EARLY DIAGENETIC SILICA DEPOSITION IN ALGAL CYSTS AND SPORES: A SOURCE OF SAND IN BLACK SHALES?

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ABSTRACT

Devonian black shales that were deposited on the North American craton contain abundant Tasmanites cysts. Although these are typically flattened because of compaction, a small proportion of cysts is filled with diagenetic silica. The latter are spherical to ellipsoidal (0.1-0.5mm), and filled with chalcedony, micro- and megaquartz, and with single quartz crystals. Chalcedonic cyst fillings are preserved best in chert and phosphate nodules, whereas megaquartz and single quartz crystals are most common in shale matrix. Together with colloform textures, this suggests that the various silica types originated from recrystallization of early diagenetic silica deposits.

Thin sandstone beds that are found in the Chattanooga Shale (e.g., Bransford Sandstone) contain abundant quartz sand that is much coarser than the detrital quartz component of underlying black shales. Because of this, their quartz component is thought to have been transported over considerable distances from the basin margin. However, because certain shale horizons contain as much as 10% silicified cysts that upon reworking could have yielded quartz grains of fine to coarse sand size, the quartz component of these sandstone beds may actually have formed in situ.

Indeed, petrographic examination of the sandstone beds shows them to contain quartz grains with morphological and textural features of "cyst" quartz (e.g. rounding, sphericity, chalcedony, pyrite inclusions, lobate grain margins). Thus, silica deposition in algal cysts may provide a significant component of intrabasinal quartz sand in shale sequences. Distinction of this type of quartz from extrabasinal detrital quartz is important to the reconstruction of the depositional history of shale sequences.

INTRODUCTION

Mudrocks contain the largest share of quartz in the sedimentary column (Blatt, 1970). Quartz grains in mudrocks are thought to be an extrabasinal detrital component, carried into the basin by flowing water and winds. Potential sources are 1) fine-grained low-grade metamorphic rocks, 2) fracturing of coarser grains during weathering and soil formation; 3) abrasion during transport; 4) formation of quartz during clay diagenesis; 5) recrystallization of biogenic opal (Blatt, 1987), as well as combinations thereof. Of these, the first is considered the main source of quartz in mudrocks, whereas recrystallization of biogenic opal is not thought to contribute significantly (Blatt, 1987). Within mudrocks and shales, large detrital grains are thought to provide particularly valuable information concerning provenance and dispersal patterns (Potter et al., 1980). For example, coarse quartz sand in the middle of a shale basin would imply that the sand was derived from the shoreline and moved offshore by currents for possibly hundreds of kilometers.

I demonstrate here that in shales, diagenetic silica deposition in algal cysts and similar microfossils can produce quartz grains in the fine to coarse sand grain size range. With quartz grains of that size present, winnowing of a shale by waves could produce sandstone beds without the necessity of strong currents to move material over large distances.

GEOLOGIC SETTING

This study is based on petrographic examination of black shale samples from the Late Devonian Chattanooga Shale (central Tennessee and southern Kentucky) and New Albany Shale (southern Indiana). These shales were deposited in the Appalachian Basin, and their exposed thickness is approximately 10m in central Tennessee and 35m in southern Indiana. The shales commonly are interpreted as having accumulated in stagnant and comparatively deep water e.g. Potter et al., 1982). Recognition of undulose submarine erosion surfaces and hummocky cross-stratified (HCS) silt and sand beds (Schieber, 1994), however, as well as the presence of widespread bone beds (Conkin and Conkin, 1980), suggests relatively shallow water.

These black shales were deposited at the distal end of a westward thinning clastic wedge. Throughout it, they contain sporelike microfossils that commonly are referred to as Tasmanites (e.g. Winslow, 1962). In the thinnest and most distal portions of this clastic wedge, in central Tennessee and south-central Kentucky, the average accumulation rate of these shales was on the order of 10^3mm/year. This figure is based on thickness of stratigraphic sections, conodont data (Ettensohn et al., 1990), and age calibrations of Devonian conodont zones (Harland et al., 1990, Fordham, 1992). The very slowly deposited black shales of above distal areas contain the Tasmanites cysts with internal deposits of diagenetic silica that are described in this paper.

Tasmanites probably represents the cyst stage (phycoma) of fossil algae with affinity to modern planktonic green algae (Prasinophyta; Tappan, 1980). The latter can take on two distinct appearances during their life cycle, changing from motile quadriflagellate cells to cysts in which new motile cells develop (Tappan, 1980). Whereas the motile cell has no skeletal mineralized structures and consequently has little chance to become fossilized, the cyst walls consist of a complex "lipoid" substance that resists chemical breakdown (Tappan, 1980). What is found in the geologic record are probably cysts that settled to the bottom after their contained motile cells were released (Tappan, 1980).

Tasmanites and similar forms (Family Tasmanitaceae) are found in deposits from the Precambrian to the Holocene. Spherical prior to compaction, they are characterized by thick walls that are perforated by canals that open as pores to their interior (Tappan, 1980). In Late Devonian rocks of eastern North America, Winslow (1962) recognized several different species of Tasmanites, ranging in size from 0.05-0.81mm.

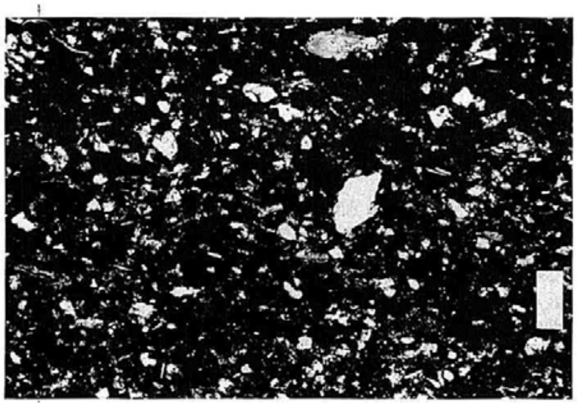

Figure 1: Photomicrograph of Chattanooga black shale that shows the typical size distribution of quartz grains. The one unusually large quartz grain just to the right of the center of the photomicrograph is 0.13mm long. It shows embayments and lobate/pointed projections, morphological features that are suggestive of an origin as a diagenetic cyst fill (compare to Figs. 2, 3, 4B, and 9). Scale bar is 0.1mm long.

