Seeing is Believing; the Importance of Trace Minerals to the Reservoir Properties of Shales Determined by Electron Imaging and Mineral Mapping*

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Search and Discovery Article #42050 (2017)**
Posted April 10, 2017

*Adapted from oral presentation given at AAPG 2016 Annual Convention and Exhibition, Calgary, Alberta, Canada, June 19-22, 2016

Winner of the George C. Matson Award for the “Best Oral Presentation” at the 2016 AAPG Annual Convention and Exhibition in Calgary.

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Abstract

Studies of conventional reservoirs routinely apply optical petrography to determine the association of minerals, pores, and occluding cement. This approach is not feasible in shale reservoirs because the resolution of optical petrography does not allow imaging of the nano-to microscale grains and pore systems characteristic of shale. Given the common view that shale is largely homogenous, bulk measurements such as powder X-ray diffraction or gas sorption are most commonly employed to characterise unconventional reservoirs. While these techniques often reveal the presence of trace minerals and microscale porosity, in situ studies of pores using electron imaging has revealed results that could not have been predicted based on bulk properties, such as the presence of pores in specific phases such as organic matter. Here we show an analogous refinement in understanding of mineralogical reservoir properties using electron mineral mapping to locate trace minerals identified in bulk powder analysis. Electron image based mineralogical data are compared between two late Permian aged shale reservoirs in South Australia; the lacustrine REM interval of the Cooper Basin and adjacent marine Stuart Range Formation in the Arckaringa Basin. Both show systematic distributions of early carbonate cements. The low sulfur REM typical of lacustrine settings resulted in early diagenetic Fe carbonate (siderite) cements that preferentially formed in coarser grained laminae. These cements parse the reservoir, restricting migrating hydrocarbons to finer grain size intervals. By contrast, S sourced from seawater in the Stuart Range led to sequestration of Fe in pyrite, barring the formation of siderite and allowing sulfurization reactions that preserved lipid-rich type II organic matter. Pyritic intervals alternate with Mn-carbonate cemented intervals dominated by type III (refractory terrestrial) OM in varves resulting from oscillations in basinal redox conditions. The dominance of one cycle over the

other influences hydrocarbon potential as well as brittleness and reservoir compartmentalization where Mn-carbonate intervals increase. While Mn-carbonate and siderite were present in trace amounts in many of the samples analysed by powder X-ray diffraction, the spatial data from the in situ technique provided the environmental significance and the ability to better understand basinal trends in source, reservoir, and rock properties.

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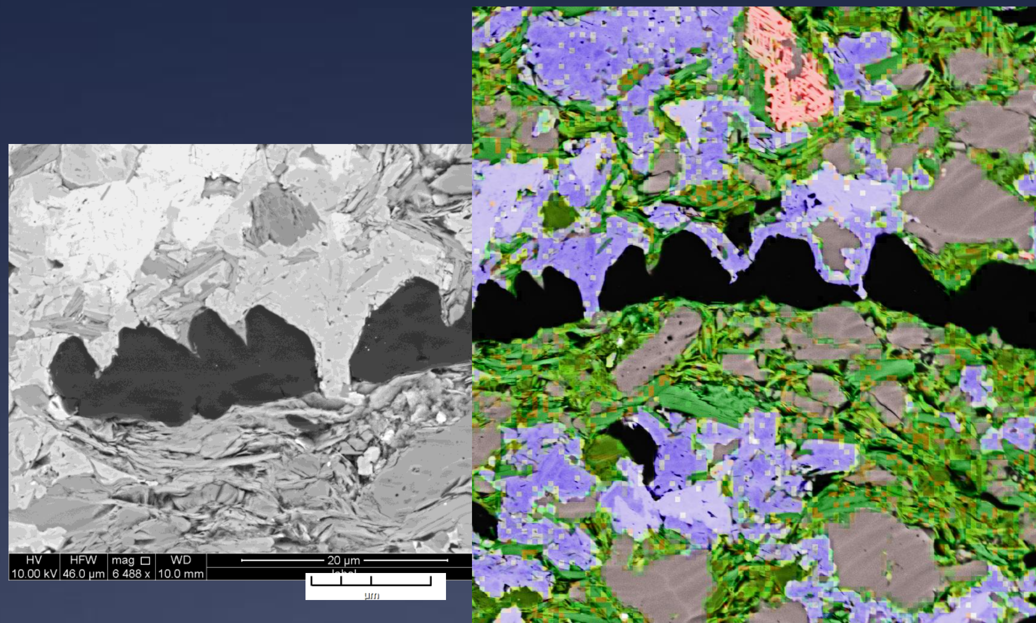
Seeing is believing; the importance of trace minerals to the reservoir properties of shales determined by electron imaging and mineral mapping



