Quartz Cementation in Mudrocks: How Common Is It?

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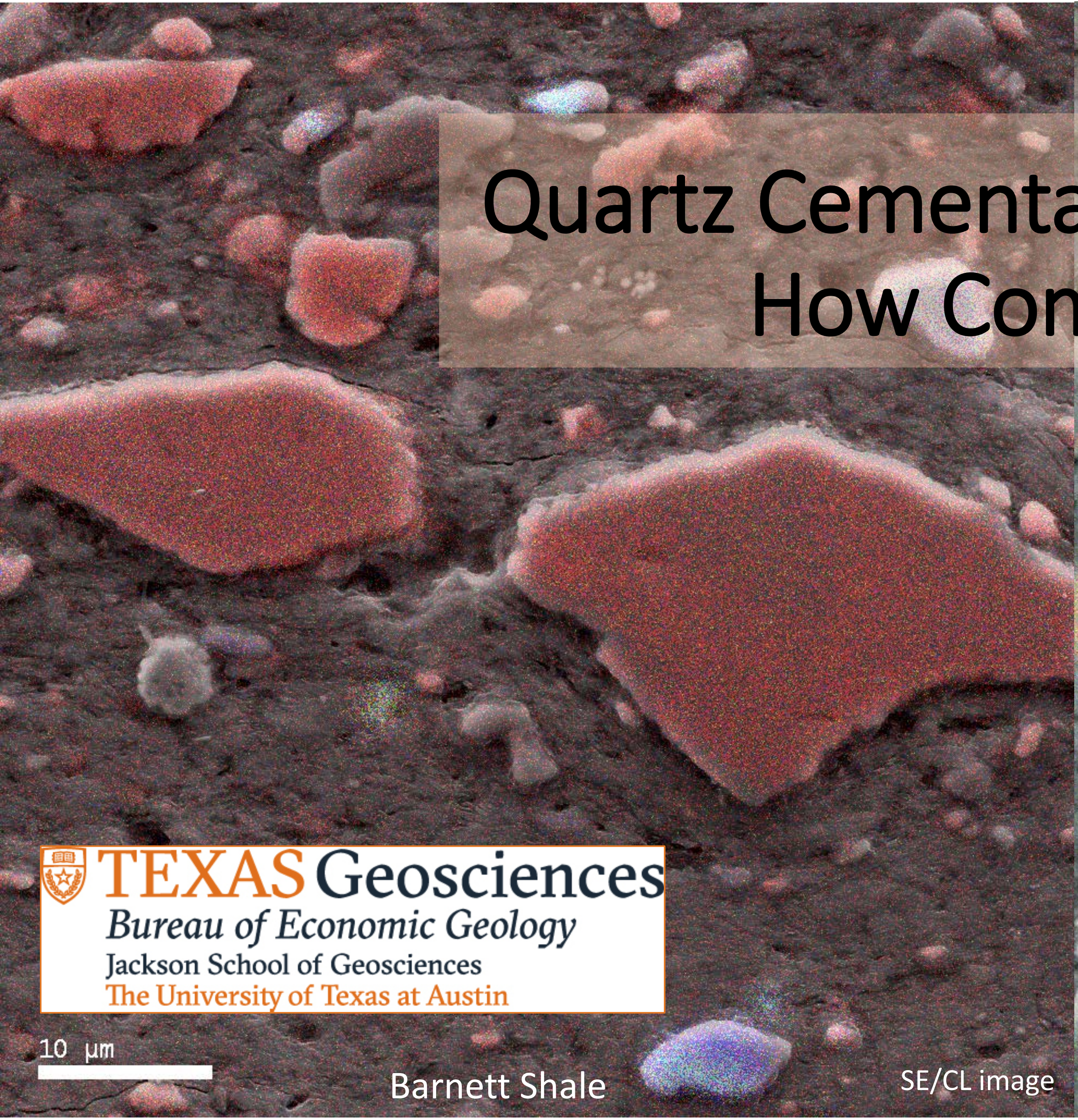
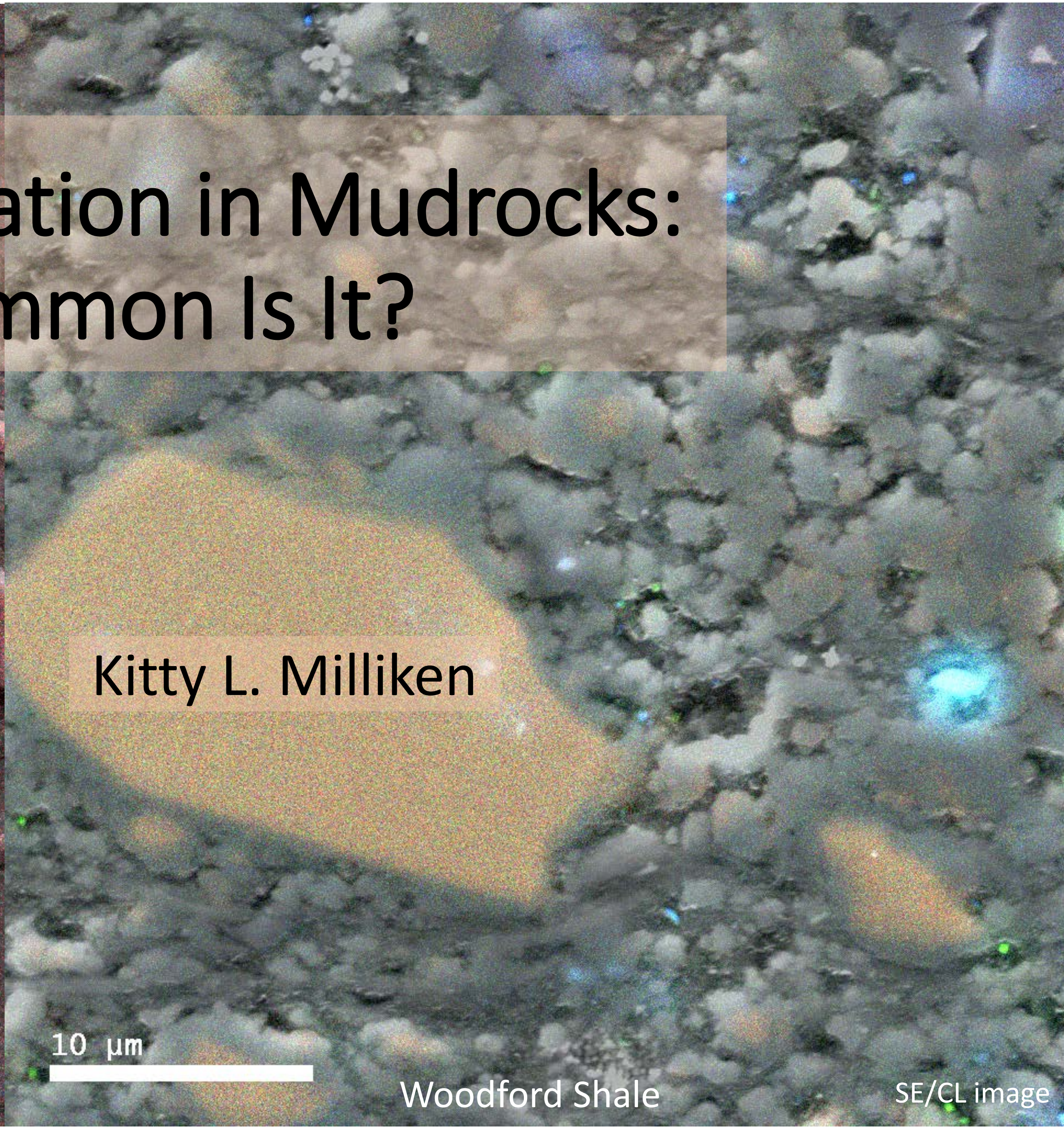




Cements are Pore-filling Precipitates

Specific definition differs with research specialty:

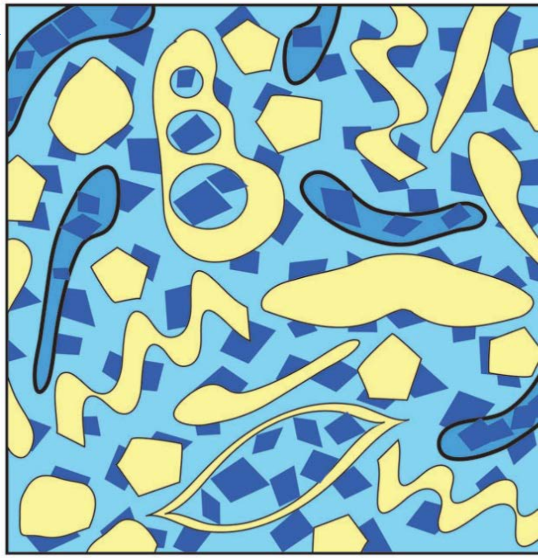
- Sandstones: strictly intergranular authigenic precipitates
- Limestones: *any* authigenic precipitate in primary intergranular, primary intragranular, or secondary pores (grain dissolution).
- Mudrocks: similar to limestone definition(see Milliken and Olson, 2017)
- Other concepts:

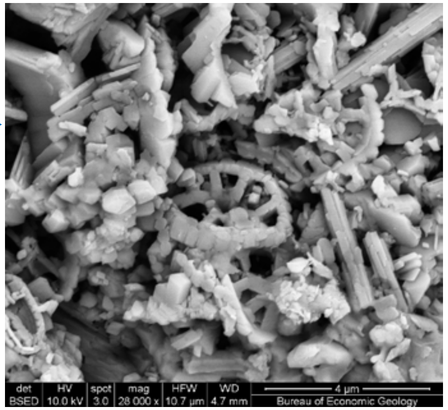
  Grain binders: some non-mineral; some polymineralic

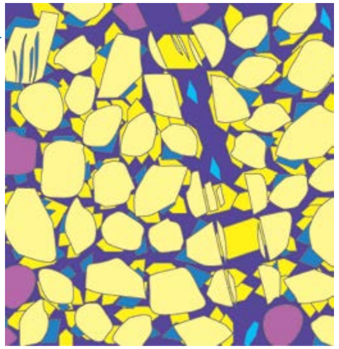
  Fracture fills

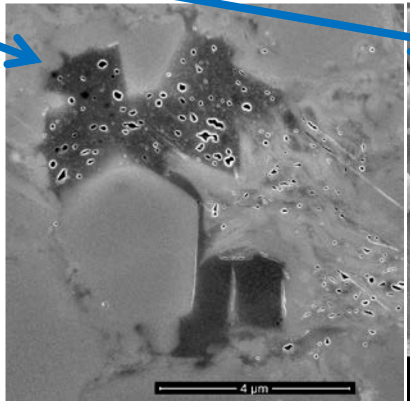
$$COPL = P_i - \frac{(100 - P_i) * IGV}{100 - IGV}$$

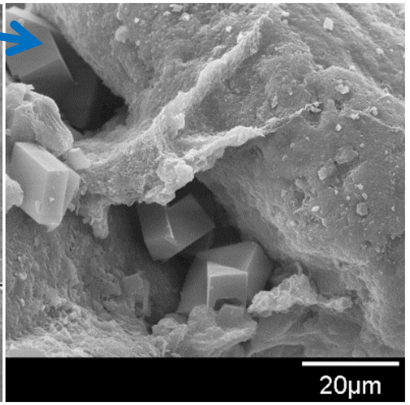
$$CEPL = (P_i - COPL) * \left(\frac{C}{IGV}\right)$$