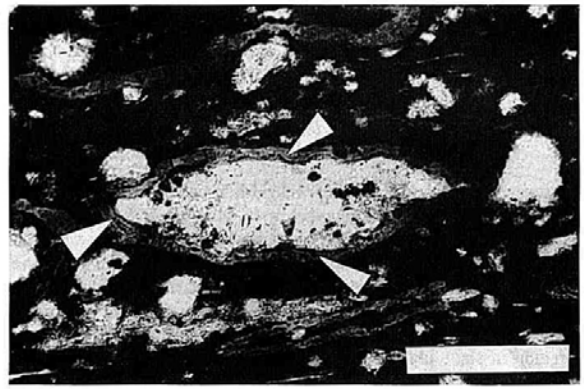

Figure 2: Photomicrograph of collapsed Tasmanites cyst. Cyst walls (arrows) are of medium to dark gray color. Center of photo shows cyst with internal diagenetic mineralization. Clear mineral is microquartz, opaque mineral is pyrite. Scale bar is 0.1mm long.

OBSERVATIONS

Late Devonian black shales that were collected for this study contain quartz grains that range from 0.002- in size (Fig. 1). The great majority of these quartz grains (at least 80%) are angular and fall into the 0.002-0.02mm size range (Ettensohn et al., 1988).

Although most Tasmanites cysts are completely collapsed due to compaction, in many thin sections one can find at least a few cysts that show some internal mineralization (Fig. 2). The latter often consists of pyrite, either as single crystals (0.005-0.015mm) or small clusters. In some thin sections cysts are completely filled with pyrite and have retained their spherical shape. Pyrite crystals within cysts are of the same size and morphology (octahedra and cubes) as those that are observed as dispersed grains and framboids within the shale matrix throughout the extent of the Chattanooga Shale.

Cysts that contain silica are comparatively less abundant than those that contain pyrite. Sampling of outcrops and stratigraphic sections in Tennessee and Kentucky showed that certain beds or horizons of shale that contain large (3-10 times the average) concentrations of Tasmanites may contain as much as 10% (by volume) silica filled cysts (Fig. 3). In contrast, other portions of the sequence may contain only a few scattered siliceous cysts.

Cyst walls surrounding sites of silica (or pyrite) deposition are in many instances still clearly visible (Figs. 4A and 4B). They are of amber color in thin section, and there is clear contrast of color and texture between cyst walls and their internal silica deposits, as well as between cyst walls and the surrounding rock matrix (shale or concretion). In some concretion samples, however, oval to irregular silica filled spaces (same size range as cysts) were observed where an enclosure by cyst material can not be documented (Fig. 5).

In thin sections, silica filled cysts range in size from 0.1-0.6mm. Their morphology is variable and ranges from perfectly spherical (Fig. 4A) to partially compressed (Fig. 4B). Spherical cysts are predominant in nodules (phosphate and chert) and in dolomitic shale, whereas cysts in normal shale matrix are usually flattened (Fig. 3). Phosphate nodules occur in most of the studied outcrops in variable amounts (Conant and Swanson, 1961), but chert nodules are very rare and only two were collected in the course of this study. All of the examined nodules (phosphate and chert) contained siliceous cysts. The latter vary in abundance from a few cysts per thin section to as much as 5%. The best preserved cysts and cyst fills are found in chert nodules, whereas in phosphate nodules cyst margins may be obscured due to recrystallization of phosphate. Within both types of nodules the majority of cysts (60-70%) shows oval to spherical outlines. Differential compaction of shale around nodules suggests that nodules formed in mud with 70-80% pore space, porosities typical for freshly deposited muds (Müller, 1967). In several nodules clearly identifyable remnants of radiolaria (Spumellarian forms) were observed.

Several different textural types of silica are found within cysts. Chalcedony, in many cases radial fibrous (Fig. 6A), length fast, and with colloform textures (Figs. 6B and 6C), is most common in cysts within chert and phosphate nodules. Chalcedony of this type may in places also show concentric growth bands that are perpendicular to the chalcedony fibers (Fig. 5). Nodules also contain cysts filled with microquartz (crystal size 0.02mm or smaller), megaquartz (crystal size larger than 0.02mm), and single quartz crystals. In thin sections where abundant silica filled cysts occur, all four types of silica may be present in variable proportions. Chalcedony and microquartz are generally the predominant quartz varieties in nodules. In contrast, siliceous cyst fills in shale matrix are strongly dominated by megaquartz and single quartz crystals. Microquartz, as well as small megaquartz grains, may show undulose extinction.

Pyrite also is found in silica filled cysts, and may occur along the margins of the cyst wall, in the central portions of the cyst, or both (Fig. 2). In a few cysts the silica fill consists of a chalcedonic rim and a center filled by megaquartz (Figs. 6A and 6C) or a single quartz crystal. In even rarer cases, bitumen may give microquartz and chalcedony fills a brownish appearance in thin section, and may also fill the central portion of cysts (Fig. 6B).

Because of the originally spherical shape of Tasmanites cysts (Tappan, 1980), many of the silica infills in nodules have rounded outlines and good sphericity. In shale matrix however,

where compression is more evident and many cyst fills consist of single quartz crystals, it is not uncommon to see unusually shaped quartz grains. Quartz grains may have irregular outlines and/or have embayments (Fig. 7), or they may show pointed to lobate projections (Fig. 4B). A number of silica filled cysts were observed where the originally spherical cyst wall has been indented, and silica extends outside of the cyst to form a spherical deposit (Fig. 5).