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A Tale of Two Shales:
Early Permian Cooper Basin VS Arckaringa Basin

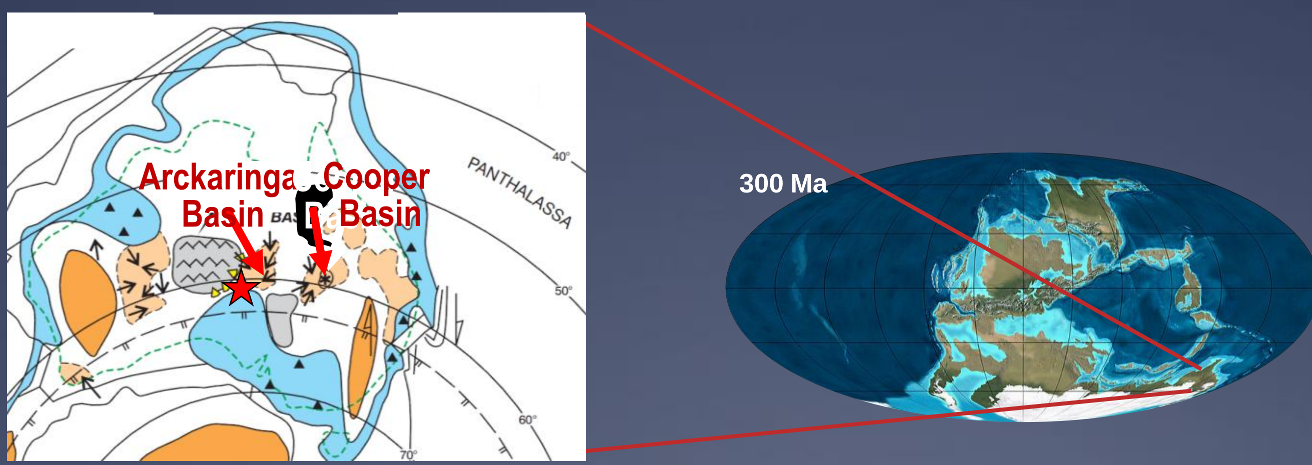
What controls the difference in organic carbon content and unconventional potential

Similar:

age, stratigraphic position, sediment composition

Difference:

Lacustrine, Marine, Burial



(Menpes 2012)

Cooper VS Arckaringa Basin

Lacustrine VS Marine

world class source rock VS successful unconventional play

What is the difference between these?

Arckaringa Basin

Australia's Best Source Rock(?)

TOC < 13%
HI > 500
Ro=0.6
Type II Kerogen
Live oil in core

NO production

Arckaringa Basin

Australia's Only producing Shale play & worst source rock

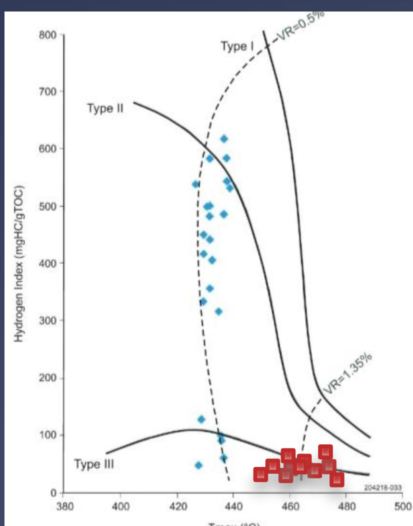
TOC < <5 %
HI < 25
Ro= >1
Type III Kerogen
Bitumen in core

