[PS]Intraorganic Nanoquartz Associated with Algal Bituminite within the Devonian Marcellus Formation, Ritchie County, West Virginia: Potential Origins and Implications*

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Abstract

The association between organic matter (primary hydrocarbon reservoir) and authigenic quartz (brittleness indicator) is a critical relationship to understand when assessing reservoir quality in unconventional resource plays like the Marcellus Shale in the Appalachian Basin. Argon-ion milling and field emission scanning electron microscopy/energy dispersive X-ray spectroscopy was performed on a Marcellus sample (11% TOC by weight; 24% TOC by volume) from Ritchie County, West Virginia. Within much of the kerogen, interpreted as algal bituminite, nanometer-scaled quartz crystallites (~125 nm aggregates of smaller <50 nm 'blobs') were observed in a chain morphology – likely a 'lattice' in 3D. Nanoquartz lattices (NQLs) were often observed emanating from authigenic 'in situ' quartz silt, suggesting a genetic relationship between the two. The NQLs observed bear remarkable similarity in both scale and morphology to extracellular biomineralization generated by iron-reducing bacteria, which suggests the possibility of a microbial origin for biogenic quartz within the Marcellus. Where present, NQLs constitute a previously unrecognized volume of quartz which, due to the individual cystallites' nanometer-scale and the intimate association with organic matter, is unobservable with light microscope, standard automated SEM analyses (e.g. QEMSCAN), and likely even XRD. Concerning reservoir quality evaluation, NQLs may outline potential cleavage planes within otherwise ductile organic matter. These cleavage planes could act as pre-propped permeability paths connecting intraorganic nanoporosity to hydraulically stimulated fractures. The prevalence of the NQL phenomenon in the Marcellus is unknown; more extensive sampling is necessary. Future analysis is needed to ascertain the origins (isotope work, if possible on micrometer and nanometer-scaled minerals) and implications (rock mechanics) of NQLs.

Intraorganic Nanoquartz Associated with Algal Bituminite within the Devonian Marcellus Fm., Ritchie Co., WV: Potential Origins and Implications

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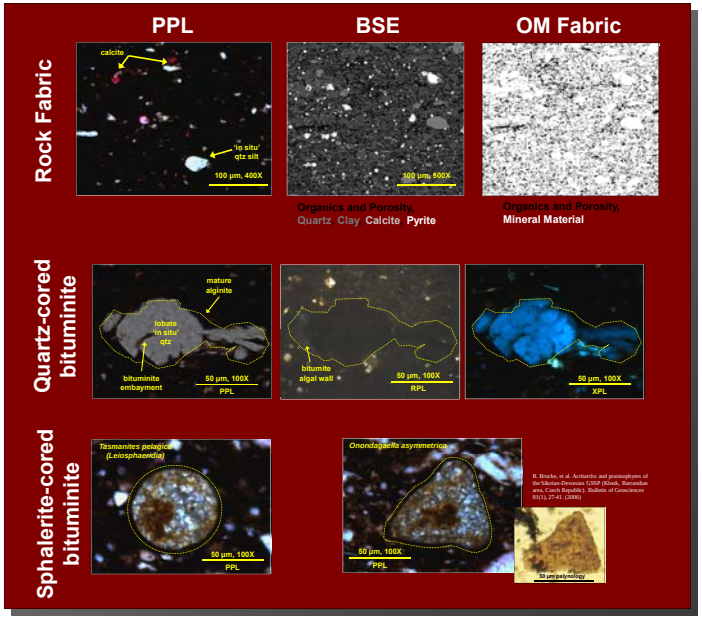
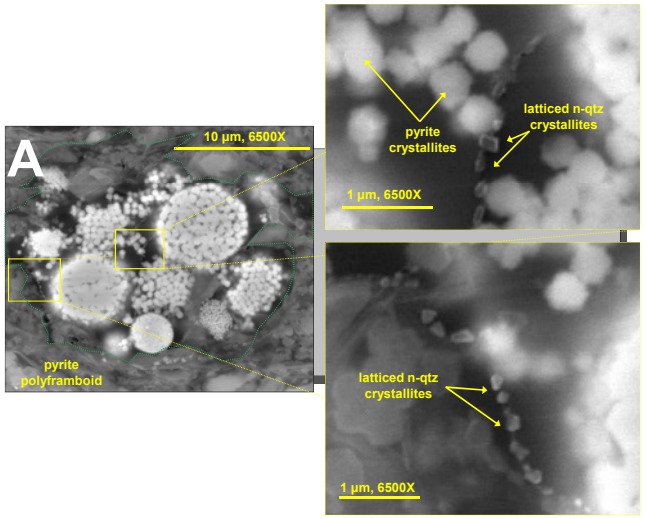
ABSTRACT