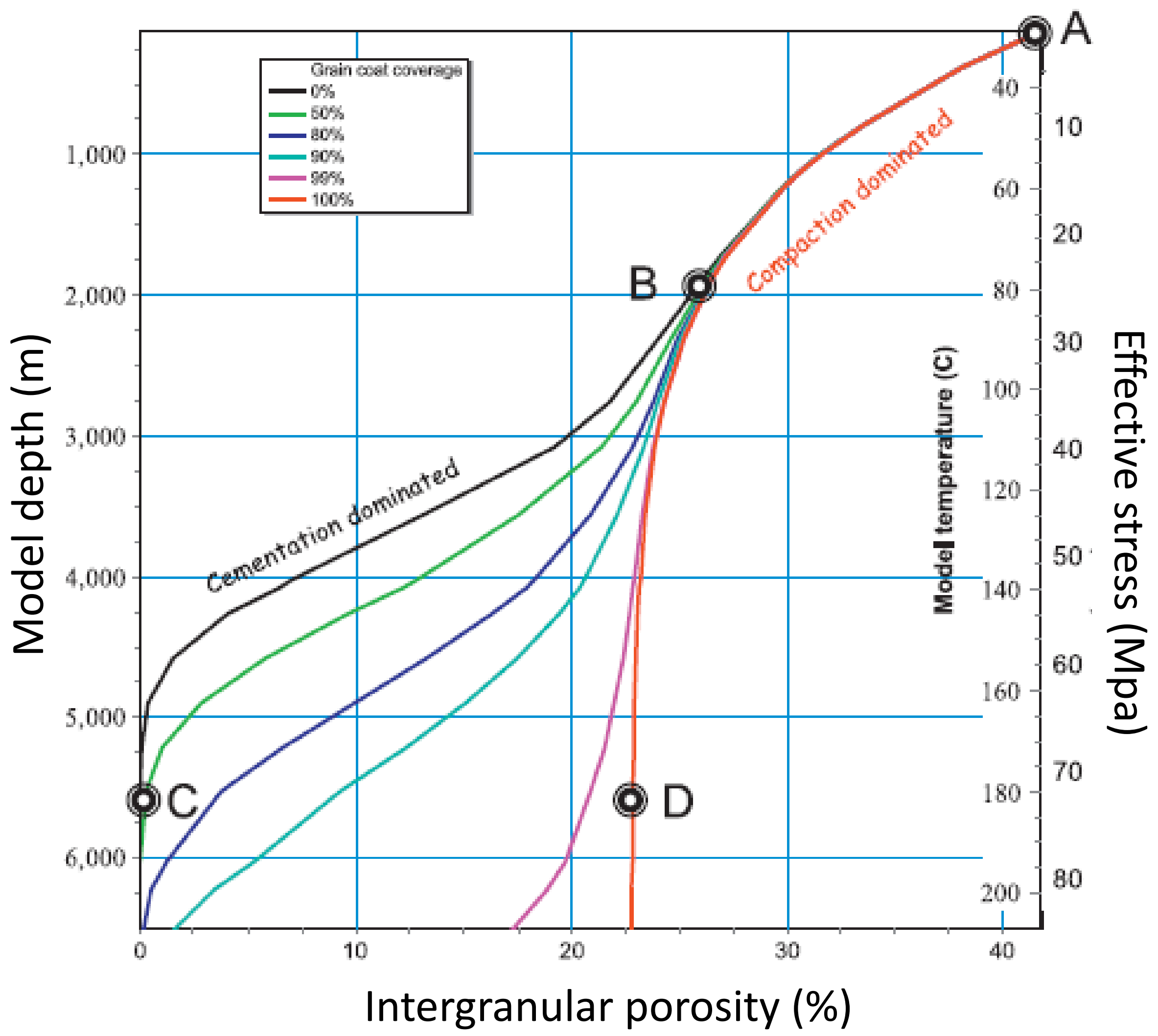
Compaction is another mechanism of pore loss, distinct from cementation.

- A bulk volume loss
- Measured as 1-D strain perpendicular to bedding.
- Takes place by physical rearrangement of primary detrital particles
- Involves no addition or subtraction from solid rock components (pore loss only). *Does not involve cementation.*

Why do we care about cementation in sandstones and mudrocks?

- Affects porosity evolution by pore occlusion
- Affects compaction and mechanical property evolution by grain binding.
- Affects bulk chemical composition by addition of authigenic components to bulk rock.
- Requires fluids and solutes: Places quantifiable constraints on fluid flow history and elemental mobility.
- Combined with compaction can be used to make a reasonably complete model of porosity evolution in the subsurface.

A hybrid empirical-chemical/mechanical model for porosity prediction in sandstone reservoirs.



Ajdukiewicz & Lander, 2010

Foundational techniques:

- Blue-dyed epoxy.
- Light microscopy.
- CL-imaging.
- Fluid-inclusion analysis.

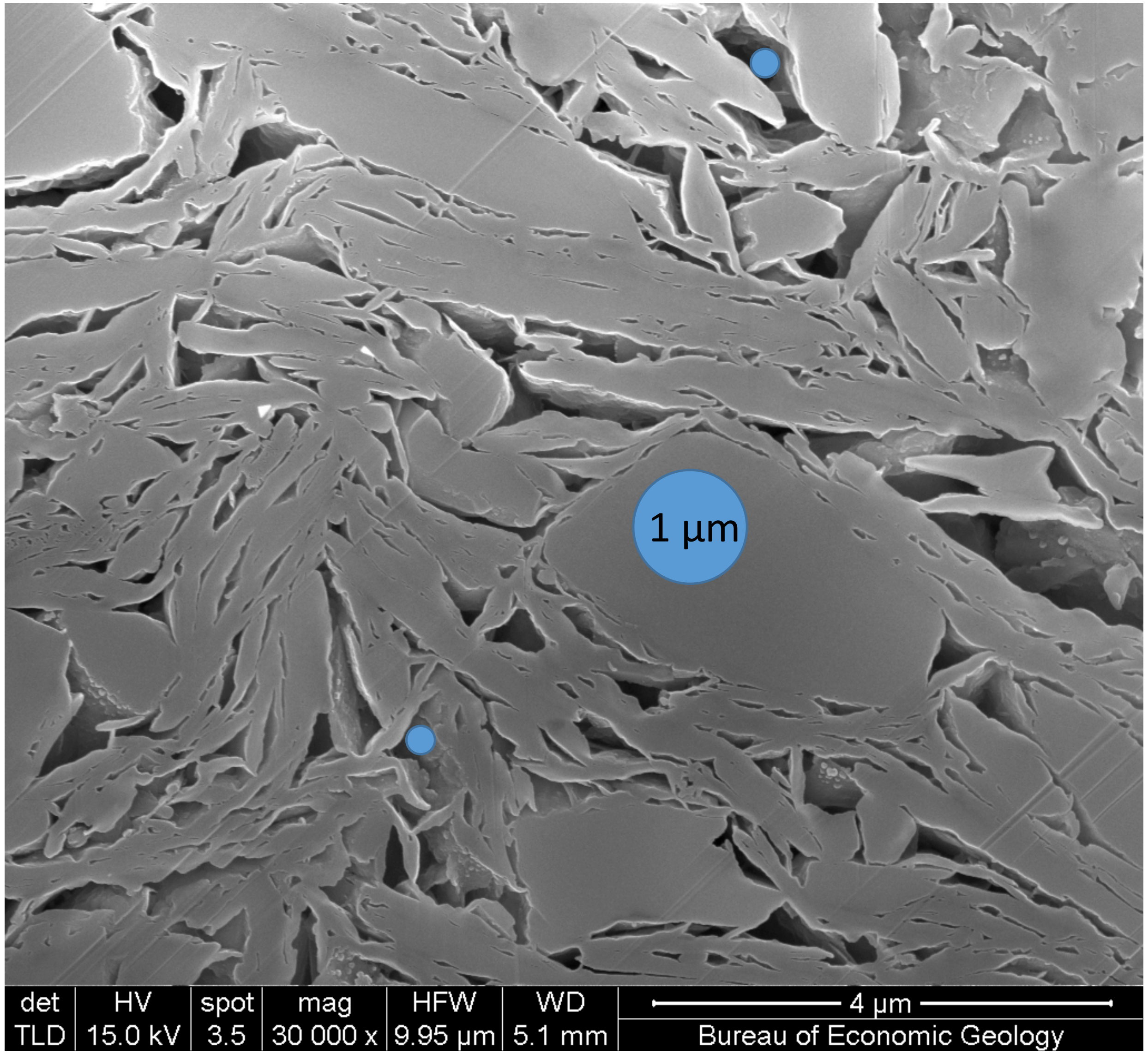
See Milliken and Curtis, 2016 for historical review.

The composition of the detrital grain assemblage is a primary control on the pathways of porosity evolution.

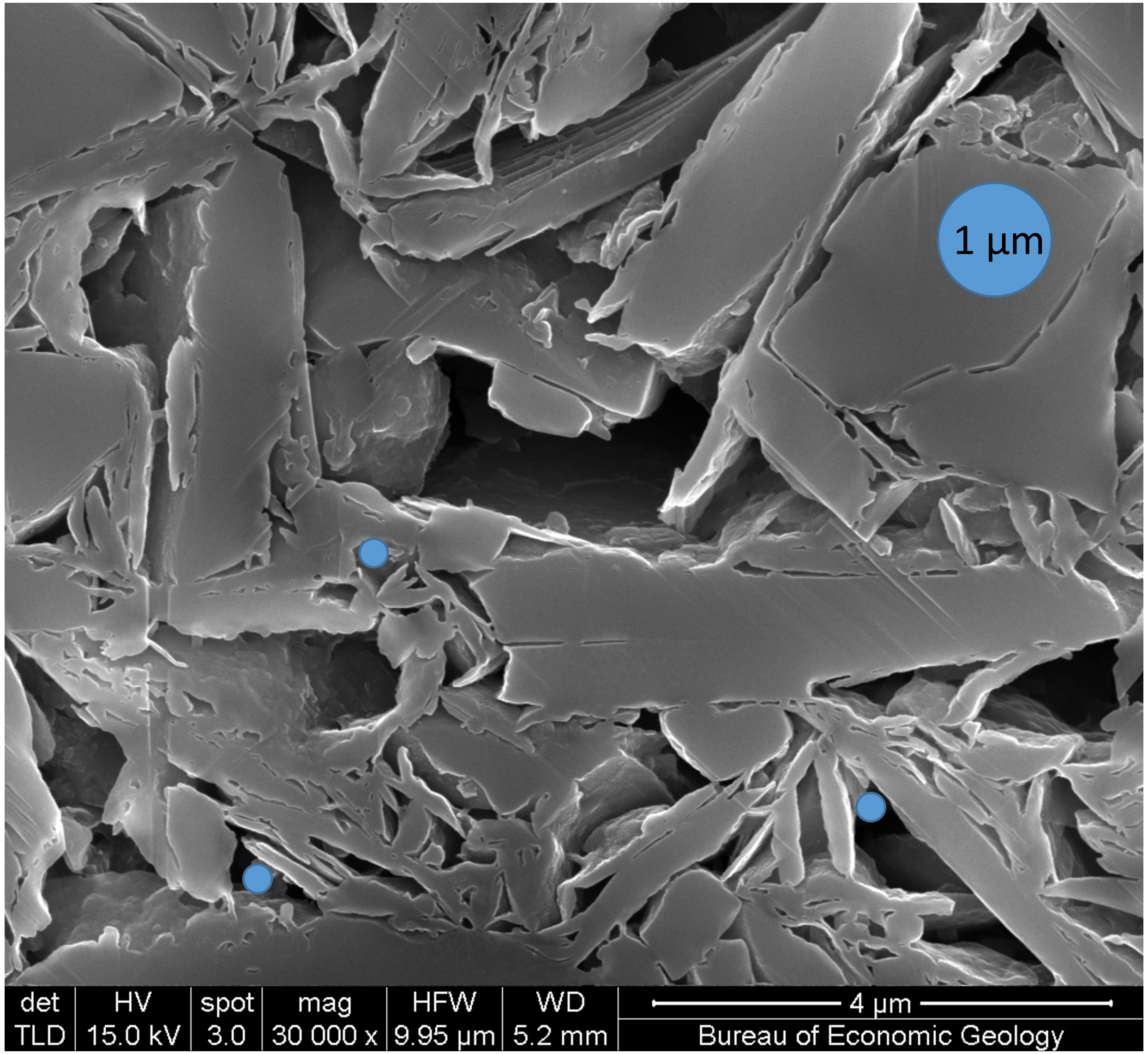
Questions about porosity evolution in mudrocks (guided by things that led to quantitative models for sandstones):

- How do grain assemblges vary in composition?
- How does lithification happen? Compaction? Cementation? Both?
- How does the grain assemblage composition affect the path to lithification?
- When does lithification happen? At what depth and temperature?
- Are there secondary pores in shales?
- What techniques do we need to figure out all of the above?