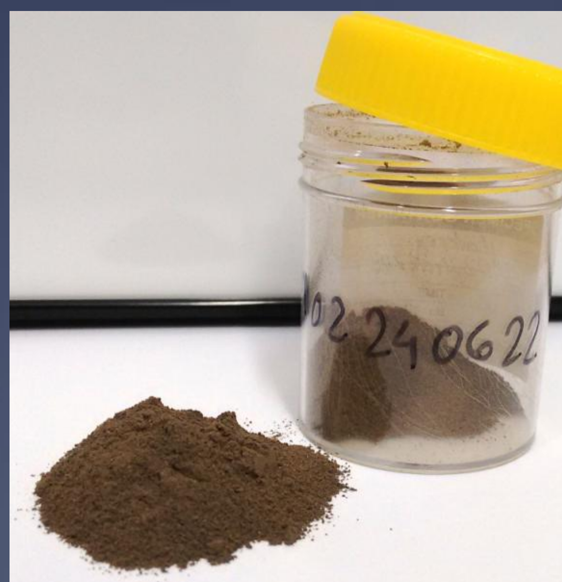
Gas production

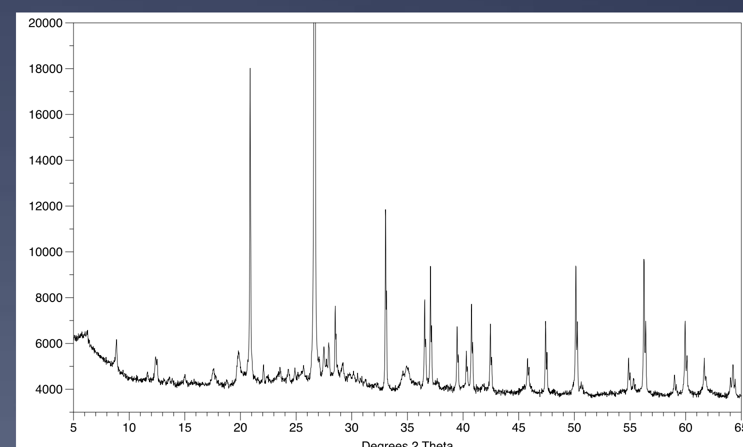
1. Bulk rock data (mostly relevant for source rock prop.)

The approach to unconventional plays is guided by 40 years of studying source rocks in conventional plays:

- Source rock intervals were rarely cored (stop at reservoir)
- Geochemical analysis of expelled products most important and determined on bulk rock powders
- Petrographic relationships of source interval were less relevant





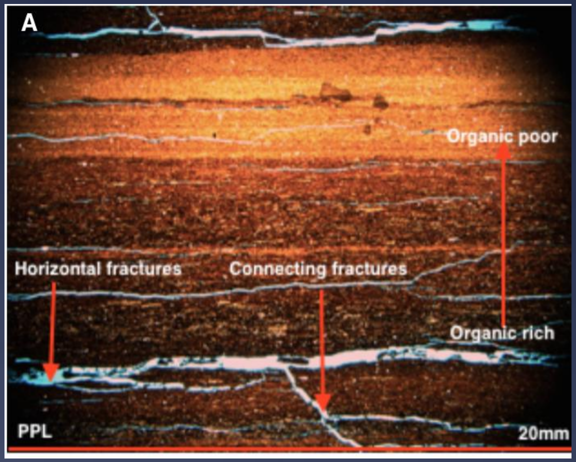


Critical Information missing to step from source rock to unconventional potential

Bulk Rock studies provide only inferred information about:

* rock properties (average from XRD),
* reservoir potential (porosity measures),
* digenetic history, (XRD, maturity)
* Depositional environment (bulk mineralogy)
* Organic composition (pyrolysis)

