduce the original organic woody structures. Since the organic matter can be removed by oxidising agents, it is clear that the siliceous lithomorph is quite porous which, in the diagenetic environment, would make it an ideal substrate for further deposition of silica.

Laboratory duplication of natural chert which contains micro-organisms is very much easier because diffusion distances are much smaller. Oehler and Schopf<sup>28</sup> (1971) silicified specimens of filamentous algae by embedding the algae in silica gel and then autoclaving it at 2-4 Kb for 2-4 weeks at 150°C. Under these conditions the gel undergoes syneresis until completely solid then it crystallises to a cryptocrystalline cherty form preserving the algal filaments.

#### *The replacement of shells by opal*

The significance of the replacement of calcareous shells by opal is that this is direct and positive evidence of replacement by the "little balls", the actual charged particles of polymeric silica, which exchange for gelatinous hydroxy carbonate species. Particle exchange by hydroxide and sulphide charged particles can be just as important as ion exchange or 'molecule by molecule' exchange in effecting replacement.

The complete diagenetic hydrolysis or "gelation" of fossil shells is usually indicated by plastic distortion of the entire calcareous fossil (Figure 86), their 'weld-



**Figure 86.** A distorted carbonate fossil is from pyritic black shales at Mt. Bulga N.S.W. The plastic or semi-fluid nature of the distortion indicates the way in which the original carbonate had been hydrolysed to hydroxy carbonate at the time of distortion. This is confirmed by its partial replacement by sulphide which requires hydrolysis (or gelation) before the sulphide particles can diffuse into the material to substitute for the hydroxycarbonate they are displacing.

ing' together and re-crystallisation, dolomitisation, or replacement by galena, pyrite, glauconite, or silica.

The calcium ion,  $\text{Ca}^{++}$ , does not hydrolyse appreciably in aqueous solution because of its extraordinarily high hydration energy. However, in neutral or slightly alkaline solution it readily exchanges to reach an equilibrium with  $\text{Na}^+$ ,  $\text{Mg}^{++}$ , and other ions so that a range of stable gelatinous mixed Ca-Na, Ca-Mg, and Ca-Al hydroxy carbonates are formed. Actual species in these amorphous mixed hydroxy-carbonates are not easily defined but a few of those which have been identified and named are listed in Table 2.

Occurrences of oolitic limestones (Figure 57) and large calcareous concretions in shales (Figure 69) clearly indicate the extensive hydrolysis of carbonates in the diagenetic environment and confirm the fact that equilibria in the pore fluid chemistry favours the hydrolysed species and stable gels for a long period of time during diagenesis.

It is important to recognise that substantial fossil shells like brachiopods and molluscs can hydrolyse completely in this environment and can therefore be replaced by silica as in Figure 87. In fact, Newell et al.<sup>29</sup> (1953), point out that in many cases the macro-fossils are selectively replaced by silica in preference to their limy matrix. Most readily silicified are bryozoans, tetracorals, tabulate corals, punctuate brachiopods, followed by non-punctuate brachiopods, molluscs, where replacement is usually spongy and imperfect, and finally echinoderms,

TABLE 2. Hydrous Carbonate Minerals

HYDROXYCARBONATE (Hydrolyses to gel under aqueous conditions)	COMPOSITION (Formulation is usually indefinite due to highly variable hydration)
GAYLUSSITE	$\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$
PROTODOLOMITE	Gelatinous partly ordered hydrous Ca - Mg Carbonate.
PIRSSONITE	$\text{CaCO}_3 \cdot \text{NaCO}_3 \cdot 2\text{H}_2\text{O}$
ALUMINOHYDROCALCITE	Hydrated carbonate of calcium and aluminium.
GAJITE	Hydrous calcium-magnesium carbonate.
NESQUEHONITE	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$
ARTINITE	$\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
HYDROGIOBERTITE	$\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
HYDROMAGNESITE	$3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
DAWSONITE	$\text{Na}_3\text{Al}(\text{CO}_3)_3 \cdot 2\text{Al}(\text{OH})_3$
TRONA	$\text{Na}_2\text{CO}_3 \cdot \text{HNaCO}_3 \cdot 2\text{H}_2\text{O}$
THERMONATRITE	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
NATRON	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

foraminifers, and calcareous sponges where silicification is often limited only to the surface.