Depth = 7.21 mbsf; porosity = 68.3 %



Depth = 28.12 mbsf; porosity = 54.3 %



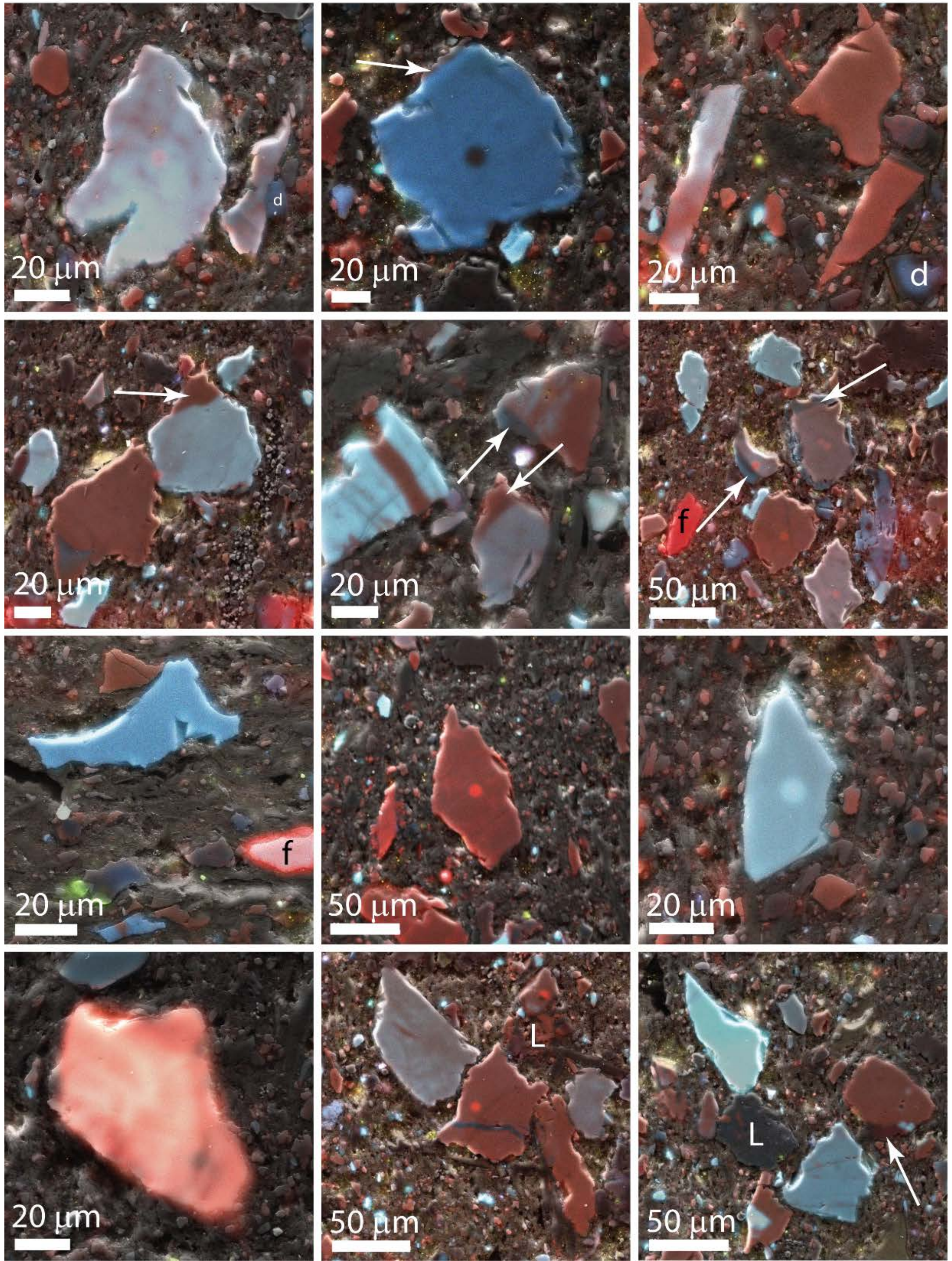
Pleistocene, eastern Indian Ocean, secondary-electron images. Samples prepared by Ar-ion cross-section polishing.

Pores in muds are very small even in the earliest stages of compaction.

Finding intergranular cements in mudrocks:

- Need a field-emission scanning electron microscope (FE-SEM).

- How to tell cements from grains:
    - Spatial distribution
    - Size, shape
    - Composition
        - X-ray mapping
        - CL imaging (in the case cements and grains have the same bulk composition)



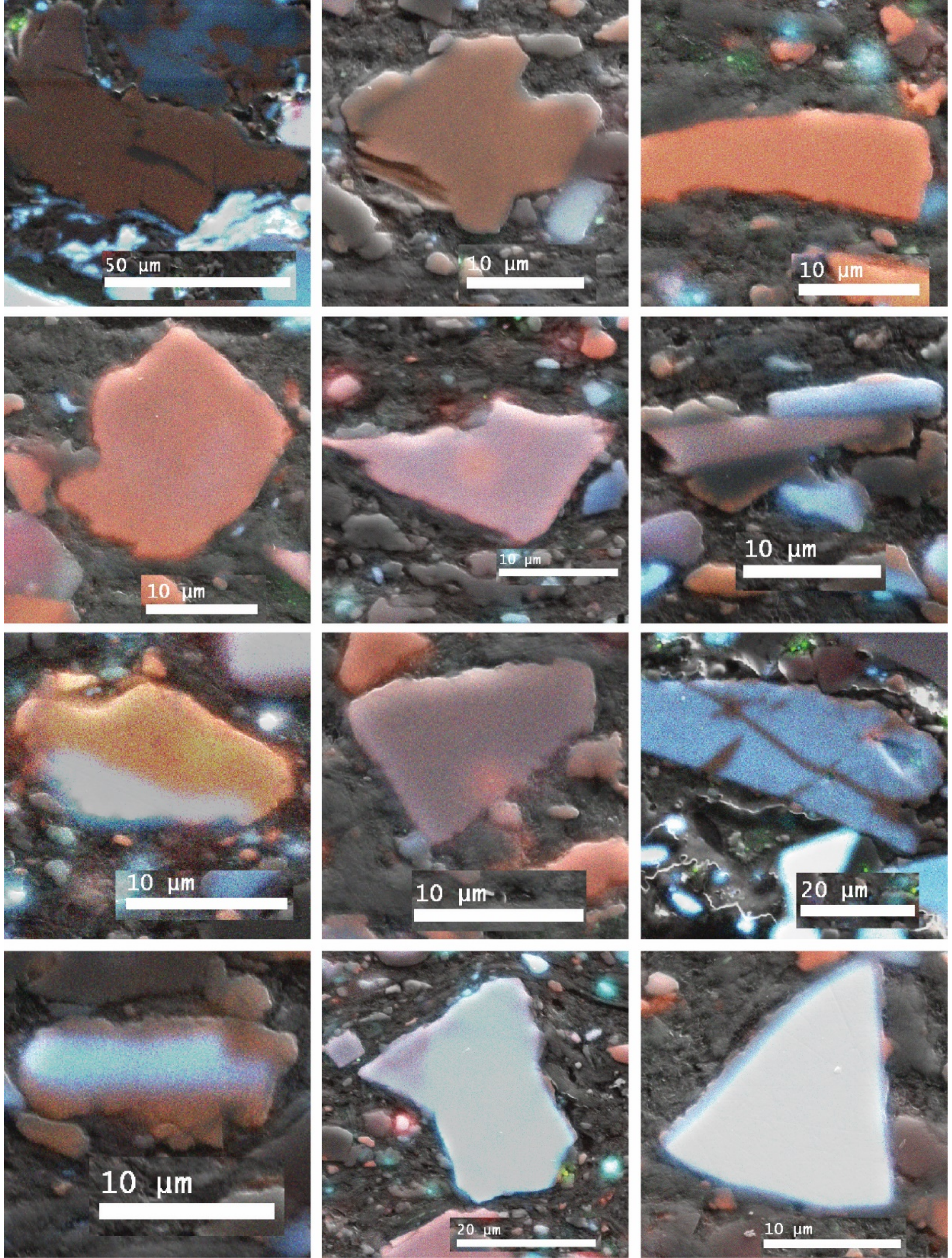
Wilcox Formation, Eocene, Gulf of Mexico Basin, USA and Mexico; Day-Stirrat et al. 2010

Most of detrital quartz is interpreted as extrabasinal.

- Most < 20 μm
- Some clay-size
- Angular shape
- Variable color, brightness, and texture in cathodoluminescence
- Some have transported overgrowths (too big for pore-fills).