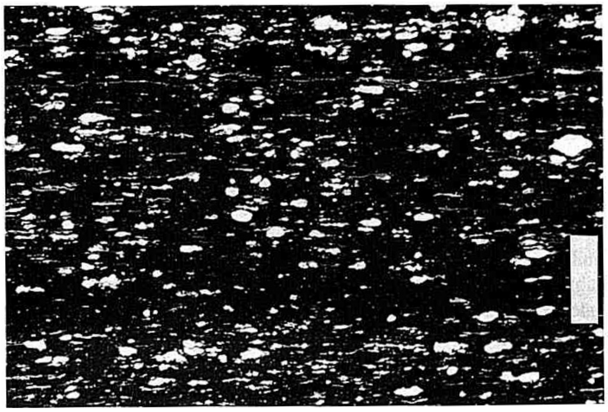

Figure 3: Photomicrograph of shale with abundant silica filled cysts (bright spots). Most cysts have been partially compressed. Scale bar is 0.5mm long.

erosive base, are friable, and are often difficult to see in outcrop. Field work during the summer of 1994 shows that in some instances in excess of 1 meter of shale have been eroded below them. In addition to fine to coarse grained quartz, these sandstone beds contain conodonts, fish bones, Lingula shells, and glauconite grains. Small quantities (less than 1%) of the latter grain types occur scattered throughout the Chattanooga Shale, but sandstone beds may contain up to 30%. In conjunction with the finding that these sandstone layers can contain conodonts from several successive conodont zones (Ettensohn et al., 1990), the above observations indicate that at least the fossil debris and the glauconite have been reworked from the underlying black shales. Some sandstone layers may also contain feldspar, zircon (Conkin and Conkin, 1980), and tourmaline grains, as well as silicified fossil debris that appears to have been derived from stratigraphic units older than the Chattanooga Shale (Conant and Swanson, 1961).

Examination of petrographic thin sections of these sandstone layers revealed the presence of abundant rounded quartz grains. Most of these are monocrystalline, but a number of them consists of several quartz crystals, chalcedony (length fast), and microquartz. Some of the chalcedonic grains may show colloform textures (Fig. 8A). Other quartz grains show irregular outlines, embayments, or pointed to lobate projections (Fig. 8B). A few sand grains were found that are still surrounded by cyst material (Fig. 8C). Some quartz grains also contain pyrite inclusions.

DEPTH AND TIMING OF SILICIFICATION

The observation that siliceous cysts are flattened in the shale matrix, but rounded when found in nodules, indicates that silica deposition commenced prior to nodule formation, and that nodule growth prevented cyst collapse during burial and compaction, and allowed completion of silica deposition in cysts (Fig. 9). Studies of

modern sediments suggest that phosphate nodules typically form immediately below the sediment-water interface (Blatt, 1992), probably no deeper than 10-20cm (Burnett, 1977). Likewise, differential compaction around phosphate nodules of the Chattanooga Shale suggests that these nodules formed in freshly deposited mud (see above). These observations indicate that silica deposition in cysts must have occurred very early in diagenesis.

The question how these cysts could have maintained their shape after early burial also bears on the timing of silicification. Because cyst walls are porous, and because by analogy to modern counterparts those cysts that settled to the bottom had probably released their content (Tappan, 1980), it seems unlikely that internal fluid pressure supported their original spherical shape upon burial. Alternatively, decay gases from decomposition of cyst material may have formed cavities (Reineck and Singh, 1980) that prevented collapse of cysts. That not the cyst walls, but rather an associated gas bubble supported the surrounding sediment, is suggested by the observation that deformed and partially collapsed cysts are found within spherical sites of silica deposition (Fig. 5). In that context, presence of silica deposits without a documentable cyst enclosure (Fig. 5) opens up the possibility that silica deposition could also occur within simple gas bubble cavities (not associated with cyst).

An analogous mechanism (mineral deposition in gas

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An analogous mechanism (mineral deposition in gas bubble cavity) has, for example, been proposed for formation of pyrite framboids in

muds (e.g. Rickard, 1970; O'Brien and Slatt, 1990). Observations on modern sediments suggest that spherical gas bubbles are most likely found very close to the sediment surface (Förstner et al., 1968). Above observations strongly suggest that silica deposition in

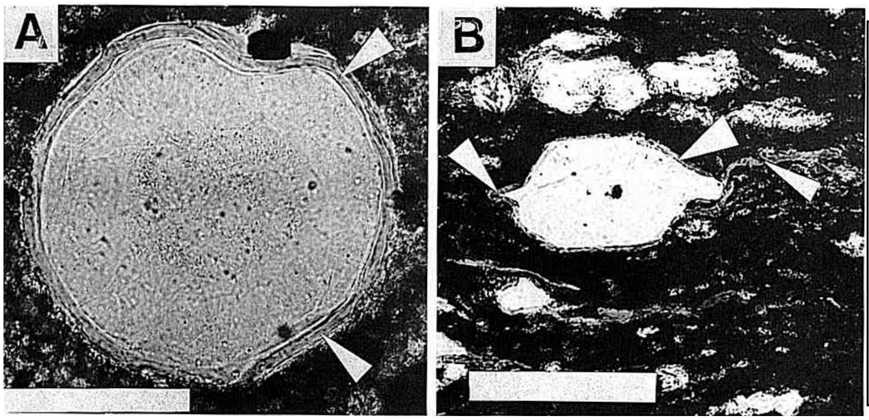

Figure 4: (A) Photomicrograph of spherical cyst fill in dolomitic shale. Arrows point out the organic cyst walls enclosing the quartz grain. Scale bar is 0.1mm long. **(B)** Closeup of partially compressed cyst. The cyst is filled with a single quartz grain. Arrows point out the organic cyst walls enclosing the quartz grain. Scale bar is 0.1mm long

Tasmanites cysts occurred (1) very early in diagenesis, and (2) very close to the sediment-water interface (cm's to tens of cm's).