The association between organic matter (primary hydrocarbon reservoir) and authigenic quartz (brittleness indicator) is critical relationship to understand when assessing reservoir quality in unconventional resource plays like the Appalachian basin's Marcellus shale. Argon-ion milling and field emission scanning electron microscopy / energy dispersive X-ray spectroscopy was performed on a Marcellus sample (11% TOC by weight; 24% TOC by volume) from Ritchie Co., WV. Within much of the kerogen, interpreted as algal bituminite, nanometer-scaled quartz crystallites (~125 nm aggregates of smaller <50nm 'blobs') were observed in a chain morphology – likely a 'lattice' in 3D. Nanoquartz lattices (NQLs) were often observed emanating from authigenic 'in situ' quartz silt, suggesting a genetic relationship between the two. The NQLs observed bear remarkable similarity in both scale and morphology to extracellular biomineralization generated by iron-reducing bacteria [9] [10], which suggests the possibility of a microbial origin for biogenic quartz within the Marcellus. Where present, NQLs constitute a previously unrecognized volume of quartz which, due to the individual cystallites' nanometer-scale and the intimate association with organic matter, is unobservable with light microscope, standard automated SEM analyses (e.g. QEMSCAN), and likely even XRD. Concerning reservoir quality evaluation, NQLs may outline potential cleavage planes within otherwise ductile organic matter. These cleavage planes could act as pre-propped permeability paths connecting intraorganic nanoporosity to hydraulically stimulated fractures. The prevalence of the NQL phenomenon in the Marcellus is unknown; more extensive sampling is necessary. Future analysis is needed to ascertain the origins (isotope work, if possible on micrometer and nanometer-scaled minerals) and implications (rock mechanics) of NQLs.

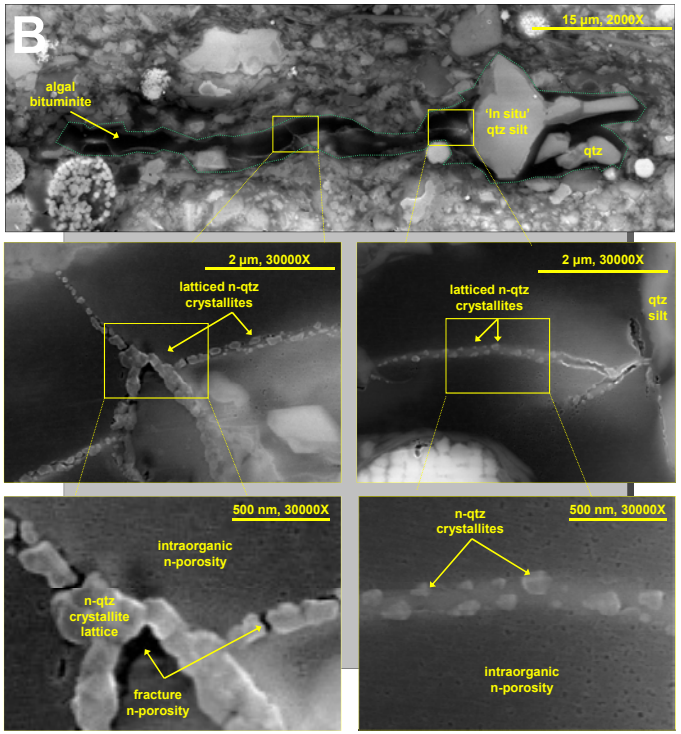
LIGHT MICROSCOPE OBSERVATIONS



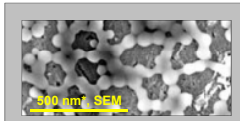


AIM / FESEM OBSERVATIONS

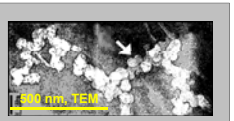
All images taken with FEI Quanta 650 FEG: SEI, 20 kV
Argon-ion milling with JEOL SM-09010 Cross Section Polisher



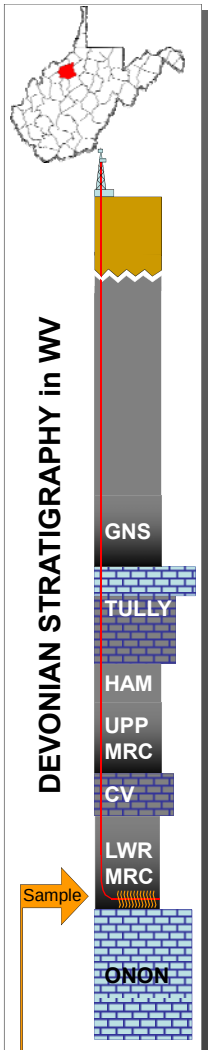
LABORATORY EXPERIMENTS



Kröger et al. (2002) – *in vitro* silica globule 'lattice' formation after 5 minutes in solution of silaffins and polyamines (found in bacterial extracellular polymeric substances).
*Image scaled ¾ to account for *in vitro* conditions.