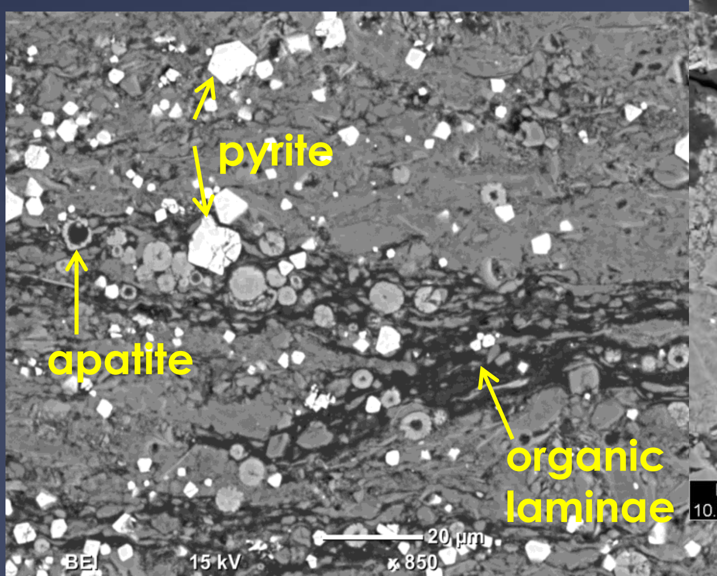
Shale petrology using optical methods; limited for fine grained sediments

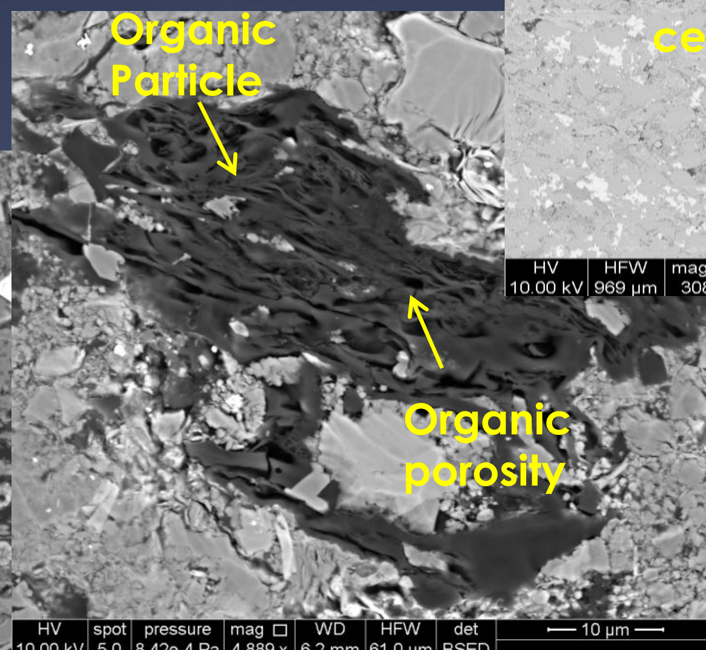


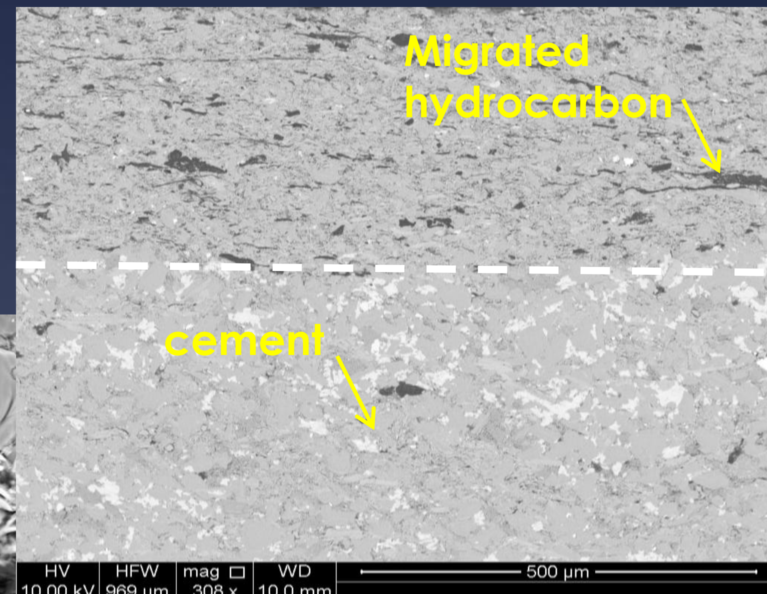
- Thin sections are many tens of crystal layers thick
- Optical wave length does not resolve relations below 5µm (grain scale features are sub micron)
- Ideal for establishing sedimentological constraints