SOURCE OF SILICA

Diagenetic silica deposition in algal cysts requires a source of dissolved silica. Pore waters can gain silica from (1) the alteration of volcanic ash (e.g. Surdam and Boles, 1979); (2) the transformation of smectite to illite (e.g. Hower et al., 1976); (3) the recrystallization of illite to muscovite (Totten and Blatt, 1993); (4) the dissolution of silicate minerals (e.g. detrital quartz, feldspars, heavy minerals; Füchtbauer, 1978); and (5) the dissolution of siliceous tests and spicules (e.g. Siever et al., 1965; Hurd, 1972). Because only a few volcanic ash beds are known from the Late Devonian of eastern North America (de Witt et al., 1993), and because samples examined for this study were from areas where no ash beds are found in the sequence, alteration of volcanic ash can be eliminated as a silica source. Because of very early diagenetic silica deposition, the smectite/illite transformation, which usually occurs at depths of 2-4 km’s (Hower et al., 1976) and temperatures between 55 and 200^{0}C (e.g. Freed and Peacor, 1989), can also be excluded as a potential source of silica. Likewise, silica release during late diagenetic to low-grade metamorphic recrystallization of illite to muscovite (Totten and Blatt, 1993) can be dismissed because conodont alteration (CAI < 1.5) indicates that these rocks were most likely never heated to even 90^{0}C during burial (Harris, 1979). Detrital quartz in mudrocks can undergo partial dissolution during diagenesis, possibly related to the presence of sheet silicates (Füchtbauer, 1978, 1979). This process however requires at least some overburden pressure (e.g. Bloch and Hutcheon, 1990), and is therefore incompatible with silica deposition close to the sediment-water interface. Feldspars and heavy minerals may dissolve as well in the course of diagenesis, but not at the very shallow depths (tens of cm’s) indicated by textural observations (Füchtbauer, 1978, 1979),

Dissolution of siliceous tests can be an important source of early diagenetic silica in sediments (e.g. Siever et al., 1965; Kastner, 1981). In the case of the Chattanooga Shale, however, remnants of siliceous fossil material (radiolaria) have only been identified in nodules. One possible explanation lies in the fact that seawater is at present strongly undersaturated with respect to silica (e.g. Calvert, 1974), and probably has been so at least since the advent of radiolarians (Schopf, 1980) in the Ordovician (e.g. Ramsay, 1977). In pore waters of modern sediments this causes extensive dissolution of biogenic (opaline) silica (e.g. Gieskes, 1983). Thus, the best chances for preservation of siliceous tests (e.g. radiolaria) are probably in those sediments where large initial concentrations of unstable amorphous silica (opaline skeletons, volcanic glass) lead to early supersaturation and reprecipitation of diagenetic silica in pore spaces between siliceous tests (e.g. Hein et al., 1990), or in early diagenetic concretions that encase unstable primary constituents before they can be dissolved (e.g. Massaad, 1973). Comparable observations were made by Murray et al. (1992), who found that highly corroded (albeit rare) radiolarians in shale interbeds of bedded chert sequences attested to diagenetic silica redistribution from shale to chert beds.Other than the radiolarian remains observed in this study, poorly preserved radiolaria were also found in phosphate nodules of the Chattanooga Shale (Conant and Swanson, 1961). In the laterally equivalent Late Devonian Woodford and Ohio Shales (Conant and Swanson, 1961) radiolaria have been observed as well (Holdsworth et al., 1982; Foreman, 1959). As in the Chattanooga Shale, radiolaria were only observed in early diagenetic nodules, and are absent in the black shale surrounding them. These observations suggest that preservation of biogenic silica in

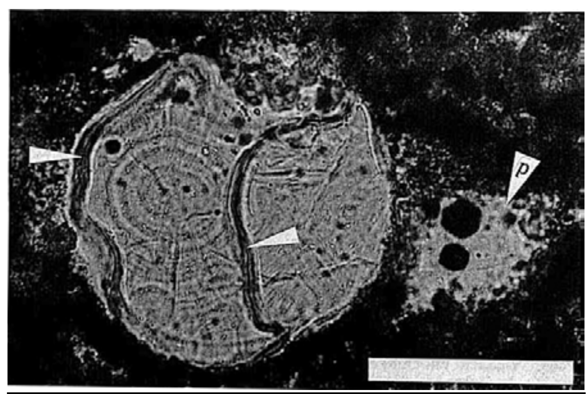

Figure 5: Photomicrograph of spherical quartz grain (chalcedony, length fast) in dolomitic shale. Cyst walls (arrows) have been indented, yet silica "fill" is still spherical. This suggests that silica actually filled a gas bubble associated with the decaying cyst. The silica fill within the cyst (left half of sphere) shows concentric growth rings and fibrous texture of chalcedony. With crossed polarizers a well developed extinction cross is visible. Arrow P shows an area of silica deposition that seems not associated with cyst material. Scale bar is 0.1mm long.

these black shales was very low. Radiolaria found in this study, as well as those described from the Ohio Shale (Foreman, 1959, 1963), are all thin-walled and delicate (primarily Spumellarians, plus some Nassellarians in the Ohio Shale). These forms are generally very susceptible to early diagenetic dissolution (e.g. Hein et al., 1990). Above observations, as well as the fact that both, the Chattanooga and the Ohio Shale were deposited in the same basin (Conant and Swanson, 1961), indicate that radiolaria were continually among the planktonic community of the Chattanooga sea, but only had a chance of preservation in early diagenetic concretions.