SE/CL images

Yangchang Formation, Triassic, Ordos Basin, China; Milliken et al., 2017



SE/CL images

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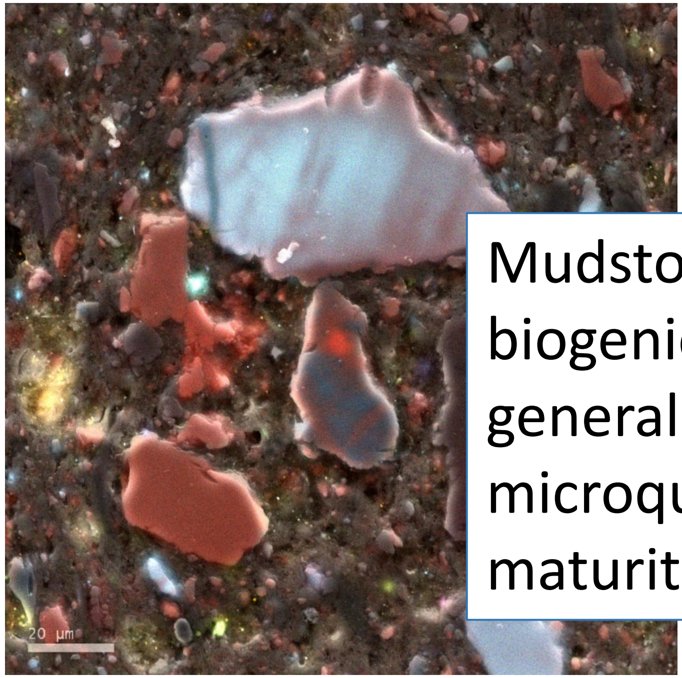
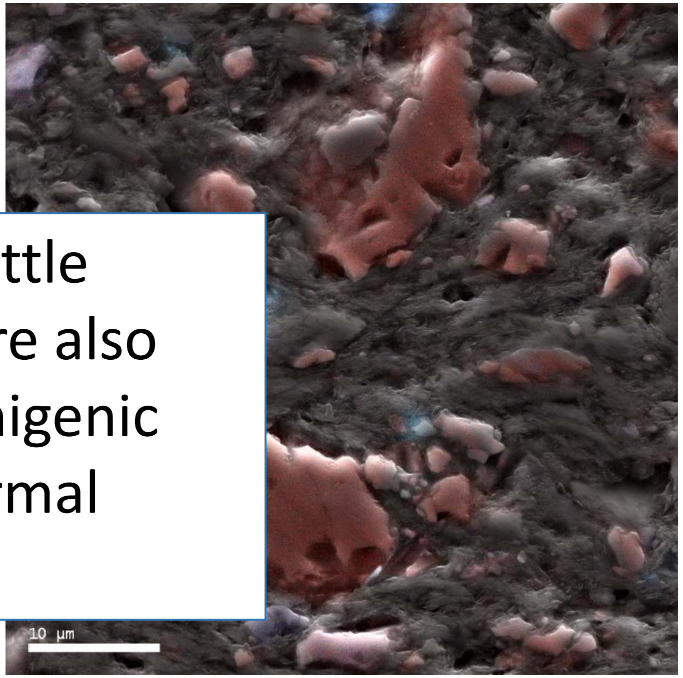
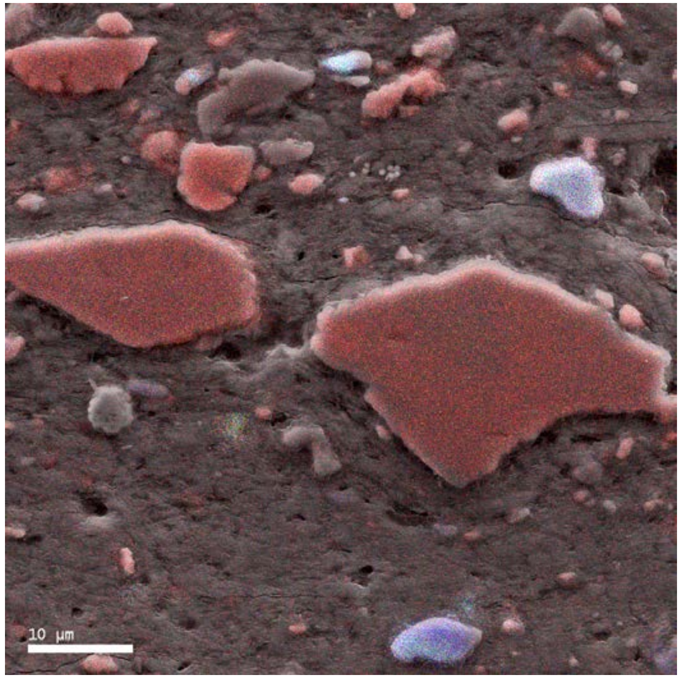


Wilcox Formation, Eocene, Gulf of Mexico Basin

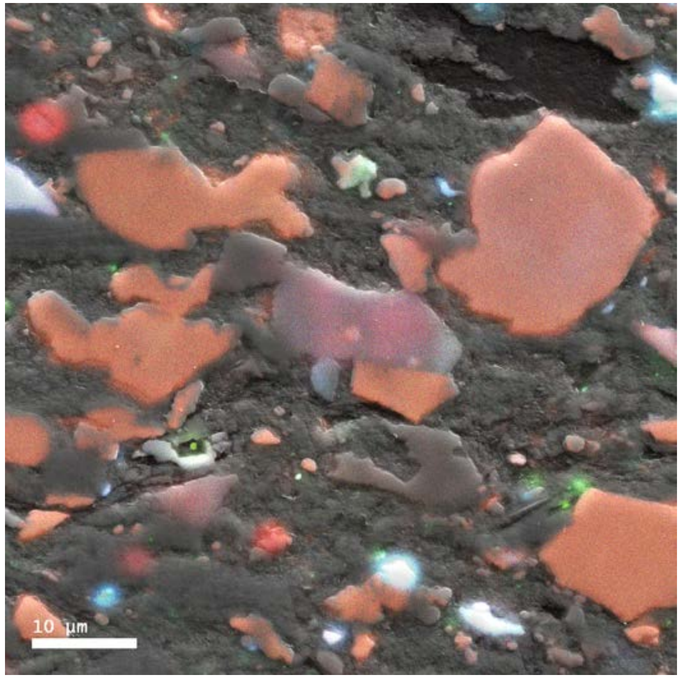
Mudstones containing little biogenic debris (tarls) are also generally lacking in authigenic microquartz---at all thermal maturities.



Baltic Basin



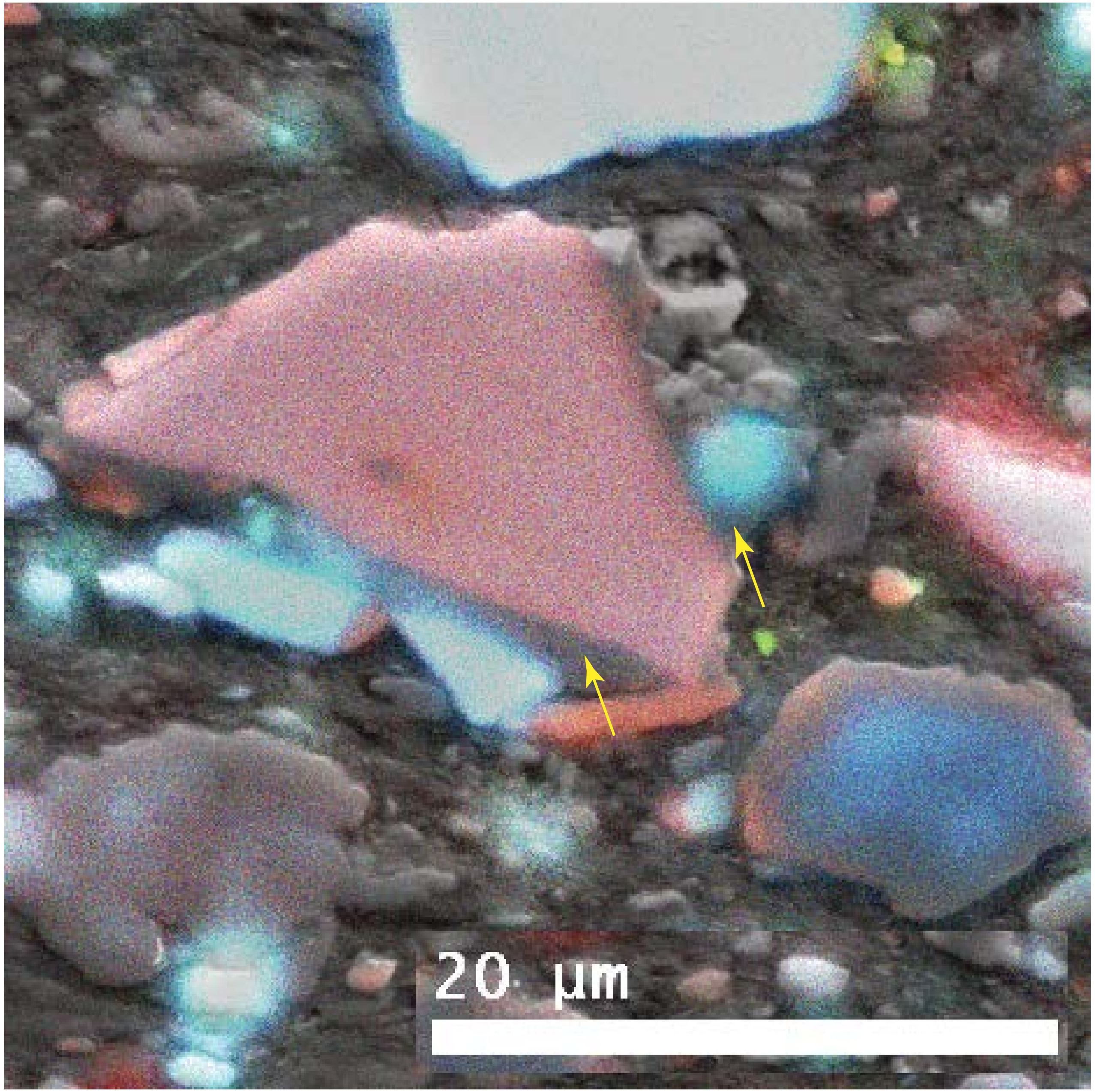
Barnett Shale, Mississippian, Ft. Worth Basin



Yanchang Formation, Triassic, Ordos Basin

SE/CL images

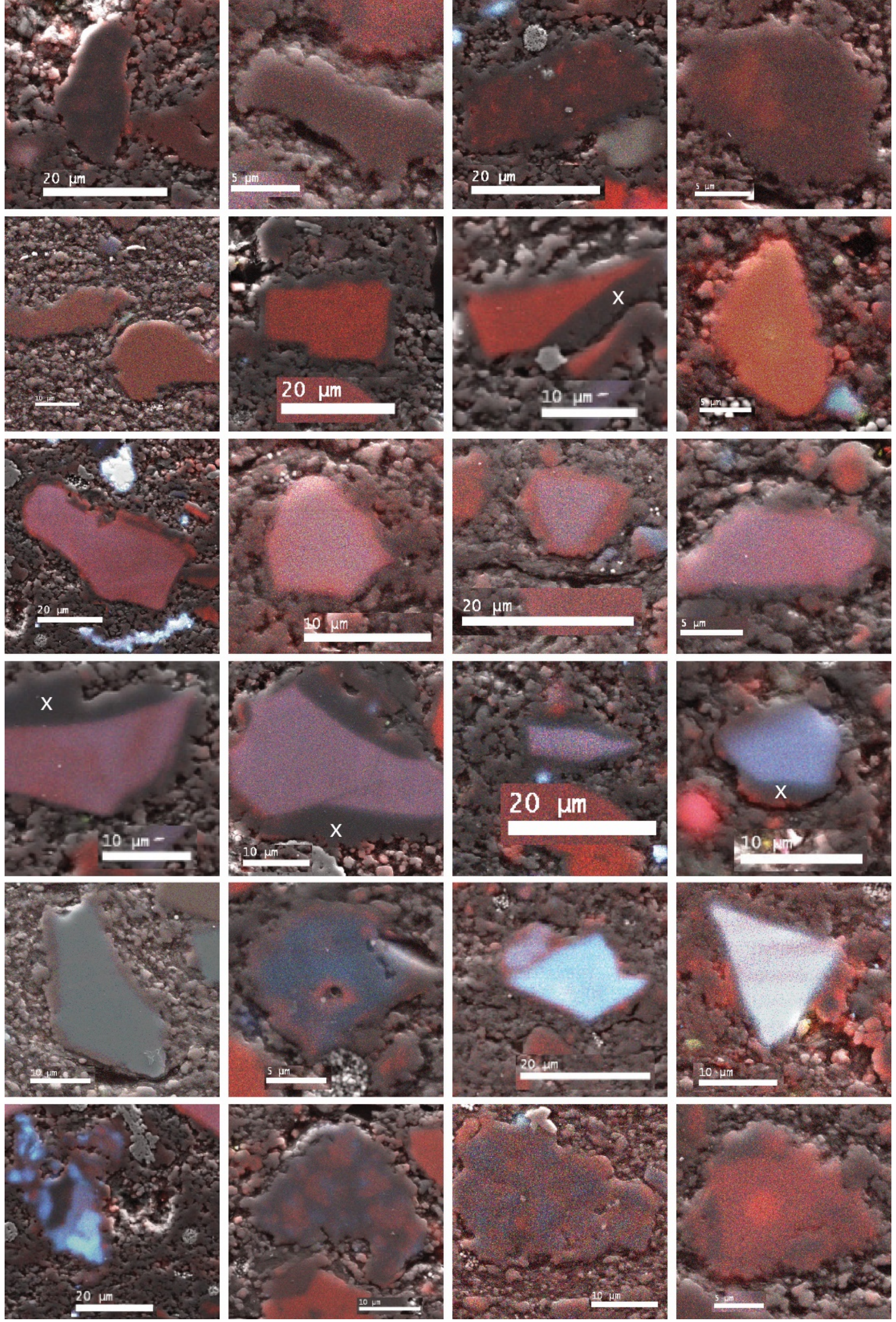
Yangchang Formation, Triassic, Ordos Basin, China; Milliken et al., 2017



Tiny overgrowths at grain contacts (yellow arrows) are typically the only visible quartz cement in silty mudstones that lack biogenic debris (tarls).