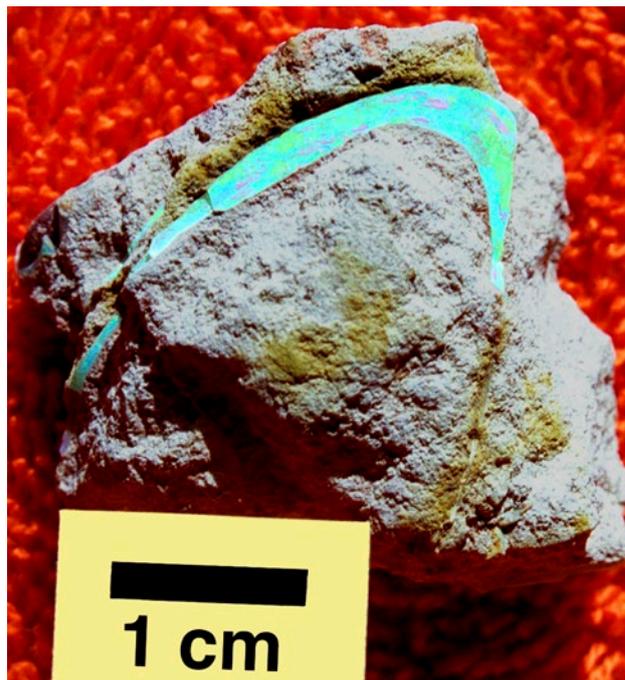
The hydrolysis which in most cases appears to be extensive and often complete, proceeds whether or not the fossils are replaced, or partly replaced by silica. This complete or extensive hydrolysis of fossil shells, calcareous remains, etc., 'gelatinises' the original microcrystalline carbonates which then coarsely re-crystallise when the sediments finally dehydrate and lithify.

Such fossils and debris distort or disintegrate if the sediments are disturbed while they are plastic. They 'weld' together and some develop rims like 'sooty' pyrite, glauconite, or haematite, and partial replacement by small patches of chalcedony in their centres or marginal to such fragments has also been observed (Chilingar et al.<sup>30</sup> 1967, p. 243). Remains like crinoid ossicles re-crystallise in optical continuity with patches of their limy matrix (Adams et al.<sup>31</sup> 1984, p. 44), or where the surrounding matrix is extensively re-crystallised in optical continuity with several crinoid plates or fossil remains, it is called "syntaxial overgrowths" (Adams et al.<sup>31</sup> 1984, p. 57).

The main point is that for replacement to occur, any fossil, buried log, shale layer, bedding laminae, or mineral precursor must be porous and gel-like so that the replacing ions, molecules, or silica particles can gain access to all parts of it by simple diffusion.

#### Other examples of replacement

A great many gelatinous mineral precursors can be 'replaced' at the diagenetic stage but actual replacement



**Figure 87.** A calcareous fossil shell (brachiopod) has been completely hydrolysed to a gelatinous hydroxy carbonate into which silicic acid [probably  $\text{Si}(\text{OH})_4$ ] has been able to diffuse to entirely replace the original shell with opal. This specimen is from Coober Pedy in South Australia.

within such permeable media involves exchange of a mobile ion for one adsorbed; of an ion for a charged particle (macromolecule); or a charged particle for an ion or another charged particle; or of a chemical radicle or group for a similar chemical radicle or macromolecular group freed by the reaction at the exchange site.