DIAGENETIC PROCESSES

Fibrous growth, colloform textures (Figs. 6A, B and C) and growth bands (Fig. 5) suggest that silica deposition started on the

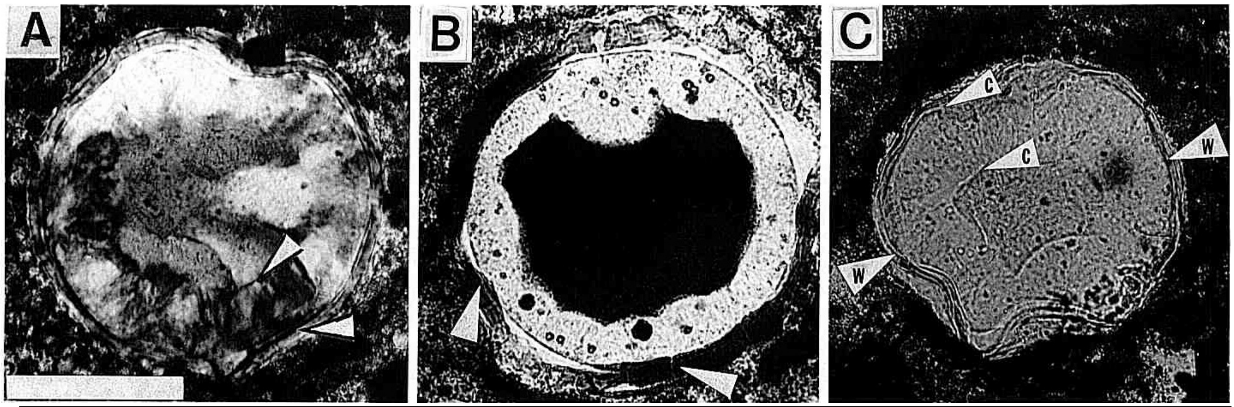

Figure 6: (A) Photomicrograph of same cyst as in Fig. 4A, but with crossed polarizers. Cyst shows a rim of chalcedony (between arrows) and a central fill of blocky megaquartz. Scale bar is 0.1mm long, all three photomicrographs in this figure have the same scale. **B)** Photomicrograph of spherical cyst in chert nodule. It is filled with chalcedony along the rim, and solid bitumen in the center. The bitumen/chalcedony margin outlines colloform texture. Organic cyst wall is pointed out by arrows. **(C)** Photomicrograph of spherical cyst in dolomitic shale. Cyst is filled with fibrous chalcedony along the margin (between arrows C), and with blocky megaquartz in the center. The chalcedony/megaquartz margin outlines colloform texture. Organic cyst walls pointed out by arrows W.

inner wall of cysts and gradually moved inward. The association of chalcedony with above features suggests that chalcedony was the initial silica deposit in these cysts. That chalcedony is a common deposit in sediment voids, nucleating on void surfaces and then growing inwards, was documented by Folk and Weaver (1952), and since then has been confirmed in numerous other studies (e.g. Heath and Moberly, 1971; Meyers, 1977; Frondel, 1978; Milliken, 1979; Noble and Van Stempvoort, 1989).

Most of our present knowledge concerning early silica diagenesis in fine-grained sediments comes from studies of siliceous oozes and resulting rocks, such as radiolarites, diatomites, and spiculites (e.g. Keene, 1976; Murata et al., 1977; Riech and von Rad, 1979; Isaacs, 1981). Considering that the silica for the cyst fills was most likely derived from dissolution of radiolarian tests (opal-A), it is tempting to think that, as in siliceous oozes, silica recrystallized from opal-A over opal-CT to chalcedony via a solution-precipitation mechanism (Murata et al., 1977; Kastner, 1979). Direct precipitation of quartz (chalcedony) without an opal-CT precursor, however, is also possible in situations where the dissolved silica concentration is below the solubility of opal-CT (Kastner et al., 1977). Textural features indicate that silica deposition in cysts of the Chattanooga Shale occurred very close (cm's to tens of cm's) to the sediment/water interface, and that the sediments at that point in time had 70-80% porosity. Thus, it is likely that buildup of dissolved silica in pore spaces of these sediments was constantly counteracted by diffusion of silica into the association of silica with pyriteurnishes an additional argument in support of that view. Fine-grained pyrite as seen in the Chattanooga Shale is a common feature of modern and ancient carbonaceous sediments, and is generally considered to occur very early after burial, when diffusion of seawater sulfate into the underlying sediment is essentially unimpeded (Berner, 1970; Berner, 1984, Sweeney and Kaplan, 1973). Thus, the observation that silica deposition coincides with early diagenetic pyrite formation, corroborates the above inference of essentially unimpeded silica diffusion between surface sediments and water column. Because of this it is quite likely that silica concentrations in pore waters of these shales never reached the solubility of opal-CT, and that, as initially concluded from textural features, chalcedony was the first precipitate in void spaces (Kastner et al., 1977). Additional factors that could have prevented or retarded early diagenetic opal-CT formation in these shales are their clay content (Kastner et al., 1977; Isaacs, 1982) and the abundance of organic matter (Hinman, 1990).

Thus, textural observations, the likely depth of silica deposition, as well as the above considerations regarding silica diffusion and solubility of silica phases, all lead to the conclusion that the silica is a very early diagenetic void-filling cement.

Assuming a net accumulation rate for these shales on the order of 10^{-3}mm/year, an initial porosity of 80%, and silica deposition at 20cm depth, silicification of cysts might have been in progress within 40,000 years after burial. Compared with other estimates for the age of early diagenetic silicification (e.g. Siever, 1983, millions of years; Bohrmann et al., 1990, hundredthousands of years), this is a short time indeed. In light of above conclusions, two further questions need to be addressed. What chemical conditions could have caused precipitation of chalcedony at such shallow burial depth's (cm's to tens of cm's), and what are the possible controls on the sites of silica deposition? These questions are addressed in the following paragraphs.

