Diagenetic Origin of Quartz Silt in Mudstones and Implications for Silica Cycling

By

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Mudstones are the most abundant sedimentary rock type[1], containing most quartz in the sedimentary record[2]. This quartz is largely in the silt size range and has long been considered detrital, derived from continental crust[1]. Quartz silt in Late Devonian black shales of the eastern US was examined with backscattered electron and scanned cathodoluminescence imaging, and oxygen isotopes (+26 to $+30^{o}/_{oo}$ d $^{18}O_{V\text{-}SMOW}$) were measured with an ion microprobe. It appears that a substantial proportion of the quartz silt (up to almost 100%) is not detrital, but instead precipitated very early in diagenesis in algal cysts and other pore spaces, with silica derived from the dissolution of radiolarian or diatomic opal[3]. If other mudstone successions are found to contain comparable quantities of "in situ" quartz silt, various aspects of the sedimentary record in mudstones, such as estimates of paleoproductivity and perceptions of the dynamics and magnitude of global biogeochemical cycling of silica, may have been misinterpreted in the past.

Containing the bulk of recorded earth crustal history, mudstones are important for interpreting the geologic record. One critical source of information is determination of provenance (origin, source) of rock constituents, which in the case of mudstones are primarily quartz silt and clay minerals. Quartz grains are chemically and mechanically resistant, ideal characteristics for preservation of provenance record, whereas clay minerals are chemically labile and difficult to interpret.

We examined quartz silt grains (4-62µm) in mudstones from the Late Devonian Chattanooga and New Albany Shales of the eastern US with scanning cathodoluminescence (SEM-CL), because recent studies reveal textures that can be used to determine quartz provenance even in very small grains[4,5]. Gray scale pictures were produced using mono-CL rather than color-CL, as mono-CL is much faster at producing images with textural details at a spatial resolution of ~1μm, and for this study textural features are far more critical than color or CL wavelength. Two principal types of quartz silt were differentiated (Fig. 1): (1) grains with uniform to mottled luminescence (Fig. 1B), and (2) grains that were essentially non-luminescent (Fig. 1B). Whereas grains of type (1) compare well to metamorphic quartz described in a prior SEM-CL study[4], and were expected because of abundant metamorphic source rocks in the Acadian orogen to the east[6], the source of the essentially non-luminescent grains of type (2) is more problematic. Quartz of this type has not been observed previously by SEM-CL[4], but in light microscopic CL studies low luminescent quartz has commonly been interpreted as of low temperature authigenic/diagenetic origin[7,8].

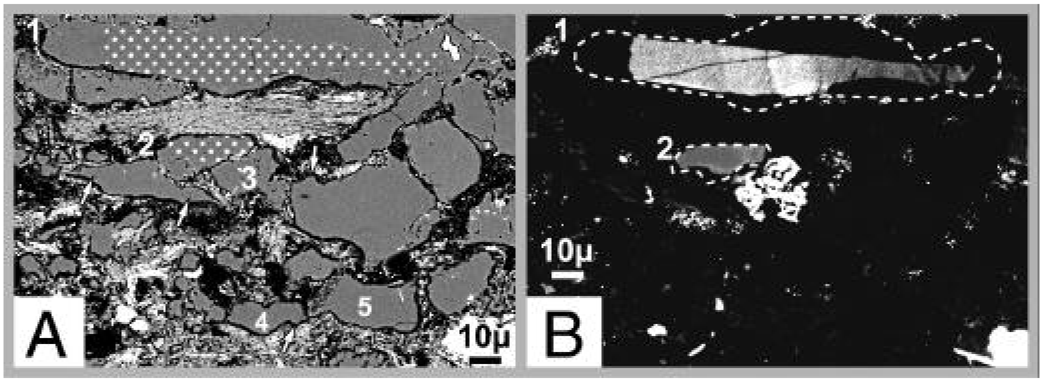

Figure 1: Quartz grains in a silt layer from Devonian mudstone succession. (A) BSE image (quartz grains are medium gray), (B) SEM-CL. Note in (A) embayments and lobate to pointed projections on a number of grains (white arrows), a first indication that they formed as diagenetic cyst fills. In contrast, quartz silt grains of detrital origin experience little rounding during transport and typically have angular outlines (Fig. 2B) with sharp corners[1]. (B) shows that there are only 3 grains that have strong luminescence. Stippled areas in (A) mark position of presumed metamorphic grains numbered 1 and 2. Dashed outlines in (B) mark BSE outlines of quartz grains with metamorphic core. The cores of grains 1 and 2 have SEM-CL characteristics typically found in metamorphic quartz[4], and grain 3 appears to be a metamorphic rock fragment with intergrown quartz, mica, and feldspar. Grain 1 and 2 have noticeable overgrowth of diagenetic quartz. About 80% of the quartz visible in (A) is essentially non-luminescent and presumed to be of diagenetic origin. The grains marked as number 4 and 5 in (A) are shown enlarged and enhanced in Figure 4C and 4D.