Finding these takes careful searching!

SE/CL image



Mowry Shale, Cretaceous, Rocky Mountains, USA; Milliken & Olson, 2017

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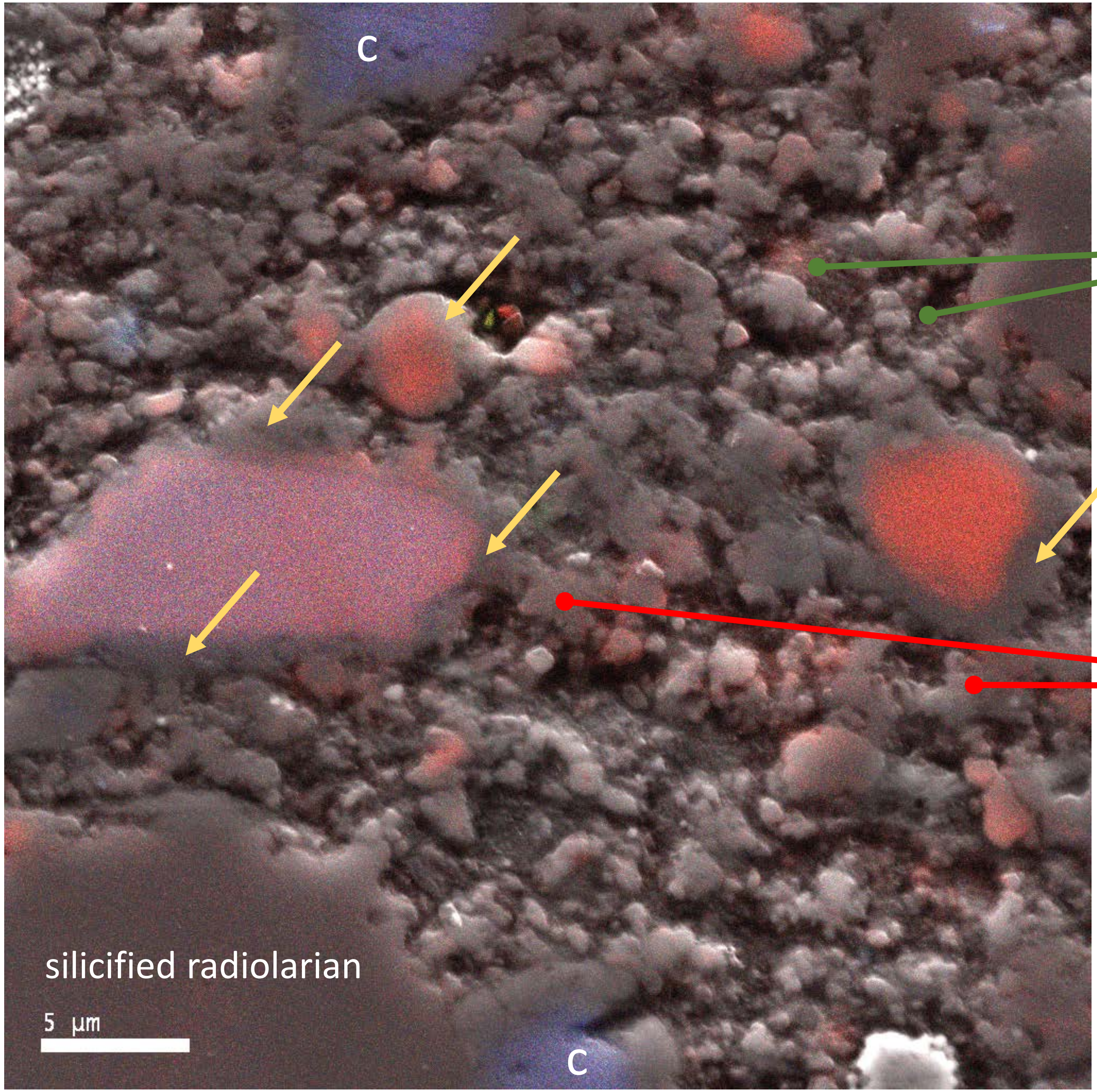
SE/CL images

Mowry Shale, Cretaceous, Rocky Mountains, USA (Milliken & Olson, 2017)



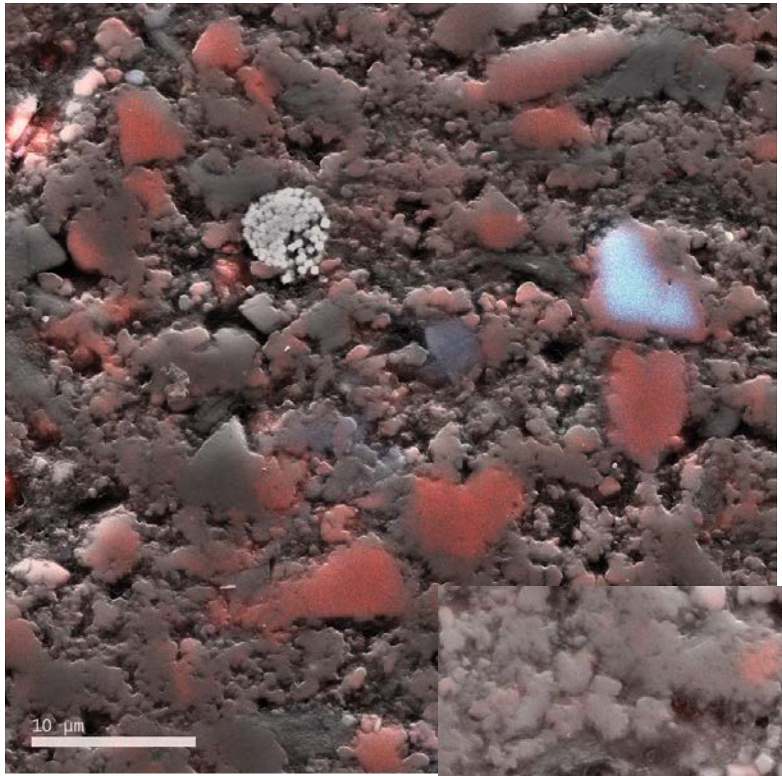
detrital clay mineral matrix

authigenic microquartz:
1 to 3 µm crystals and
and crystal aggregates

C = calcite grain; yellow arrows = authigenic microquartz distributed as overgrowths on detrital quartz grains.