This could be confused with infill concretion where material infilling the gel meshwork or particle interstices is merely added to available spaces. Replacement actually substitutes for, and liberates to the dispersed phase, some part of such meshwork or adsorbed particle system. Many minerals like the common precursor silica gels in quartz veins become denser by simple "one-way traffic" diffusion (only water comes out in the reverse direction) of additional molecular species into the consolidating mineral mass. The diffusion gradient is maintained by release of surface adsorbed ionic species or by chemisorption which simply releases water as a reaction product.

The most obvious examples of silica 'replacement' are those where biogenic material or fossils have been replaced. The two examples illustrated are:

- 5 km SW of Calistoga in the Napa Valley in California, or some 12 km due south of Mount St Helena, is a petrified forest where a number of large red-

wood trees (*Sequoia sempervirens*) were felled by an ancient (3.4 Ma) nuée ardente. The very large tree trunks buried in the volcanic ash have been completely silicified (Figure 85).

- Calcareous fossils have been selectively replaced by silica with more extensive replacements recorded in bryozoans, tetracorals, tabulate corals, punctuate brachiopods (Newell et al.<sup>29</sup>, 1953; and Figure 87).

'Replacement' or silicification is a very real phenomenon which has been widely recognised for many years. The physico-chemical interactions by which it is achieved have remained somewhat obscure and ill-defined but replacement processes become clear and greatly simplified when the intrinsic properties of polymeric silica particle systems and the gelatinous mineral precursors of vein quartz are recognised.

### CONCLUSIONS

There is clear evidence for the conclusion that quartz veins are emplaced, not by 'hydrothermal solutions', but by gelatinous polymeric silica carried in the normal outflow of aqueous fluids and brines during diagenesis of sediments and to a greater extent from those that have been reliquefied as pastes and slurries. Fluids released during diagenesis carry suspensoids and sols of amorphous polymeric silica gel. A very limited amount of the transported silica is actually dissociated or ionic  $\text{Si}(\text{OH})_4$  at any stage.

Early in diagenesis fluids which escape from basin sediments tend to be more dilute suspensoids. These episodically 'break across' formations or form dykes and veins injected by hydraulic fracture from overpressured zones as the entrapped fluid-rich suspensoids containing the soluble and suspended matter thixotropically re-liquefy and break out.

The rapid re-setting or solidification which suspends wall rock fragments or contained mineral matter and which preserves the shape and form of the veins, is due to rheopexy of the hydrous polymeric silica. Once established, the crosscutting precursor veins, 'elvans', ore pipes, silicified zones, stockworks, lodes, stringer zones, etc. are permeable and continue to augment the general diffusion of fluids upwards and out of de-watering sedimentary materials.

Much, if not most of the silica accumulates in the quartz veins, pipes, or lodes, during this 'static' or 'slow seepage' stage. Pore fluids tend to be saturated with monomeric and oligomeric species of silicic acid and since these react preferentially with larger polymers rather than with other monomers or oligomeric spe-

cies, the open meshwork or more fluid-rich gels infill and become denser. Each successive mobilisation of precursor quartz vein material is a thicker or denser gel. It becomes whiter and 'cleaner' due to rejection during fluid flow of other differently shaped colloidal particles.

The aqueous chemistry of silica involves not only the dissolution of mono silicic acid but a sensitive equilibrium over a wide range of parameters to the oligomers and polymerisation to colloidal silica.

The crystallisation of quartz in veins and lodes is from dense polymers during final dehydration and long after the veins were emplaced. Crystallisation of these dense polymers entraps fluid inclusions (including some oil and organic matter), Boehm lamellae, and helicitic structures. Residual hydroxyl groups cause displacements and 'strain' in quartz crystal lattices so that virtually all naturally occurring quartz is 'strained' and has an undulatory extinction under the petrological microscope. The extinction in deformed and folded quartz is unrelated to any schistosity or regional cleavage.

All the observations relating to the occurrence and behaviour of quartz and silicification in nature are consistent with its aqueous chemistry and the formation of a wide range of particulate polymeric species from which quartz most commonly crystallises.