Furukawa and O'Reilly (2009) – silica globule chain formation (after 7 days) observed in iron (III) reducing bacteria extracellular polymeric substances. image inverted to highlight silica globules.



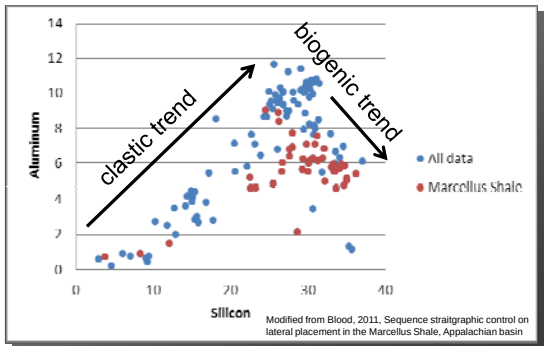
Wt. / Vol. % XRD

11 / 24% Organics
48 / 38% Quartz
1 / 1% K-Feldspar
3 / 3% Plagioclase
4 / 4% Calcite
3 / 3% Dolomite
1 / 1% Apatite
13 / 5% Pyrite
7 / 6% Smectite
4 / 3% Chlorite
16 / 12% Illite

Geochemistry SRA

T_{MAX} : 474
HI: 45.1
OI: 5.2
%Ro : 1.4

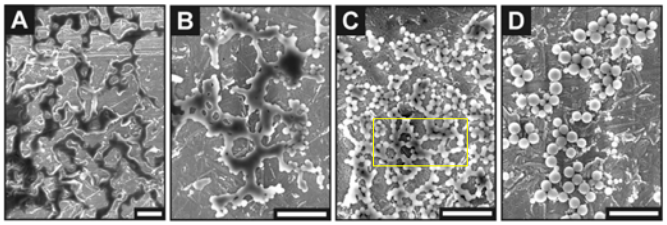
MARCELLUS BIOGENIC QUARTZ



Modified from Blood, 2011, Sequence straitgraphic control on lateral placement in the Marcellus Shale, Appalachian basin

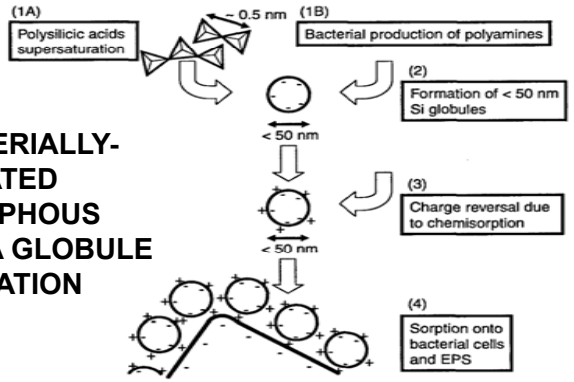
MICROBIAL MECHANISM

in vitro SILICA LATTICE FORMATION



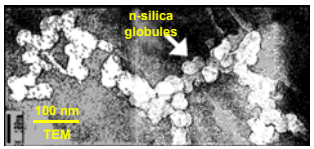
Kröger et al (2002) Figure 4 Modified. SEM images of in vitro amorphous silica morphogenesis, to imitate biomineralization. 'Latticed' structures formed at (A) 3.5 minutes, (B) 4.5 minutes, (C) 5 minutes, and (D) 8 minutes after addition of silaffins to a buffered monosilicic acid solution. Silaffins (and polyamines) are zwitterionic and induce silica polycondensation. Scale bars are 2 microns. Silica is confirmed with EDX. The in vitro environment of this experiment resulted in silica spheres 4-7 times larger than found in nature.