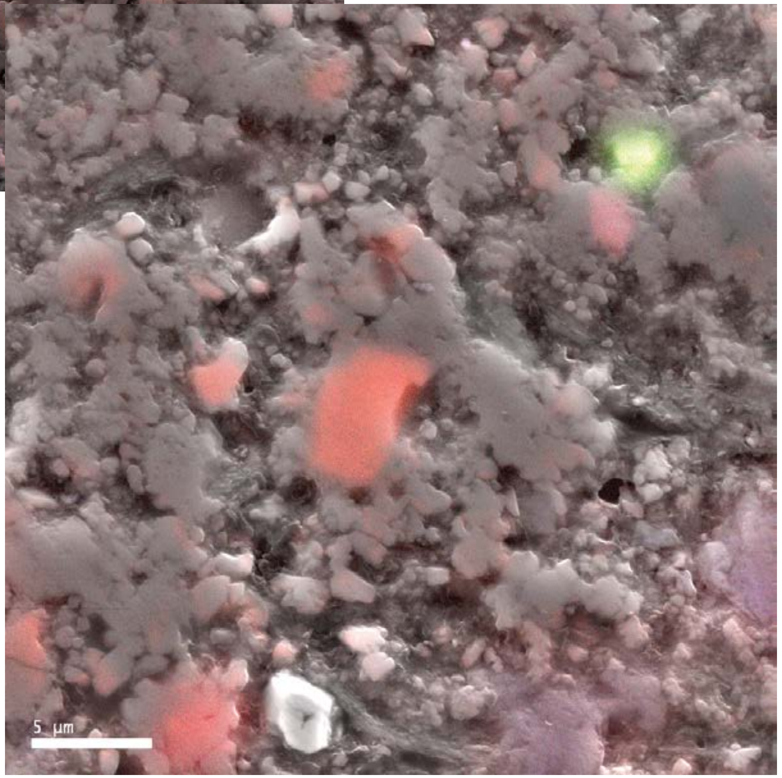
SE/CL image

Barnett Shale, N. Texas



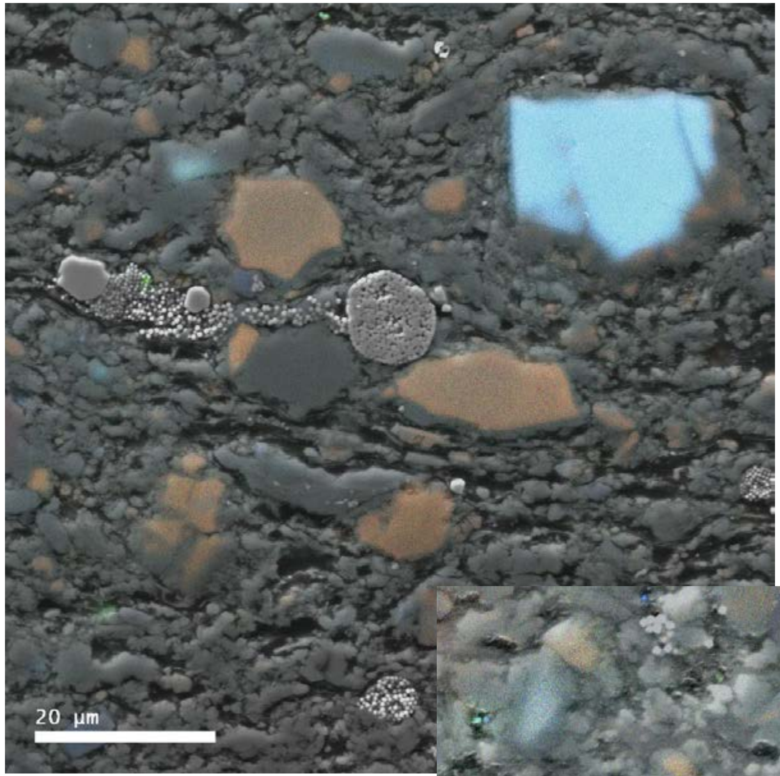
Massive authigenic microquartz

Silurian, Poland

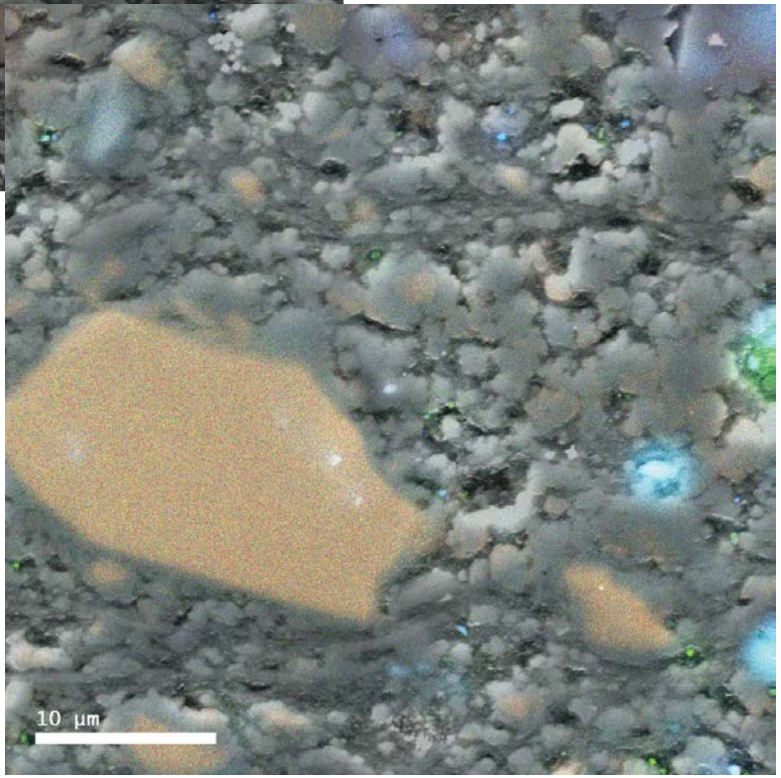


All contain biosiliceous grains. “quartz-cemented siliceous tarl or sarl”

Bakken Formation, N. Dakota



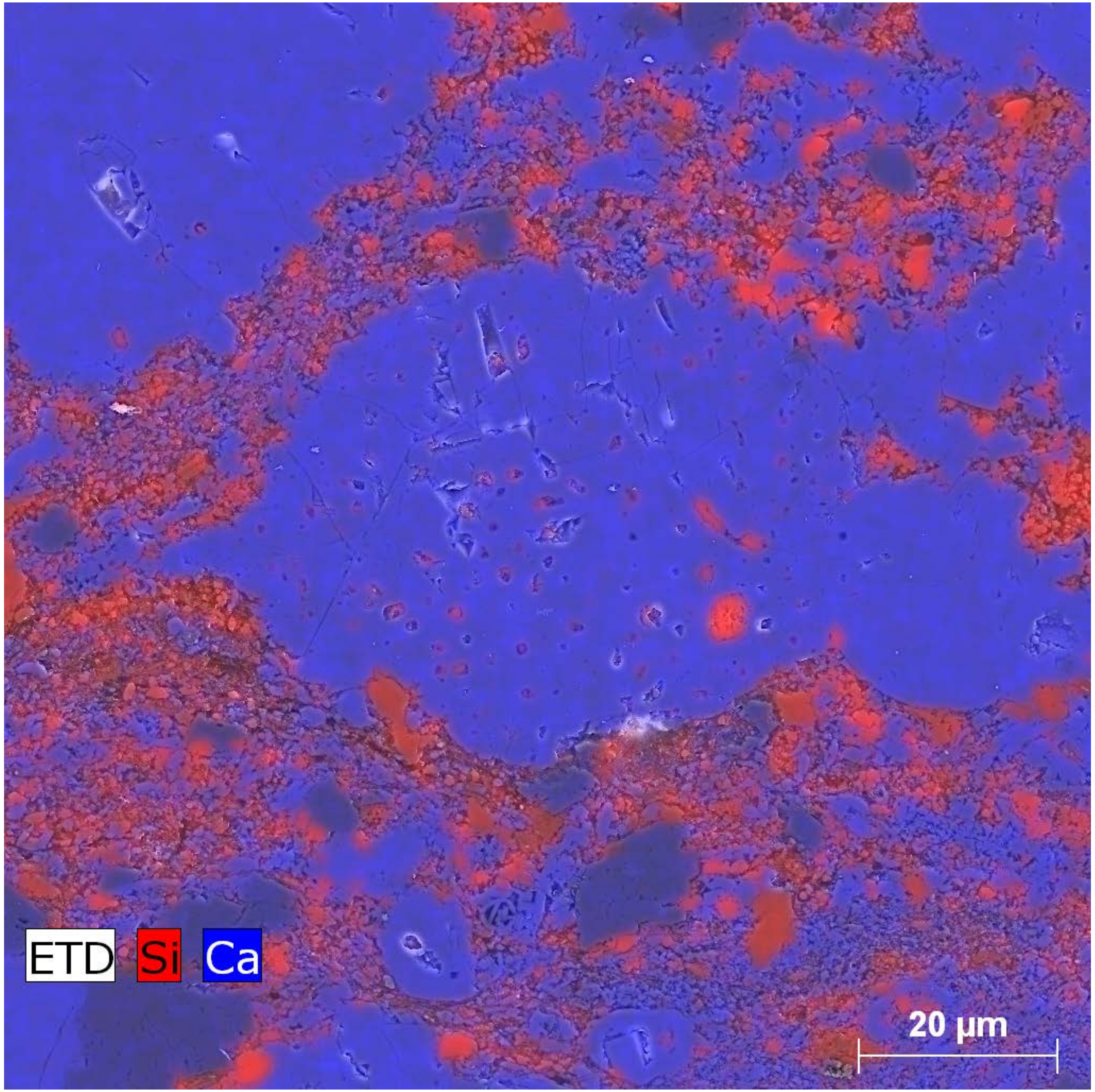
Woodford Shale, W. Texas



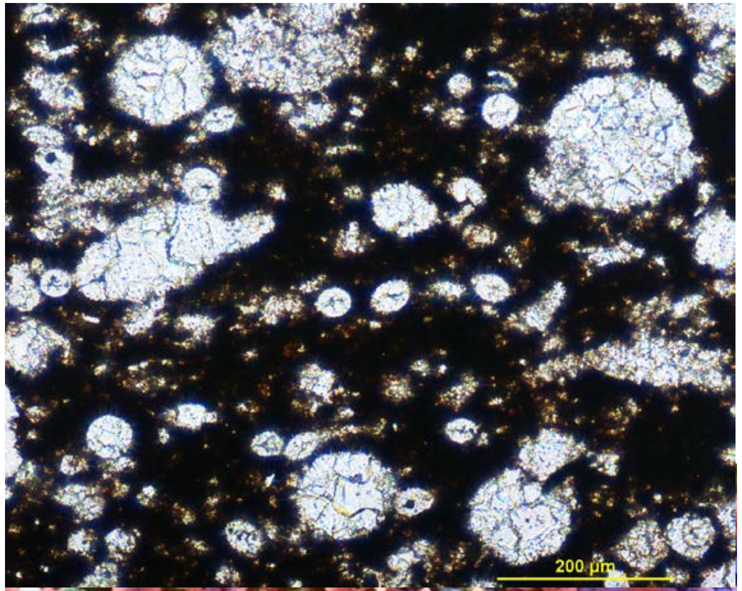
“argillaceous chert”

SE/CL images

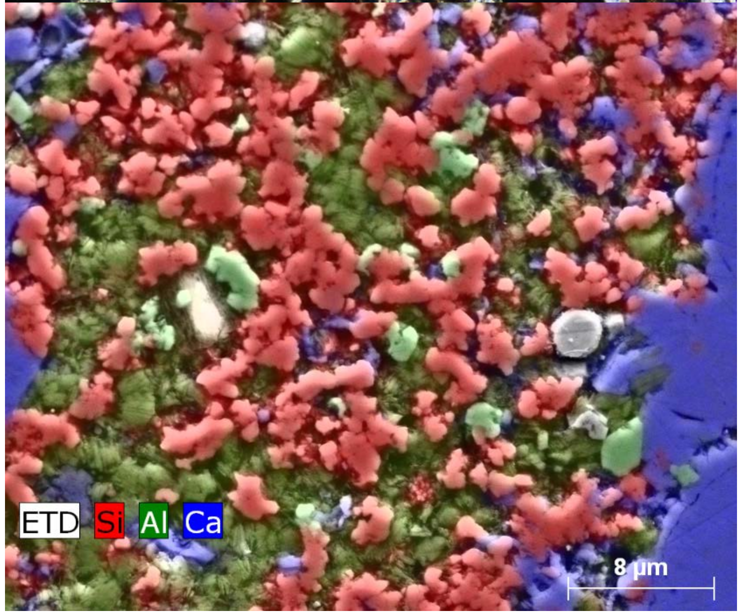
Eagle Ford Formation, Cretaceous, South Texas, USA; Milliken et al., 2017



EDS image



plane-polarized light image



EDS image

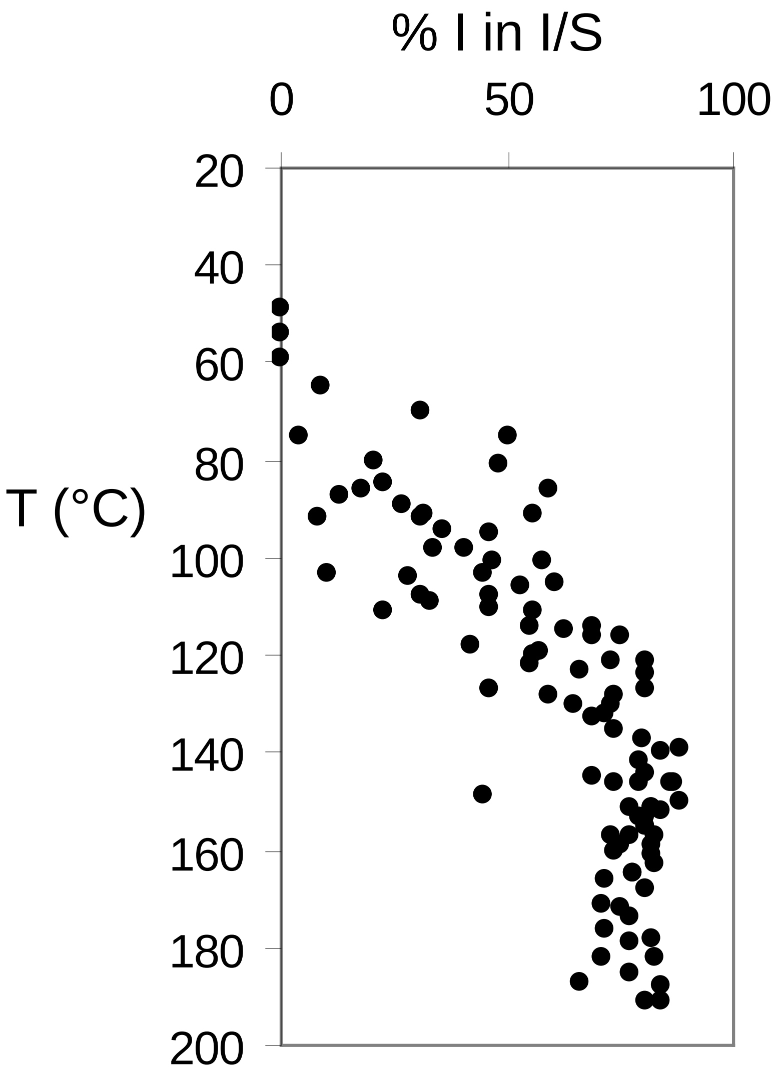
siliceous mudrocks	microcrystalline quartz cement	matrix (clay-size grains + pores)	cement/ total matrix
	vol %	vol %	
Barnett Shale	35.4	40.9	0.46
Woodford Shale	46.8	29.3	0.61
unnamed unit; Baltic basin	35.4	54.3	0.40
Vaca Muerta	25.2	34.5	0.42
Mowry Shale*	41.0	39.6	0.51
	36.8	**39.7**	**0.48**
*Average of 5 samples from Milliken and Olson, 2017			

Where present, authigenic microquartz in mudrocks makes up nearly 40% of whole rock and 50% of matrix.