To verify this, quartz identified as authigenic by other methods in previous studies of these rocks[3,9] was examined using SEM-CL. In partially quartz cemented siltstone beds[9], metamorphic quartz is always considerably lighter than the dark authigenic quartz, although careful examination of this authigenic quartz reveals subtle CL variability and fine structure (Fig. 2B). Very early diagenetic quartz also fills large, sand size (0.1-1.0 mm) algal cysts in these rocks[3]. These cysts, remains of planktonic green algae, have walls that consist of complex lipoid-like substances that are highly resistant to chemical breakdown and bacterial degradation[10]. Dissolving radiolarian tests, still preserved in carbonate and phosphate concretions within these mudstones[3], provided silica for initial chalcedony precipitation in these cysts and associated pore spaces. Later on these chalcedony grains recrystallized to single crystal quartz grains[3]. Large silica filled cysts represent a source of "in situ" quartz sand and occur concentrated in lag deposits on erosion surfaces and sequence boundaries[9]. Thus, even though these sand size authigenic quartz grains constitute less than 1 percent of the deposited sediment volume, they are important for reconstructing the depositional history of these mudstones[3]. Although largely non-luminescent (Fig. 3A), these quartz sand grains also show fine structure through zones of variable luminescence (Fig. 3B). Other features that distinguish them from detrital sand grains are embayments and lobate to pointed projections[3] that resulted from deformation of the cyst walls during early burial.

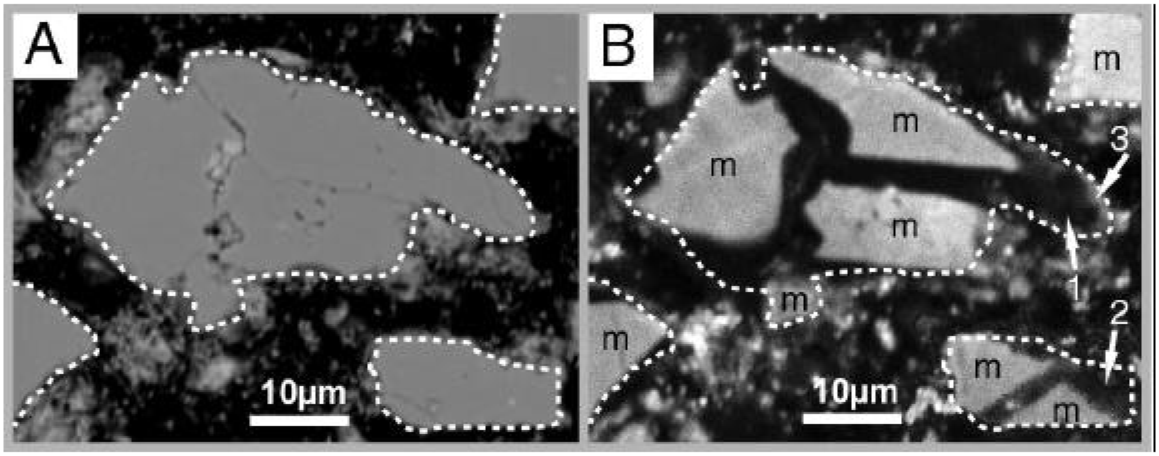

Figure 2: Detrital quartz silt with pore filling diagenetic quartz. (A) BSE image where quartz grains (outlined with dashed white line) are essentially uniform medium gray. (B) SEM-CL image that shows how metamorphic quartz grains (marked m) with light gray, uniform to mottled luminescence, have been fused together and overgrown by authigenic quartz of black to dark gray color (± non-luminescent). Arrows 1 and 2 show how quartz deposition not only occurred in the space between detrital grains, but also in the adjacent pore space. Arrow 3 points to a lighter colored rim (zonation) within pore space filling quartz.