The abundance of organic matter and the early diagenetic pyrite testify to an environment with bacterial sulfate reduction and concomitant reduction of iron oxides and hydroxides (Berner, 1984).

The latter process tends to increase the pH of the system (Hesse, 1986) and enhance silica dissolution (Blatt, 1992). The relationship between silica solubility and pH is such that a small decrease in pH can cause a drastic reduction of silica solubility (Blatt, 1992). The latter may well be bacterially mediated, because experimental evidence suggests that metabolic processes of sulfate-reducing bacteria, through localized lowering of pH, promote silica precipitation (Birnbaum and Wireman, 1984, 1985). Equally well, silica complexing with sulfate might explain the apparent connection between sulfate-reducing bacteria and silica precipitation (Marshall and Chen, 1982). A mechanism of that kind would be consistent with the observed coincidence between early diagenetic precipitation of pyrite and silica. A possible connection between early diagenetic sulfate reduction and silica deposition has also been pointed in other studies (e.g. Wells, 1983; Ziljstra, 1987; Noble and Van Stempvoort, 1989).

Decomposition of organic material can, in a general sense, lead to local lowering of pH (Hesse, 1986) and consequent silica precipitation. Thus one might hypothesize that decomposition of Tasmanites cysts is the direct cause of silica precipitation. The cyst walls, however, are highly resistant to chemical breakdown. They, as well as their microstructures, are well preserved in these shales (Winslow, 1962), and they also survive chemical breakdown in a mixture of sodium hypochlorite and sodium hydroxide (a process used for conodont separation) without visible damage. Although a simple scenario, it thus seems unlikely that early diagenetic degradation of cysts could have been responsible for localized lowering of pH and selective silicification of cysts.

The inference that sites of silica deposition seem to coincide with gas-bubble cavities (Fig. 5) could suggest that the pore-fluid/gas interface is of some significance. Decay gases that might accumulate in such a bubble would probably be mainly CO_2 and H_2S. Interaction of these gases with surrounding pore waters would lower the pH and promote silica precipitation. Related to this issue is the high resistance of cyst material to chemical degradation (pointed out above), which suggests that the absence of cyst material from some silica deposits in nodules (Fig. 5) is not an artifact of preservation, but rather an indication that under certain circumstances silica was also deposited in gas bubble cavities not

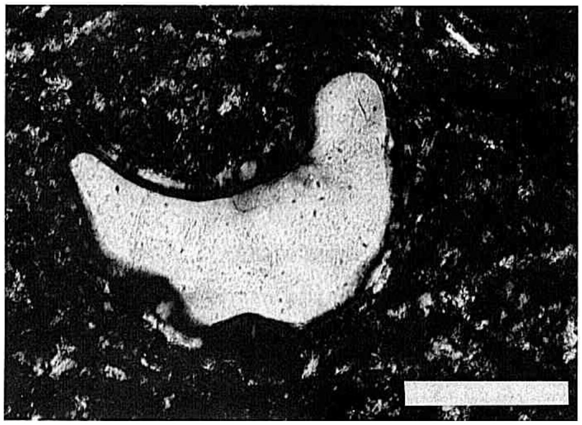

Figure 7: Photomicrograph of irregularly shaped cyst with fill of single quartz grain (crossed polarizers). Scale bar is 0.1mm long.

associated with cysts. Thus, chemical gradients at the pore-fluid/gas interface may indeed be of some significance for silica precipitation.

Petrographic observations from other studies (Holdaway and Clayton, 1982; Schmitt and Boyd, 1981) suggest that organic substrates may be preferred nucleation sites for quartz growth. The clear preference of early diagenetic silica deposition for the interior of Tasmanites cysts and associated gas-bubble cavities suggests that the cyst walls were a substrate for diagenetic silica precipitation. Thus, the composition of cyst walls or their coating may indeed have influenced silica nucleation/precipitation. Once suitable chemical parameters for chalcedony deposition had been established in the sediment, possibly mediated by sulfate-reducing bacteria, the presence of cyst material may then have hastened the onset of its deposition and largely controlled its spatial distribution.

Obviously, identifying the exact cause (or causes) for early diagenetic silica deposition in these shales poses an intriguing problem with many intricacies. It is, however, beyond the scope of this study to determine precisely which mechanism or combination of mechanisms produced the observed features. Additional studies will be needed (stable isotopes, microprobe) to address this question further.

Crystallization Sequence

Micro- and megaquartz in the center of chalcedony-rimmed cyst fills suggest that in general chalcedony formed prior to micro- and megaquartz. This general crystallization sequence has also been observed in other silica filled sedimentary voids (e.g. Folk and Weaver, 1952; Meyers, 1977; Frondel, 1978; Milliken, 1979; Noble and Van Stempvoort, 1989). Because silica diagenesis is strongly affected by temperature, pressure, time, as well as by the nature of the pore fluids (Kastner, 1979), the precise reasons for the change in crystal habit from fibrous (chalcedony) to equant (micro- and megaquartz) are difficult to discern. The general consensus, however, is that the change indicates either a decrease in silica concentration or some other change in pore water chemistry (e.g. Frondel, 1978). Indeed, the change in crystal habit may be a direct consequence of chalcedony precipitation along cyst walls. The latter would tend to lower overall silica concentration in pore waters and reduce silica access to cyst interiors. As a consequence, the rate of silica precipitation would decrease, and instead of chalcedony micro- or megaquartz would form (less defects and inclusions; e.g. Folk and Weaver, 1952; Milliken, 1979).