BACTERIALLY-MEDIATED AMORPHOUS SILICA GLOBULE FORMATION

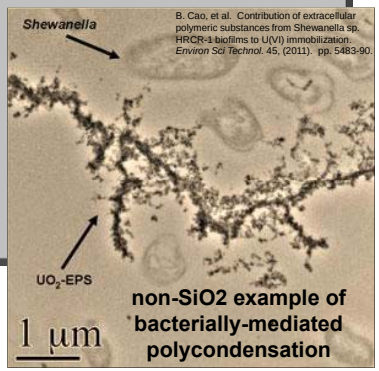


Furukawa & O'Reilly (2007) Figure 6 Modified. Proposed mechanism for the formation of observed amorphous silica globules and their association with bacteria and extracellular polymeric substances (amorphous organic matter) from experimental systems. (Step 1A) Dissolution of montronite [or, for example, radiolarians] yields supersaturation of aqueous polysilicic acids with respect to amorphous silica; (Step 1B) Fe(III)-reducing bacteria [or, for example, sulfate-reducing bacteria] produces polyamines; (Step 2) Polysilicic acids are further polymerized to form <50nm amorphous silica globules with the help of polyamines; (Step 3) Negatively charged surface of amorphous silica globules become positively charged due to chemisorption; (Step 4) Positively charged amorphous silica globules are sorbed onto net negatively charged surfaces of bacteria and extracellular polymeric substances).

SILICA CHAIN IN IRB EPS



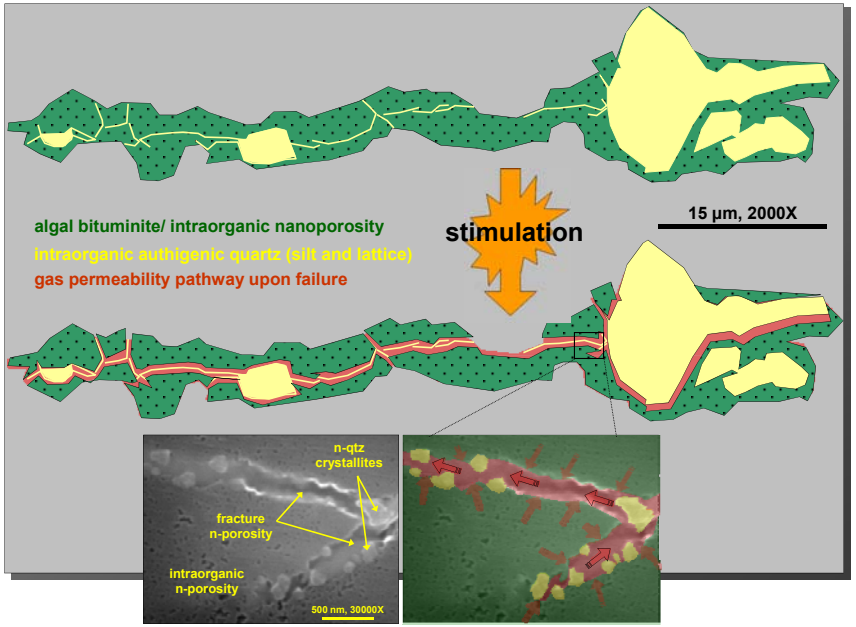
Furukawa & O'Reilly (2007) Figure 4d Modified. TEM image of rapidly formed amorphous silica globules (black; confirmed by EDXS) organized in a chain structure, in the immediate vicinity of iron(III) reducing bacteria 'extracellular polymeric substances' (i.e. gums generated by microbes)



B. Cao, et al. Contribution of extracellular polymeric substances from Shewanella sp. HRCR-1 biofilms to U(VI) immobilization. *Environ Sci Technol.* 45, (2011). pp. 5483-90.

EQT RESERVOIR TECHNOLOGY

NANO-QUARTZ LATTICE PHYSICAL IMPLICATIONS



CONCLUSIONS

1. NQLs represent a **previously unrecognized volume of quartz** in the Marcellus Formation (not readily resolvable without ion milling and SEM due to its nanometer scale and inherent relationship with opaque organic matter). Such quartz may be present in other organic-rich formations.
2. Opaline silica precipitation may have been **mediated by microbial action**, such that authigenic silica formed during eogenesis. This silica may be the precursor to the more well-formed authigenic quartz silt observed ubiquitously throughout the organic-rich portions of the Marcellus. The presence of abundant authigenic quartz therefore may be indicative of depositional environment.
3. The lattice morphology of nanoquartz may outline **potential cleavage planes** within organic matter, and therefore may represent the first open and permeable pathways between HC-filled intraorganic nanopores and stimulated fractures connected to the well bore. In this case, latticed nanoquartz may behave as a **natural proppant**.

FUTURE ANALYSES

Nano-quartz lattices have only been observed in abundance in one sample. To ascertain its prevalence, further analysis is necessary. Samples of variable kerogen type (geochemical and maceral), degree of maturation, and sequence stratigraphy could yield more insight into lattice abundance and generation.

Isotope analysis of the authigenic quartz and sphalerite would help determine if the origins are biogenic or hydrothermal; this may be experimentally difficult given the micrometer and nanometer scale.

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