At what depths do mudrocks have such porosity?

....generally less than 1.5 km burial.

The most volumetrically significant reaction in the sedimentary part of the crust.



Lynch 1997 (three papers)

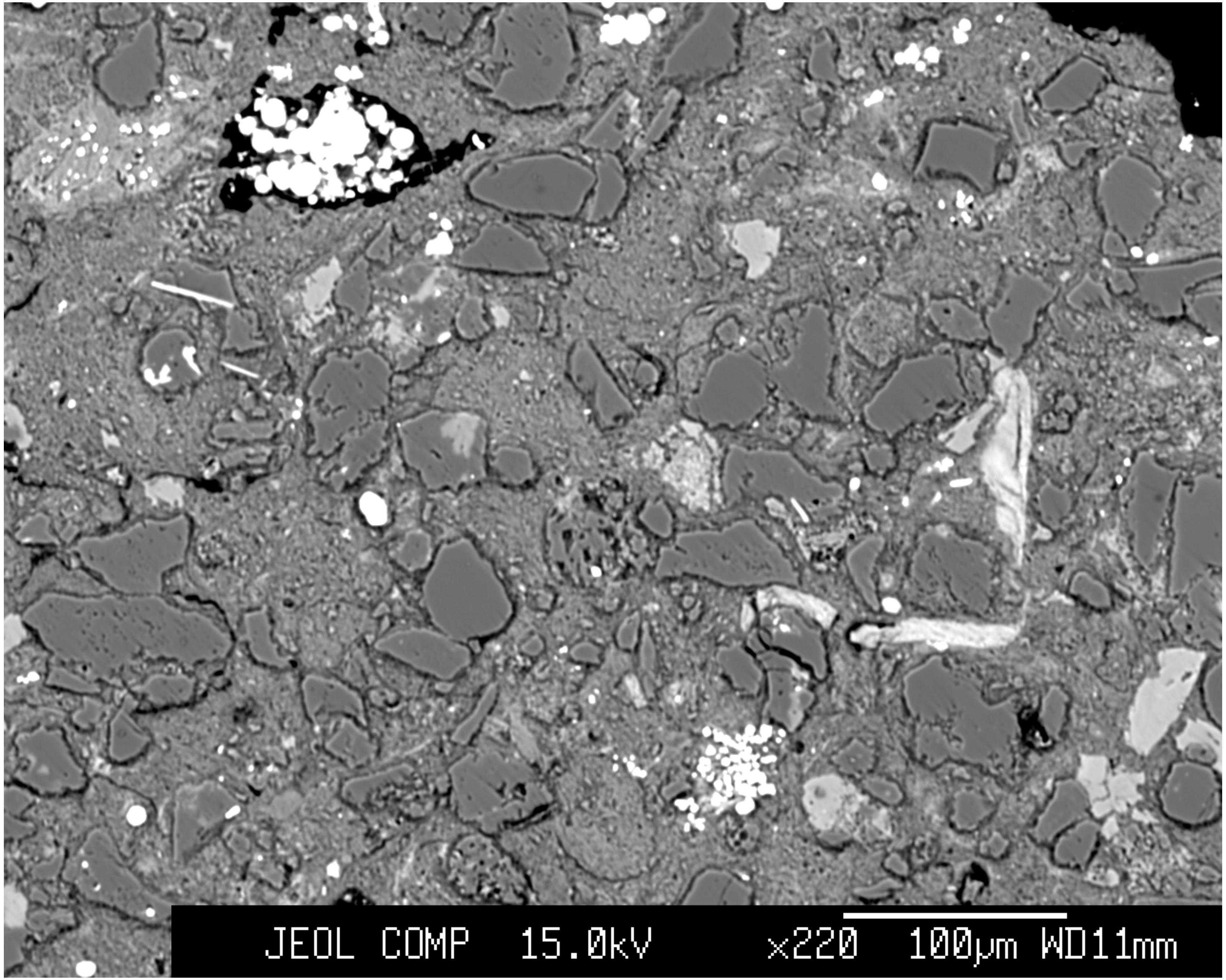
Smectite dissolution:

$K_{.12}Na_{.25}(Al_{1.41}Fe_{.22}Mg_{.41})(Si_{3.88}Al_{.12})O_{10}(OH)_2 + 9.96H_2O =$
$.12 K^+ + .25Na^+ + .22 Fe^{3+} + .41Mg^{2+} + 1.53Al^{3+} +$
$3.88H_4SiO_4 + 6.44OH^-$

Illite precipitation:

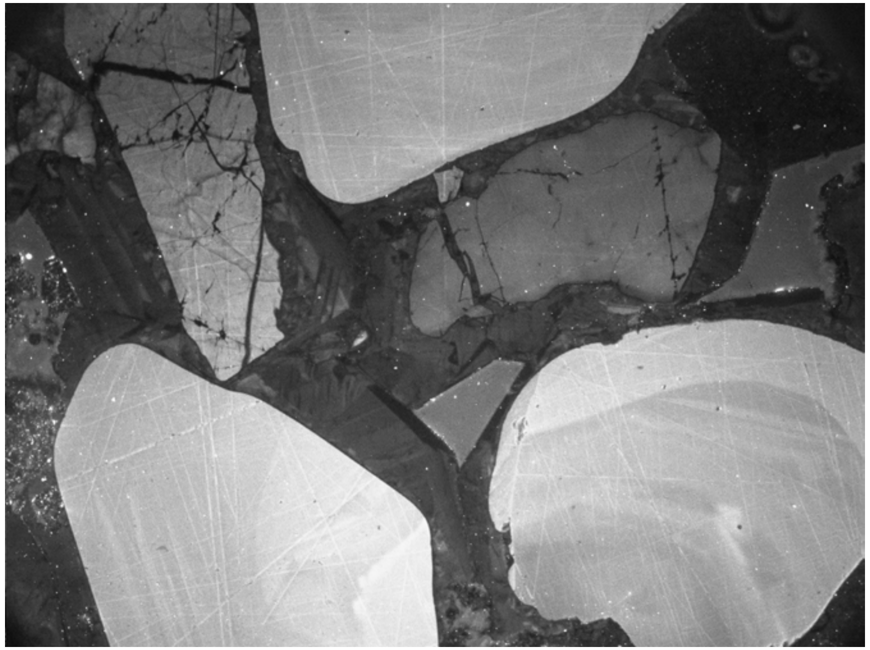
$.65K^+ + .08Na^+ + .14Fe^{2+} + .2Mg^{2+} + 3.4 H_4SiO_4 + 2.27Al^{3+} =$
$K_{.65} Na_{.08} (Al_{1.68} Fe_{.14} Mg_{.2})(Si_{3.41} Al_{.59})O_{10}(OH)_2 +$
$8.22H^+ + 2.69H_2O$

Illitization reaction in the Frio Formation (Oligocene) of South Texas.



The Frio Formation at the depths of illitization has authigenic quartz in sandstones but not in associated mudrocks. Milliken, 1994

Frio Formation sandstone, South Texas, approx. 4 km depth.



Frio Formation; South Texas, depth = 4769 m; Milliken, 1992.

Illitization Reactions

FUNDAMENTAL

smectite → elements in solution
elements in solution → illite

1:1 MOLAR BALANCE

1 mole smectite → elements in solution

elements in solution + (K^+ + Al^{3+}) → 1 mole illite + 2.06 (Si^{4+})

Al-BALANCE

1 mole smectite → elements in solution

elements in solution + (K^+) → 0.67 mole illite + 2.13 (Si^{4+})

Si-BALANCE

1 mole smectite → elements in solution

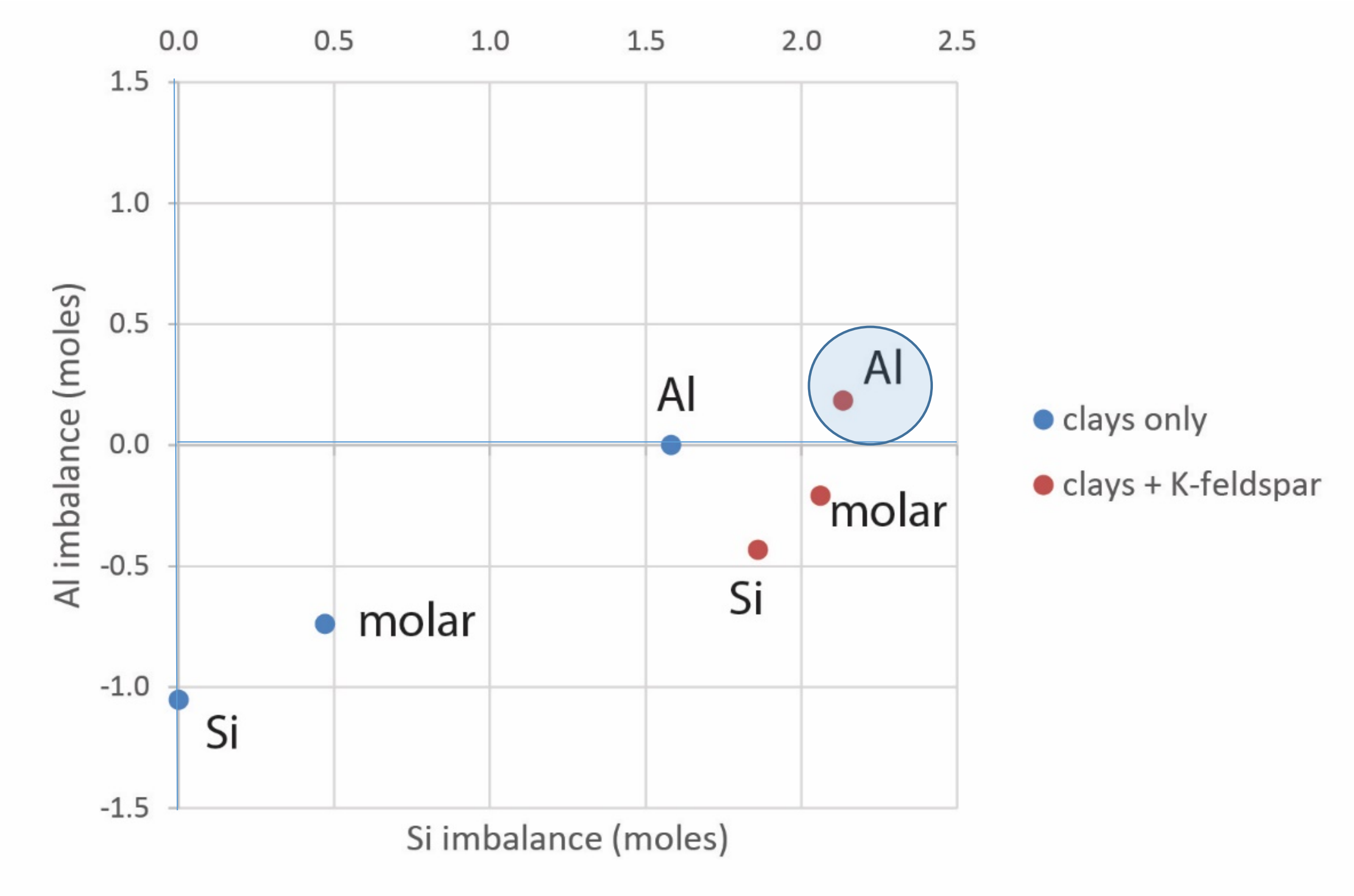
elements in solution + (K^+) → 1.14 mole illite + 1.86 (Si^{4+})

Al-BALANCE

1 mole smectite → elements in solution

elements in solution + (K^+) → 0.67 mole illite + 2.13(Si^{4+})

Maximum silica generation from an Al-balanced reaction with K provided by K-feldspar dissolution.