The observation that chalcedony and microquartz are most common in nodules, whereas megaquartz and single quartz crystals are typical for cysts in shale matrix, may reflect the ability of nodules to preserve early diagenetic mineral assemblages and textures (e.g. Potter et al., 1980). Age can also be factor in silica phase transitions, allowing for gradual change to coarser quartz varieties over time (e.g. Siever, 1983). Yet, given their Late Devonian age, one would expect that cyst fills in both nodules and shale matrix were affected similarly had time been the main factor. Because this was obviously not the case, a possible alternative explanation is that chemical conditions in areas of nodule formation differed sufficiently from those in the surrounding shale to cause differences in the type of silica deposits. The commonly observed flattening of silica filled cysts in shale matrix (Figs. 2, 3, 4B, and 7) probably reflects silica precipitation into cysts during early stages of compaction, prior to complete flattening of cysts (Fig. 9).

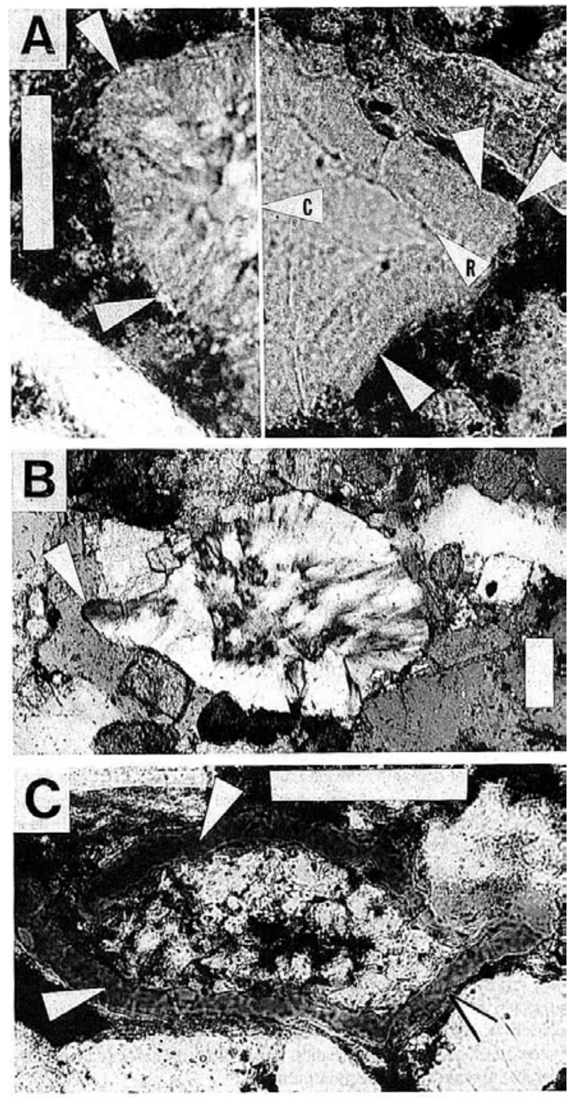

Figure 8: (A) Composite photomicrograph of quartz grain in sandstone (outer margin of grain pointed out by arrows). The portion of the photo to the left of arrow C was made with partially crossed polarizers (to show megaquartz texture), the photo of the right portion was made in plain light. This grain shows a rim of chalcedony (between arrows R), colloform texture, and a central portion consisting of megaquartz (arrow C). The chalcedony is length fast, and the basic texture is the same as in cyst fills of Figs. 7A and 7C. This is most likely a grain of reworked "cyst quartz". Scale bar is 0.05mm long. **(B)** Photomicrograph of chalcedonic quartz grain in sandstone layer of the Chattanooga shale. The pointed projection (arrow) resembles those in Figs. 2, 4A, and 9. Together with the chalcedonic texture (compare to Fig. 7A), this suggests that this is a reworked grain of "cyst quartz". Scale bar is 0.1mm long. **(C)** Photomicrograph of "cyst quartz" in sandstone layer of the Chattanooga Shale. The cyst fill consists of microquartz and some pyrite (opaque) and is still surrounded by organic cyst walls (arrows). Scale bar is 0.1mm long.

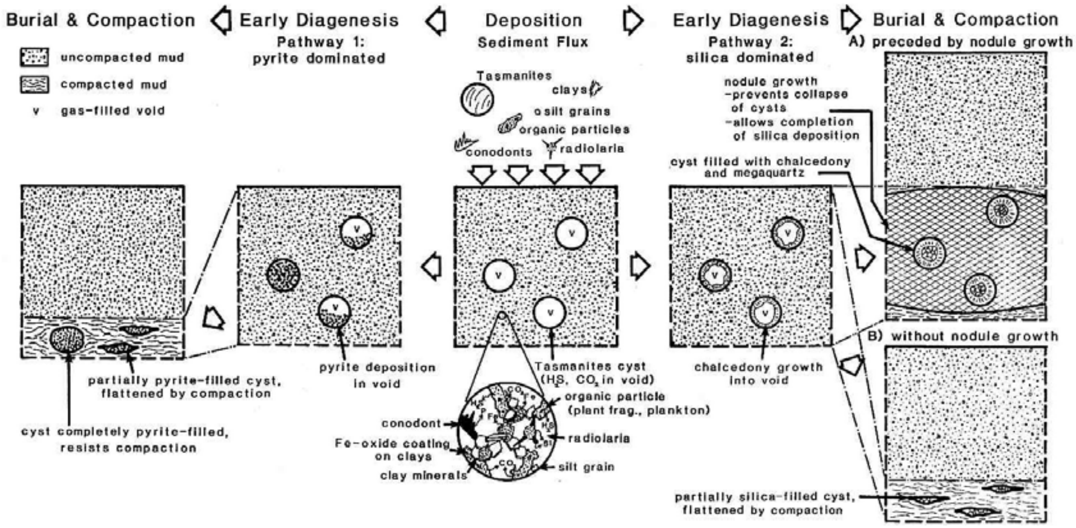

Figure 9: Schematic presentation of early diagenetic processes. Two potential pathways of mineral deposition in cysts are envisioned, one in which mainly pyrite is deposited (pathway 1), and one in which mainly silica is deposited (pathway 2). Enlarged view of initial sediment shows envisioned fabric of freshly deposited mud, and sources of early diagenetic products (CO_2 and H_2S from degradation of organic matter by sulfate reducing bacteria, silica in pore waters from dissolution of radiolarians, iron from dissolution of iron oxyhydroxides on clays, and phosphorous from dissolution of conodonts and fish debris). Which pathway is favored may depend on the initial sediment composition (few radiolaria = pathway 1; abundant radiolaria = pathway 2).