That quartz veins are actually emplaced as successively mobilised fluid particulate suspensoids of polymeric silica is indicated by:

- 1) The fluid nature of the injected vein quartz where the mobility and plasticity of the pre-crystalline quartz was clearly not due to melting or the exceedingly low solubility of quartz in water.
- 2) The actual occurrence of silica gels in some veins.
- 3) The occurrence of biogenic and carbonaceous matter, brines, and oil in small inclusions within the vein quartz.
- 4) The occurrence of vein quartz as breccia matrices for rotated angular fragments of heavier wall rock and other minerals such as magnetite, sulphides, etc. The suspension of these fragments in their quartz matrix is due to rheopexy of the pre-crystalline polymeric silica.
- 5) The re-brecciation, episodic re-liquefaction and re-intrusion of vein quartz is due to the thixotropy of the pre-crystalline polymeric silica.
- 6) The occurrence of some jasper, opal, and chalcedony veins confirms the mobility of their hydrated metacolloidal silica precursors.
- 7) The occurrence of colloform and Liesegang-type banding in some vein quartz or sections of quartz veins clearly indicates the metacolloidal and diffusive nature of the silica precursors.

- 8) The common occurrence of druse and miarolitic cavities in vein quartz and lodes is undoubtedly due to the syneresis and contraction of the original precursor polymeric silica of the veins.
- 9) The occurrence of siliceous oolites in cherts, jaspers, and vein quartz is due to syneresis of the oolite nuclei. Such concretionary rim growth can only occur in aqueous particle systems.
- 10) Surface catalysis or the enhanced crystal growth on a specific single face of very small crystallite nuclei results in the growth of slender acicular needles, rosettes, blades, spherulites, wheat sheaf structures, etc. where mineral crystals like rutile, tourmaline, chlorite, dawsonite, and magnetite are developed in vein quartz. This type of enhanced crystal growth is due to the gelatinous nature of the polymeric silica in the precursor host vein material.
- 11) Occurrences of pygmatic quartz veins clearly indicate viscosity related to fluid flow rates during intrusion of the non-Newtonian vein precursors.
- 12) Parallel striations on some faces of large quartz vein crystals reflect "crystal growth in steps" from a gelatinous surface coating.
- 13) Silica like potch, opal, or chert which replaces hydrolysed brachiopod shells clearly indicates a diffusive media in the host and a dispersed particulate phase of the replacing precursor silica.
- 14) Replacement of large tree trunks, originally largely cellulose, by silica clearly indicate the diffusive media of the decaying cellulose logs and the dispersion of the replacing particulate silica species.
- 15) Pervasive silicification of wall rocks, lode zones, stockworks, etc. and of the initially intruded polymeric vein quartz precursors is accomplished by minute dispersed monomeric and oligomeric silicic acid species which can diffuse within the silicifying host media.

The interactions and behaviour of the particulate and hydrous species of polymeric silica are more widely known and better documented than for any other colloid. This can therefore be applied to the mobilisation of silica into veins and lodes, the silicification of wall rocks, the formation of opal, the formation of pygmatic veins, the replacement of shells and tree trunks, etc. This behaviour of particulate silica species will then provide 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 selectively replace fine shale bands in syndiagenetic orebodies, etc.

## 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.

**Acicular:** describes a crystal that is needle-like in form. It is also used to describe rod-shaped sedimentary particles when their length is more than three times their width.

**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.

**Bingham Yield Point:** Charged particle systems "gelled" as cohesive, fractural, thixotropic, and viscoelastic solids may be envisaged as having many weak links between particles and fewer strong ones. Stress (application of force) disrupts weak linkages continuously and stronger linkages at an increasing rate until uniform viscous flow is achieved (the rate of shear is proportional to the shearing stress). In systems like natural sediments, viscous flow begins gradually through a plastic deformation stage. The theoretical point at which stress would be sufficient to initiate uniform viscous flow is called the Bingham yield point

**Boehm lamellae:** are chains or bands of fluid inclusions within quartz crystals that are usually deformed or folded. They are a feature of the precursor polymeric silica and unrelated to the later crystal lattice structure.