2. **SEM imaging for grain to grain relationships**
Backscatter Mode using ion polished block

- Porosity
- Cement distribution
- Mineralogy (sort of)
- Diagenesis
- Organic matter types
- Migration history

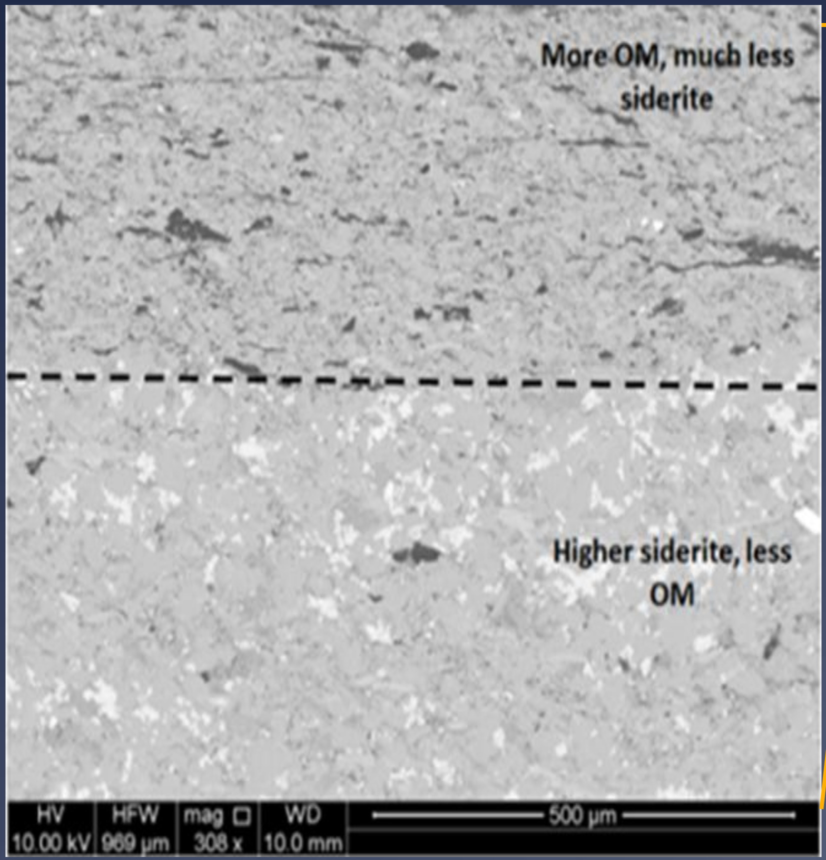


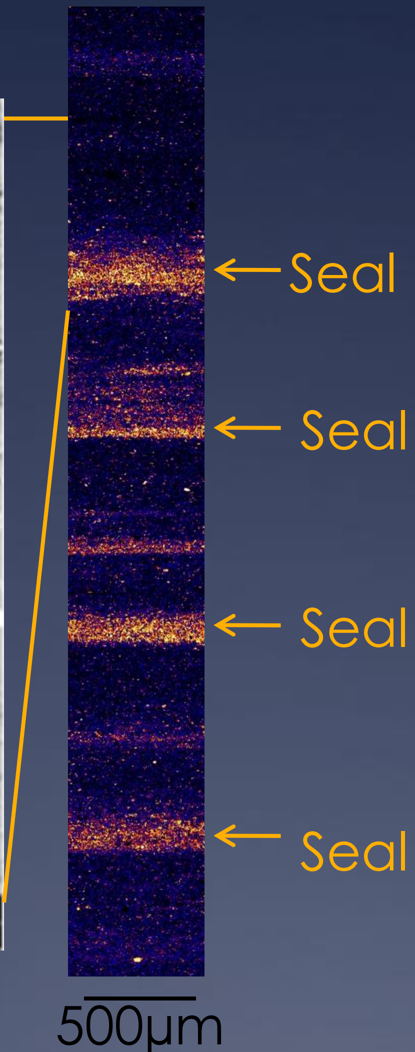




3. **Elemental mapping for phase determination**