SYNTHESIS

Textural observations, as well as consideration of likely pore water chemistry and potential diagenetic processes, strongly suggest very early diagenetic mobilization of biogenic (radiolarian) silica, and its consequent precipitation in void spaces (mainly Tasmanites cysts). Initial silica deposits were probably mainly in the form of fibrous chalcedony. As envisioned (Fig. 9), early diagenetic deposition of silica in Tasmanites cysts provides a mechanism by which quartz grains can be produced that may be as large as 0.8mm. Because they formed probably at very shallow depth, these "in situ" quartz sand grains could have been concentrated in sand layers during episodes of shale erosion and reworking. In the process, cyst walls would probably have been destroyed/removed through mechanical abrasion and oxidation.

Although the Chattanooga and New Albany Shale contain a minor component of detrital quartz sand, no medium to coarse grained extrabasinal quartz sand is present. Thus, through no conceivable process of winnowing could the observed medium to coarse sand layers in the Chattanooga Shale have been produced from underlying black shales.

For the correct interpretation of sedimentary history and basin evolution, it makes a significant difference whether a sand layer in a shale sequence has been carried to its site of deposition from the basin margins, or whether the sand layer was produced by winnowing in place. Consequently, recognition of "in situ" quartz is of importance. The most useful features that seem to differentiate "cyst quartz" from normal detrital quartz are (1) chalcedonic grains, (2) grains with colloform textures, (3) irregular grains with embayments and lobate/pointed projections, and (4) quartz grains with pyrite inclusions. Rounding is not a useful criterion because it is also common in quartz grains that were recycled or underwent eolian reworking (Pettijohn et al., 1987).Quartz grains with above differentiating features are commonly found in thin sections of Chattanooga Shale sandstone layers (Fig. 8), but they are absent for example from quartz arenites and arkoses (Pettijohn et al., 1987, and personal observations). This suggests that "cyst quartz" was indeed incorporated into sandstone layers of the Chattanooga Shale. Although at least several of these sandstone layers contain clear extrabasinal components (feldspar, zircon, tourmaline, etc.), and probably contain a mixture of intra- and extrabasinal quartz grains, some of them may very well turn out to be of purely intrabasinal origin. Yet, even in a sand layer that consists entirely of intrabasinal "cyst quartz", the above diagnostic features would only be found in a minority of grains. The majority of grains would simply consist of a single quartz crystal and be of oval or rounded shape. To determine whether the latter grain population constitutes recycled "cyst" quartz, cathode luminescence (e.g. Milliken, 1994) and oxygen isotopes may prove useful. Because O^{18}/O^{16} ratios of igneous and metamorphic quartz grains differ distinctly from those of low-temperature diagenetic quartz (Savin and Epstein, 1970), determination of O^{18}/O^{16} ratios of "cyst" quartz would probably show it to be distinct from detrital quartz silt and sand. A study of cathode luminescence and oxygen isotopes is planned for the future quantitative evaluation of the significance of "cyst quartz".

The presence of silica filled cysts in shale sequences can also be considered an indicator of (1) mobilization and precipitation of silica very close to the sediment-water interface, (2) very low rates of sediment accumulation, and (3) the potential presence of biogenic silica in the original sediment. "In situ" sand should be looked for in all black shales that contain algal cysts, spores, and similar hollow biogenic structures. Early diagenetic formation of sand-size quartz grains, as evident in these shales, also invites speculations regarding the origin of quartz grains in the silt to clay size-range. According to

Blatt and Schultz (1976), the average mudrock contains close to 30% quartz with a mean grain size from 0.006 to 0.047mm. Slates, phyllites, and very fine-grained schists are considered the most important sources of quartz (Blatt, 1987).

Quartz grains in the Chattanooga Shale (and lateral equivalents) of east-central Kentucky range in size from 0.002-0.08mm and the majority of grains falls into the 0.002-0.02mm size range (Ettensohn et al., 1988). Thus, with respect to the size of quartz grains there is not much difference between the Chattanooga Shale and the average mudrock of Blatt and Schultz (1976). With an average quartz content of 40% (Ettensohn et al., 1988), the Chattanooga Shale contains distinctly more quartz than the average mudrock of Blatt and Schultz (1976). The large quartz content is even more remarkable if one considers studies of modern muds (Devine et al., 1973; Kolla and Biscaye, 1977) and ancient mudrocks (Blatt and Totten, 1981), that show decreasing abundances of quartz with increasing distance from the shoreline. In the case of the marine epicontinental shale studied by Blatt and Totten (1981), it was found, for example, that at a distance of 270km from shore, the average quartz content had decreased to 11%. In contrast, Late Devonian black shales of east-central Kentucky were deposited more than 400km from shore (Woodrow et al., 1988), but still contain on average 40% quartz (Ettensohn et al., 1988). In light of very early diagenetic silica deposition, this observation might even indicate that a substantial portion of the silt and clay sized quartz in these shales is of diagenetic origin. For example, fine-grained quartz could have been produced through disintegration of cyst fills during reworking. or through silica deposition in very small (silt and clay sized) pores. To determine whether this indeed happened (and how), and whether substantial portions of fine-grained quartz in shales could be of diagenetic origin, will require detailed chemical and petrographic (cathode luminescence) comparisons between cyst fills and the quartz silt fraction of these shales.

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