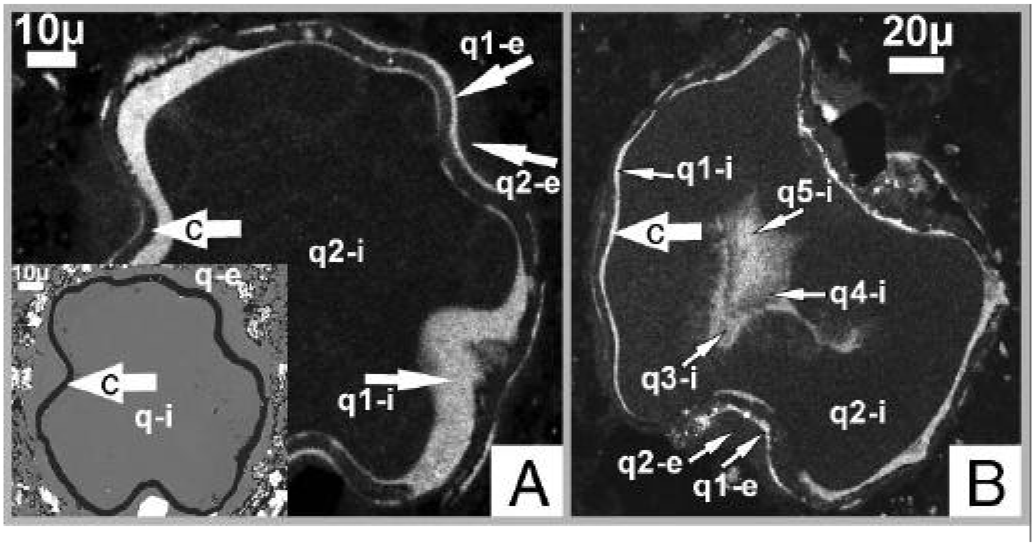

Figure 3: (A) SEM-CL image of sand size algal cyst that is filled and overgrown with quartz. The cyst underwent some deformation after deposition, and early internal silica deposition prevented collapse upon burial. Inset in lower left is a BSE image that shows the cyst wall (arrow c), quartz infill (q-i), and overgrowth (q-e). Although most of the diagenetic quartz is non-luminescent (q2-i and q2-e), there are thin rims of luminescent first generation quartz (q1-i and q1-e). (B) is similar to (A), but shows additional growth stages (q3-i, q4-i, and q5-i) with variable intensity of luminescence on the inside of the cyst (cyst wall marked with arrow C). Thus, although typically one sees only a very thin or absent first generation (q1, moderately luminescent), and a very prominent second generation (q2, non-luminescent) of diagenetic quartz, some cysts may show a larger number of concentrically growing quartz generations. During reworking the organic cyst wall and outer quartz deposits (q-e) are removed[3], and fragments of the latter are also a source of "in situ" quartz silt.