**Clay hydrolysis:** clay minerals are created by the reaction of water (hydrolysis) with more structured silicates to form sandwich-structured platelets that are fully hydrated with silanol terminations on their external surfaces. Hydrolysis of existing clay minerals therefore refers to the slow progression of hydrolysis inward along the octahedral (brucite or gibbsite) layers from the edge of the platelets. This further hydrolysis occurs during diagenesis when clay-rich sediments are 'soaking' for long periods in slightly alkaline seawater or exposed to pore fluids in thick sediment accumulations. The progression of the hydrolysis reaction between the tetrahedral and octahedral layers in clay platelets has been referred to as the "zip fastener reaction".

**Colloform texture:** describes the finely banded semi-circular or spheroidal layering of minerals that are precipitated from colloidal sols and crystallise from these gelatinous rhythmically layered precursors.

**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 medium 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.

**Crustiform:** describes a vein in which the mineral filling is deposited in layers on the wall rock.

**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. Henisch<sup>20</sup> (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 growth in a solid is usually by chemical reaction or ordered arrangement of molecules by heating or change of physical shape. Crystallisation from gas (sublimation) is by addition of molecules to active lattice sites (Pt. 1, Figure 230).

**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 Elliston<sup>1</sup>, 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 Elliston<sup>1</sup>, 2017.

**Displacive concretion:** is where the growth of the denser gel rimming layers round the synerectic nucleus displaces the surrounding weaker gel matrix.

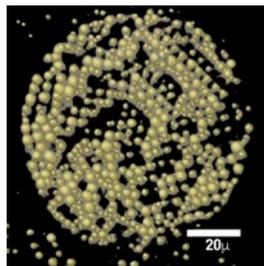


**Enhanced crystal growth:** occurs in gelatinous media because of the support for the initially delicate skeletal or needle-like crystals and the catalytic effect of certain gel coatings on solid crystal faces. The catalytic surface coating that enhances crystal growth in gels and facilitates growth and development of well faceted crystals directly from dispersed particulate species is very significant. Where the catalytic surface coating applies particularly to one facet of an initial small 'seed crystal', it can result in acicular or needle-like growth. Freedom of reactants to diffuse to and from a growing crystal face, and suppression of competing crystal nuclei also enhance the growth of crystals in gelatinous media. Yield of the medium to the developing crystal shape and conversion from the high-energy state of dispersed gel or sol particles to the low energy crystalline state also enhance the growth of crystals. For the crystallisation of synerectic accretions or concretions in deposits of gelatinous pastes or slurries, the pre-ordering due to close packing of the particles strongly accelerates crystal growth.

**Elvan:** A now largely disused Cornish term (from Celtic, "white or pale rock") for intruded rocks having the composition of quartz, quartz porphyroid, chert, etc.

and usually associated with intruded mineral deposits. An elvan may contain chlorite, tourmaline, fluorite, or topaz as accessory minerals.

**Framboids:** are globular clusters of iron hydroxy mono-sulphide in various stages of crystallisation to tiny pyrite cubes and grains that make up small raspberry-like spheroidal aggregates usually some 15 to 25 microns in size. Framboidal clusters are synergetic and they often nucleate infill concretion of additional hydroxy-sulphide mineral or form the nuclei for concretionary overgrowth. Some framboidal clusters display long range ordering patterns. Framboids are usually composed of iron sulphide but framboids of brunnkite (ZnS gel), sphalerite, native copper, digenite (CuS), chalcocite, covellite, native arsenic, and magnesioferrite or haematite have been recorded.



**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 defloccu-

lating 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 ( $\beta$  in Figure 1.7) 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 Part 1, Figure 5.