Volumetric (petrographic) implication

~~g~~/mole / ~~g~~/cm^3 = cm^3/mole (molar volume)
~~moles~~ x cm^3/~~mole~~ = cm^3 (volume)

Reaction of 1 mole smectite via an Al-balanced reaction with K-feldspar for K yields:

0.67 moles of illite and 2.13 moles of Si

187 cm^3 of illite and 48 cm^3 of quartz (0.26 cm^3 quartz/ 1 cm^3 illite)

In a shale with 50% illite by volume, there would be around 13% quartz produced as a consequence of illitization. Other reaction formulations yield less (6 to 8% quartz). If unreactive detrital illite makes up a portion of total illite, silica generation is less yet.

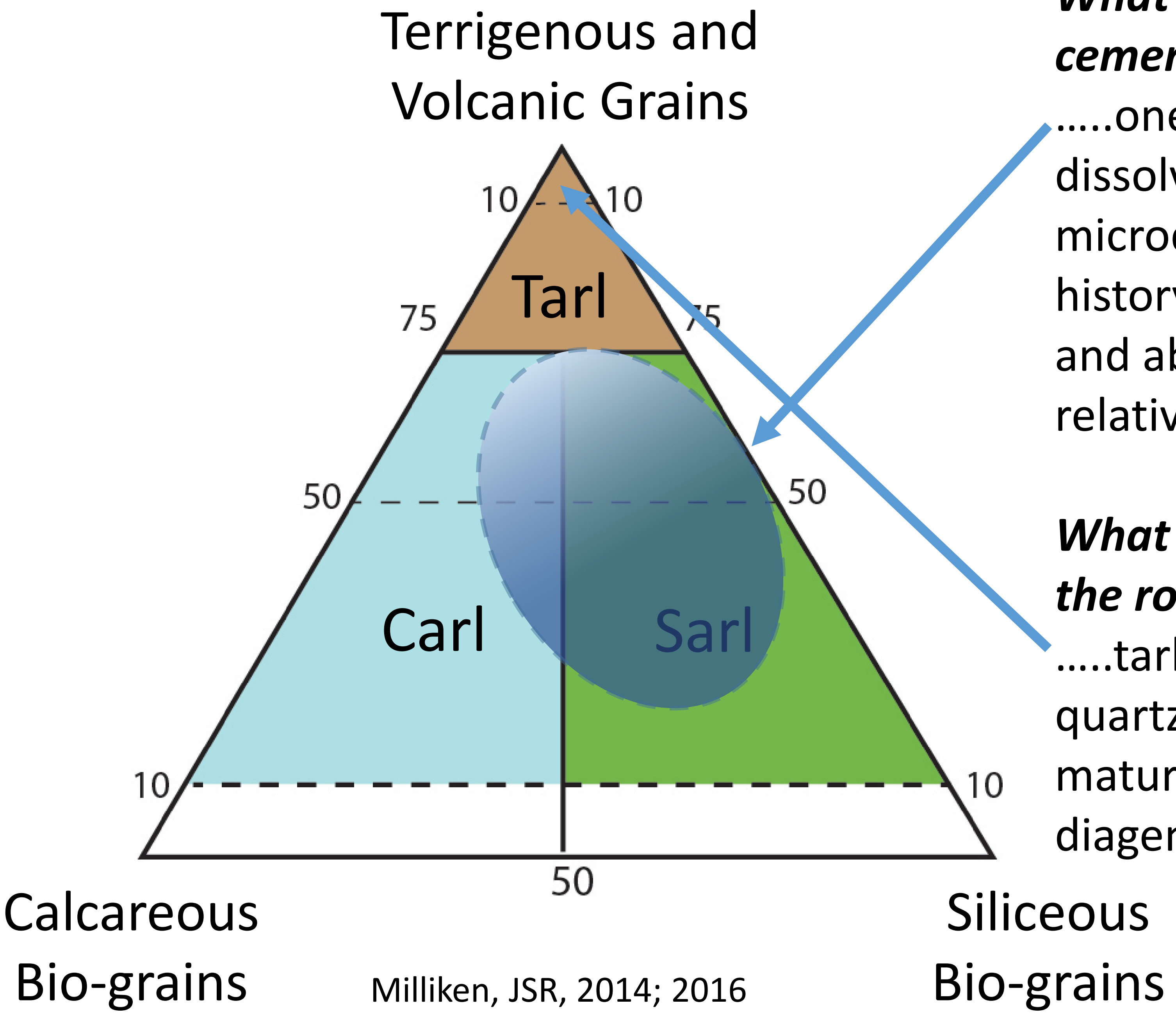
Authigenic quartz in mudrocks

Observed volumes of authigenic microquartz in quartz-cemented mudrocks are *too large* (~40 volume percent) to arise by illitization:

- Greater than the porosity at the depth of illitization
- Greater than the amount (~13%) that can be generated by illitization using the most optimistic assumptions
- Consistent with a source related to relatively early diagenetic alteration of biogenic silica

The most common mudrocks (tarls) associated with quartz-cemented sandstones display *even less* (< 1 volume percent) authigenic quartz than is potentially generated by illitization reactions (6 to 13 volume percent).

Illitization as a cause of quartz cementation in mudrocks deserves re-examination. Total elemental balance should include entire sandstone/shale system and minerals other than illite-K-feldspar-quartz (e.g., chlorite, albite).



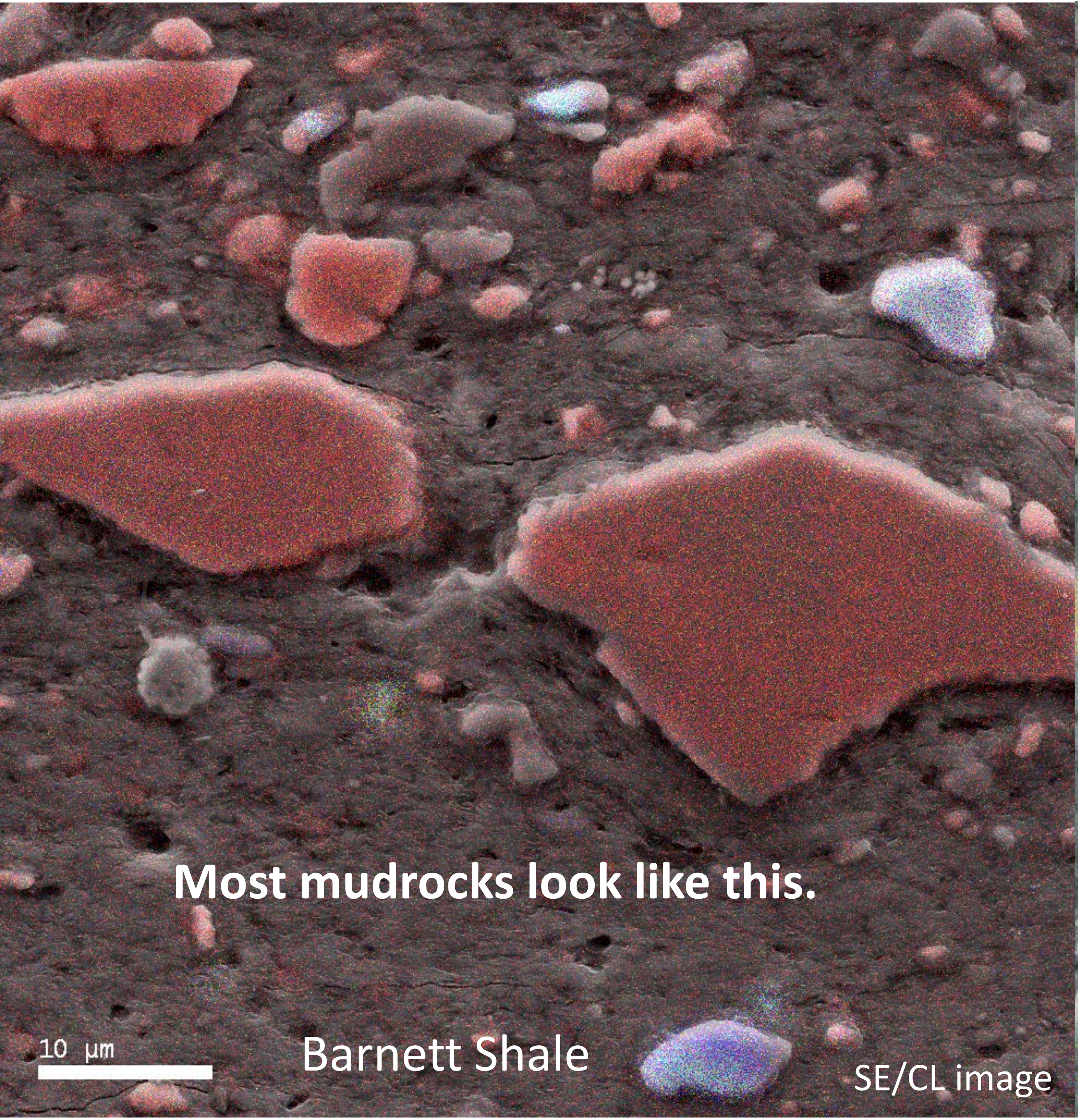
Milliken, JSR, 2014; 2016

What kind of mudrocks have quartz cement?

.....ones with bio-siliceous grains that dissolve to re-precipitate as opal-CT and microquartz relatively early in the diagenetic history. BUT sarl is the rarest mudrock type and abundant authigenic microquartz is a relatively *rare phenomenon*.

What kind of mudrock is most abundant in the rock record?

.....tarl! Tarls appear to have essentially no quartz cementation at any depth or thermal maturity. Compaction-dominated diagenesis.


Most mudrocks look like this.
10 µm
Barnett Shale
SE/CL image


A few mudrocks look like this.
10 µm
Woodford Shale
SE/CL imag

Conclusions about quartz cement in mudrocks:

- Where present, authigenic microquartz in mudrocks tends to be abundant (~40 volume percent of rock).
- Timing, distribution, and abundance of microquartz suggests the importance of biogenic silica (opaline sponge spicules, radiolaria, and perhaps diatoms) as a silica source.
- Illitization appears to generate little to no authigenic quartz in mudrocks.
- Quartz-cemented mudrocks are, overall, rare, but are significant in terms of having brittle mechanical behavior (and potentially, OM-rich compositions).

Research questions:

➢ What happens to the excess Si generated by illitization? Does it appear in authigenic phases such as chlorite or albite? Is it exported from the mudrocks?

➢ What is the quantitative relationship between cement volume and mechanical moduli?

➢ Can the basinal distribution of mudrocks rich in siliceous biogenic debris (i.e., potentially cemented mudrocks) be predicted using sequence stratigraphic principles?

➢ What is the depth of compactional stabilization in uncemented mud? Does compaction in typical tarl proceed to greater depth than compaction in sand? Is compaction more important to porosity evolution in mud as compared to sand?

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