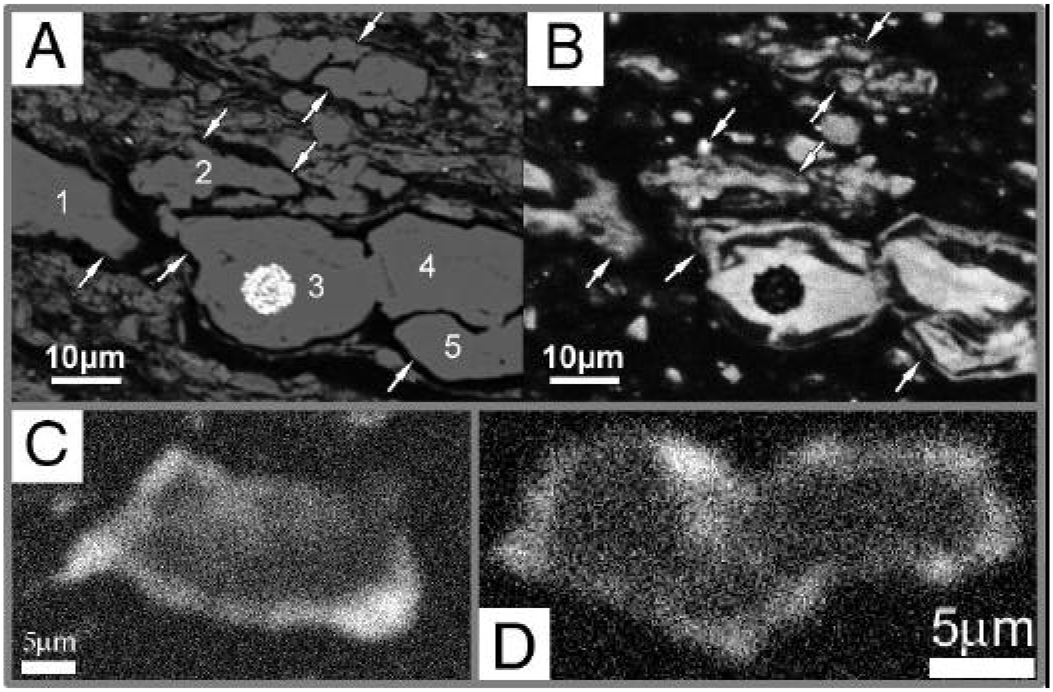

Figure 4: (A) and (B), a range of quartz grains in mudstone matrix. (A) BSE image, quartz grains are medium gray with ± uniform surface. (B) SEM-CL image of the same region. Arrows in (A) point out embayments and lobate to pointed projections that are an indication that these quartz grains formed as diagenetic cyst fills and are "in situ" quartz grains[3]. Arrows from (A) are repeated in (B) for reference. Larger grains that are marked 1 through 5 in (A) show zoned luminescence patterns in SEM-CL view, suggesting that they are of "in situ" origin (compare to Fig. 3B). Smaller grains in the upper half of the image also show zoned luminescence patterns. Quartz silt in this sample has highly positive $\delta^{18}O$ values and appears to be almost entirely of "in situ" origin. Grain 3 contains a pyrite framboid in the center, further evidence for early diagenetic quartz deposition. (C) and (D) are enlarged and enhanced images of quartz grains marked 4 (D) and 5 (C) in Figure 1. They show internal zonation and an outer zone of brighter luminescent quartz, as seen in "in situ" quartz grains shown in Figures 3. Thus, even though these quartz grains appear non-luminescent and featureless when contrasted with more luminescent metamorphic quartz (Fig. 1), they show the same internal features as found in bona fide "in situ" quartz grains.

Extrapolating these observations from the rare sand size quartz grains to the much more abundant silt size quartz grains in these rocks (Figs. 2, 3) strongly suggests that the low- to non-luminescent quartz silt grains seen in Fig. 1B are of authigenic origin as well. Textural features (Fig. 4), such as zones of variable luminescence, embayments, and lobate projections, indicate that low luminescence quartz silt probably also originated as early diagenetic infills of small algal cysts. The observation, in places, of thin, amber-colored films (the cyst walls) surrounding this type of silt grain (best seen in tapered wedges at the edge of thin sections) supports this assumption. In the studied samples, 50 to almost 100% (e.g. Fig. 4A/B) of the visible quartz silt shows the textural characteristics noted above, and we presume that it is of "in situ" authigenic origin. With an average quartz silt content of 40%[9,11], the authigenic quartz silt content of these Devonian mudstones may range from 20 to 40%. Although algal cysts were apparently the preferred locus of early diagenetic silica deposition in the case of our Devonian mudstones[3], this need not be the case elsewhere. In the absence of algal cysts, interparticle voids and other fossil pores (e.g. foraminifera tests), are alternative sites for early diagenetic silica deposition. As a consequence, some identifying textural features (e.g. grain outline) may differ as well.

Because of the small grain size and limitations of instrument resolution, textural identification of silt size authigenic quartz can not be performed at the same level of confidence than possible for larger, sand size grains. Nonetheless, our textural and CL discrimination of "in situ" authigenic quartz silt is confirmed by oxygen isotope measurements on individual quartz grains. Quartz silt grains texturally identified as either metamorphic or early diagenetic were analyzed with a modified Cameca 4f ion microprobe at Oak Ridge National Laboratory using extreme energy filtering[12]. Spot size was ~15μm, located in the center of the grain, and precision was $\pm 1\ ^{o}/_{oo}$ (1σ). Grains texturally identified as metamorphic have $\delta^{18}O_{V\text{-}SMOW}$ values of $+9.4 \pm 1.5\ ^{o}/_{oo}$ (1σ, n=7), consistent with metamorphic quartz. Grains identified as "in situ" authigenic quartz have much higher $\delta^{18}O_{V\text{-}SMOW}$ values of $+28.4 \pm 1.0\ ^{o}/_{oo}$ (1σ, n=5), typical for cherts and other types of diagenetic quartz[13]. Thus, textural identification of "in situ" quartz silt in these mudstones (Fig. 4) is confirmed by isotopic data. That a large proportion of quartz silt in mudstones may not be detrital, but rather of "in situ" authigenic origin, has significant implications for a variety of research areas, including basin modeling, paleoclimate, paleoproductivity, and biogeochemical silica cycling.

It was long thought that the quartz silt content of mudstones diminishes in offshore direction, and that the distribution of quartz silt in the mudstones of a sedimentary basin can be used to determine paleocurrents[1] and distance to shoreline[14]. If common, "in situ" quartz silt production could completely obscure expected patterns and lead to erroneous conclusions. For example, our Devonian mudstones contain between 20-50% quartz silt in nearshore settings[15], yet 300-600 km offshore quartz silt still averages 40%[9,11], clearly at odds with the expected offshore decline of quartz silt abundance[13]. Our finding that a large portion of the quartz silt can be assigned to authigenic, "in situ", silica deposition (Fig. 1) resolves this problem.