Cooper Basin: Lacustrine System

Australian Synchrotron Infrared Fe map





Siderite is early, forming within coarser siltstone laminae

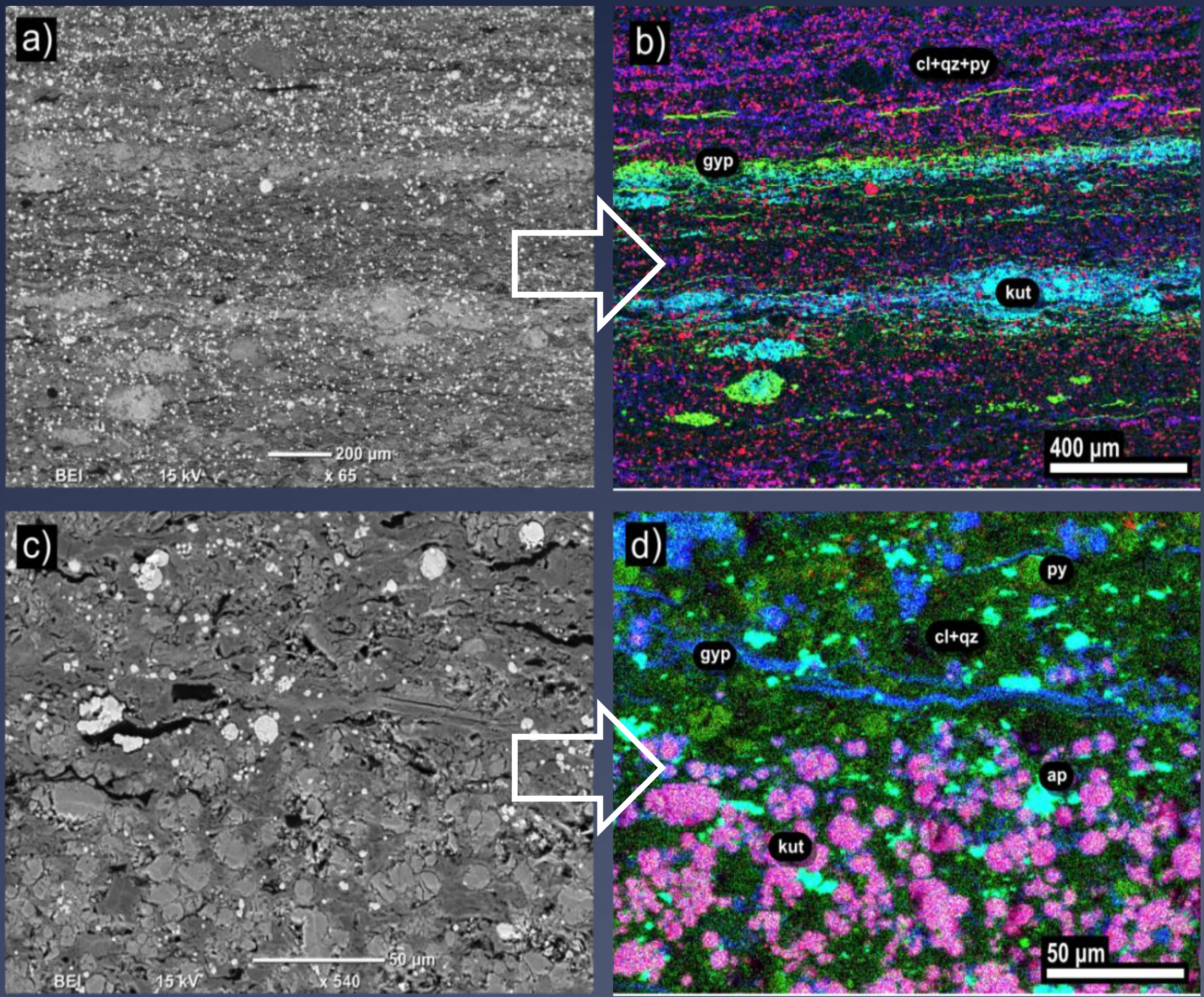
Mini seals within sequence result in a tight formation

pore filling cement predates charge and is early diagenesis.