**Hydrophobic bonding:** hydrophobic (water rejecting) colloids such as emulsions can involve the adsorption of dispersible organic particles or molecules on solid surfaces such as silica (or sulphide minerals in the important example of the floatation process). This adsorption means that the adsorbed hydrophobic molecule or particle must displace the solvent (adsorbed water monolayer) from the surface. This binding of hydrophobic molecules or particles to surfaces by short-range chemical forces or longer range (electrostatic and van der Waal’s attraction) is called hydrophobic bonding.

**Illite:** this is a general name for a group of three-layer mica-like clay minerals intermediate between muscovite and montmorillonite. Illite flakes are generally much larger than montmorillonite platelets but they do not have the expanding lattice characteristics of smectites. However, the specific adsorption of potassium ions on the hydrolysed margins of illite clay platelets is some

500 times greater than their affinity for competing ions at the same molar concentration (equivalent solution strength). Illite accretions therefore readily crystallise to potassium feldspar. Illite is also called hydromica.

**Infill concretion:**

growth of gelatinous precipitate on small syncretic nuclei within intergranular pore spaces can either displace the sediment grains or simply fill the pore spaces without displacement. Infill concretions are rounded

“blobs” or nodules of relatively coarse sediment in which the pore spaces have been filled and the grains ‘cemented’ together by concretionary growth of the intergranular gel. Infill concretions may contain concentric or rhythmic bands like displacing concretions but the bedding and granularity of the original sediment are preserved within the concretion.

**Lepidocrocite:** is a ferroso-ferric hydroxide of iron  $[\text{FeO}(\text{OH})\cdot\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}]$  that occurs as a precursor mineral in the mixture of iron hydroxides that form the intrusive lodes and veins of haematite and magnetite.

**Liesegang banding:** concentric rings or bands are developed during syneresis of pre-crystalline natural sediment colloids (such as clay, chert, hydroxycarbonates, or siliceous shale). The Liesegang banding is a response to rhythmic changes in adsorption equilibria for pigment particles coating gel surfaces. The release/resorption of pigment particles is caused by different anion and cation diffusion rates as electrolytes are exuded from syncretic material. The bands parallel surfaces from which the fluid is lost.

**Lithomorph:** is the skeletal shape or pattern of rock mineral such as silica, that is left when cell walls or organic structures have been replaced and the original decayed organic matter removed.

**Macromolecule, macromolecular:** refers to very large molecules or very small crystallites such as clay platelets that by the continuity of their chemical linkages are essentially large molecules.

**Meshwork:** in relation to particle systems ‘meshwork’ is used to describe the static situation where particles of different shapes and sizes are randomly linked to each other by coulombic and van der Waal’s forces to form a diffusible, plastic, fractural, and thixotropic visco-elastic solid.

**Metasomatism:** means the changed body of the mineral or rock. See ‘Replacement’ for further discussion of the process in terms of current chemistry.



**Minnesotaite:** is a green to brown ferromagnesian silicate mineral commonly found in chloritic or iron-rich sediments.

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

**Montmorillonite:** this is a group of clay minerals that ‘swell’ by further reaction with water (hydrolyse). Typical montmorillonites have a three-layer crystal lattice with one sheet of aluminium-magnesium hydroxide (octahedral layers) between two sheets of hydrated silica (tetrahedral layers). A synonym for montmorillonite is smectite.

**Newtonian Fluids:** melts like that of ice and most other crystalline solids behave as Newtonian fluids. The rate of flow resulting from a shearing stress (application of a force) is proportional to the stress applied.

**Non-Newtonian Fluids:** the viscosity of non-Newtonian fluids varies with the rate of flow. This fluid behaviour is typical of thixotropic ‘gels’ (pastes and slurries) where the shear strength depends on interparticle linkages. As an approximation, it can be thought of as “the faster it flows – the more fluid and mobile it becomes”. In many systems involving the flow of pastes and slurries, it is referred to as “shear thinning”.