Previously, when large amounts of quartz silt were detected in distal mudstones, a high degree of sorting in the silt fraction was used to support eolian transport as an explanation for such anomalies[16]. However, "in situ" quartz silt as described here forms in organic particles (e.g. algal cysts) that have a limited size range, and thus is inherently well sorted. Because eolian dust in mudstones is used as a paleoclimate proxy[17], mistaken identification of "in situ" quartz silt as eolian will produce errors in paleoclimate assessments.

The bulk of opaline silica produced by radiolaria and diatoms in ocean surface waters never becomes incorporated into deep sea sediments because it dissolves while settling through several kilometers of water[18]. In shallow epicontinental seas this dissolution effect is much less important, and a substantial portion of surface production can be buried. Although opal invariably dissolves in the sediment, when silica concentrations are large enough authigenic quartz will precipitate[19]. Thus, "in situ" quartz silt can be considered a testament of vanished opaline constituents, and possibly as a proxy for surface productivity. If quantified and compared to C_{org} and P contents, recognition of abundant "in situ" quartz silt in a carbonaceous mudstone could provide evidence for productivity control, and could contribute to the ongoing discussion of whether carbonaceous mudstones owe their origin to high surface productivity or to enhanced preservation in anoxic basins[20,21]. It might also help identify paleoproductivity in sediments that are not characterized by abundant C_{org} and/or P. The Devonian mudstones we studied are carbonaceous and were long considered a consequence of anoxia[22]. Recent observations in support of shallow water conditions and some oxygen in the water column[9,15] suggest instead high surface productivity as a cause of abundant organic matter accumulation. This view is supported by our observation of large amounts of "in situ" quartz silt.

Identification of abundant authigenic quartz silt in mudstones may help explain the large gap in the geologic record between the earliest fossil occurrences of diatoms (early Cretaceous, ca. 120 Ma)[10], and molecular evidence suggesting that they appeared during the Permian (ca. 266 Ma)[23] or early Paleozoic[24]. This gap has been attributed to diatom dissolution in the past[25], and our results suggest that vanished diatoms may have been preserved as "in situ" quartz silt.

Failure to recognize this authigenic component may also impact our understanding of the dynamics and magnitude of the global biogeochemical cycling of silica[17] and secular trends of silica cycling[26]. As described here, "in situ" quartz silt is linked to opaline silica flux (radiolarians, diatoms), and thus to dissolved silica flux from continents and mid-oceanic ridges[18]. Secular changes of the "in situ" quartz silt component in mudstones may therefore reflect changes in weathering and climate (continental dissolved flux), as well as changes in the rate of seafloor spreading[18].

By volume, most mudstones are deposited along basin margins[1]. In those areas terrigenous clastic deposition dominates and biogenic silica, the source of "in situ" quartz silt, will be of little consequence for the total sediment budget. Under those circumstances, quartz silt abundance is probably a useful indicator of shoreline proximity[14]. Distal mudstones, although of lesser volume, tend to cover large areas of depositional basins, occupy a disproportionate share of geologic time, and contain a more complete sedimentary record. Due to their slow accumulation, biogenic sedimentation is much more significant and the "in situ" quartz silt component, as illustrated with our Late Devonian mudstones, should be most noticeable. Late Devonian carbonaceous mudstones occur over large portions of the North American continent[27], and mineralogical data from a broad range of localities show anomalous quartz contents[28]. A study of the Late Devonian Antrim shale of the Michigan Basin even reports that more than half of the quartz silt was of authigenic origin[29]. Petrographic re-examination (by light microscope) of Late Devonian mudstones from across North America reveals abundant quartz silt grains that are texturally identical to those identified here as authigenic quartz infills of algal cysts. Apparently, "in situ" authigenic quartz silt is an abundant and widespread component of Late Devonian carbonaceous mudstones in North America. Considering that many transgressive episodes in Earth history were accompanied by slowly deposited and often carbonaceous mudstone blankets[30], it is likely that many other mudstone successions contain a significant "in situ" quartz silt component. Although it remains to be determined how abundant this component is in mudstones of varying ages, conditions that produced our Late Devonian mudstones were not unique to that period in Earth history. If authigenic/intrabasinal quartz silt is widespread, a large portion of the sedimentary record may have been misinterpreted, with important implications in a variety of research areas. Although the identification of authigenic quartz silt is not a trivial matter, its recognition offers a variety of new opportunities to better understand the geologic record.

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