**Ossicle:** is a calcified individual element or piece of a skeleton such as an echinoderm shell. The term is usually used for larger pieces but has also been used for tiny bones, etc.

**Polymeric silicic acid:** the condensation of monomeric silica  $[\text{Si}(\text{OH})_4]$  forms oligomeric silicic acids and many varieties of silica gel including the naturally occurring ‘little balls’ of amorphous silica that are adsorbed on the surfaces of most sediment substrates.

**Ptygmatic:** this word is used to describe the appearance of ‘loopy’ disharmonic folds that are obviously not due to any uniform stress field or constant direction of deformation. Internal forces within the precursor pastes of the intruded substances develop this pattern of fluidal folding as they flow into soft visco-elastic host materials. Ptygmatic folding is due to the shear thinning properties of the intruded pastes (viscosity dependent on the rate of shear) and the fold patterns are preserved by rheopectic re-setting (see Figure 74).

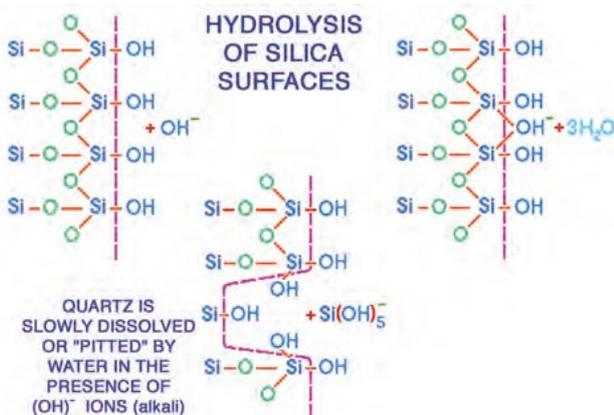
**Rheological separation:** is an important principle by which components of gel meshworks such as semi-consolidated sediments separate by differences in their fluid properties when the meshwork is physically disrupted or disturbed. The more mobile (less viscous or water-rich) components simply “flow out” of the agitated or disturbed pastes at the stage where its major compo-

nents would re-assume a non-fluid or more viscous gel condition.

**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 ( $\text{SiO}_2$ ). Other polymorphs of silica such as cristobalite or tridimite are less common.

**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” (Iler<sup>2</sup>, 1979, fig. 1.11.) This is shown diagrammatically as: -



Molecular dispersion from crystalline silica in water as  $\text{Si(OH)}_4$  is catalysed by hydroxyl ions of an alkali or base. Seawater is slightly alkaline and therefore silica (and most silicate surfaces) “disperse” by these surface reactions. In sea water and within marine sediments the small neutral  $\text{Si(OH)}_4$  molecules polymerise to short chain polymeric silicic acids called “oligomers”.

**Silicic Acid:** See Part 1, 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.

**Spherulite:** is a rounded or spherical body of acicular (needle-like) crystals radiating from a central point or small nucleus. Spherulites are a fairly common arrangement of feldspar crystals but are formed by many other minerals crystallising in diffusive media. Spherulites range in size from microscopic to several centimeters in diameter. Part 1, Figure 45 illustrates an example.

**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.

**Surfactant:** a particular class of solutes that show dramatic effects on surface tension are highly active in relation to surface adsorption and are called surfactants. They are dispersions or solutes such as soaps, detergents, long chain alcohols, and polymeric silica

**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.

**Tactoid:** is like a floc but distinguished by a high internal ordering of the particles within the cluster. In the process of manipulating the repulsive forces between particles to promote coagulation or flocculation, it is possible to achieve a structured or partly structured aggregate such as stacks of platelets, interlocking arrays of chains of particles, or bundles of aligned rods.

**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.

**van der Waals’ forces:** the strong attraction due to interaction between dipoles when small particles or molecules are in very close proximity to each other is called van der Waals’ forces of attraction. These forces exist between all matter in very close proximity.

**“Zip fastener reaction”:** see ‘Clay hydrolysis’

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