Fe-carbonate and lack of pyrite indicate S limitation in freshwater system

3. **Elemental mapping for phase determination**
Arckaringa Basin: marine system

EDX (Energy Dispersive X-ray) mapping

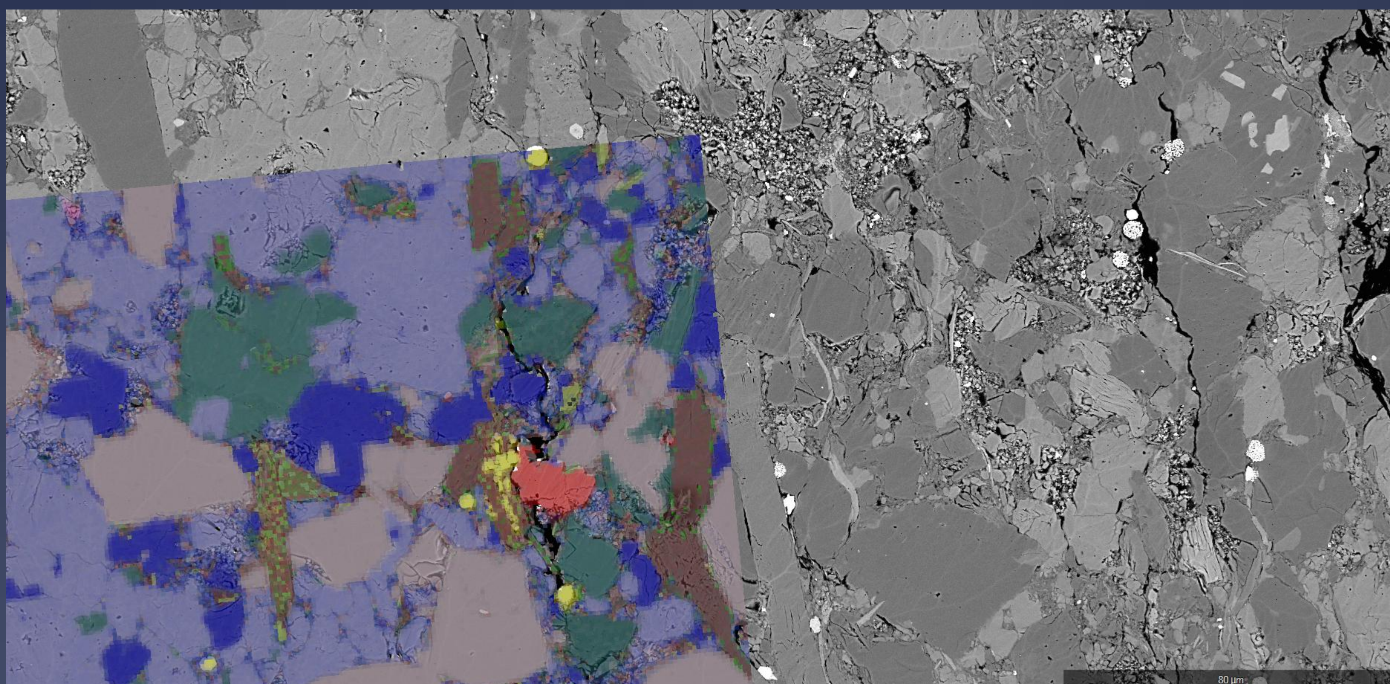


Arckaringa Composition:

- Equally cyclic
- Mn alternates with S in alternate laminae
- S is associated with organic carbon
- Mn is organic lean
- no Fe as in in Cooper
- Evidence of migration and organic particles

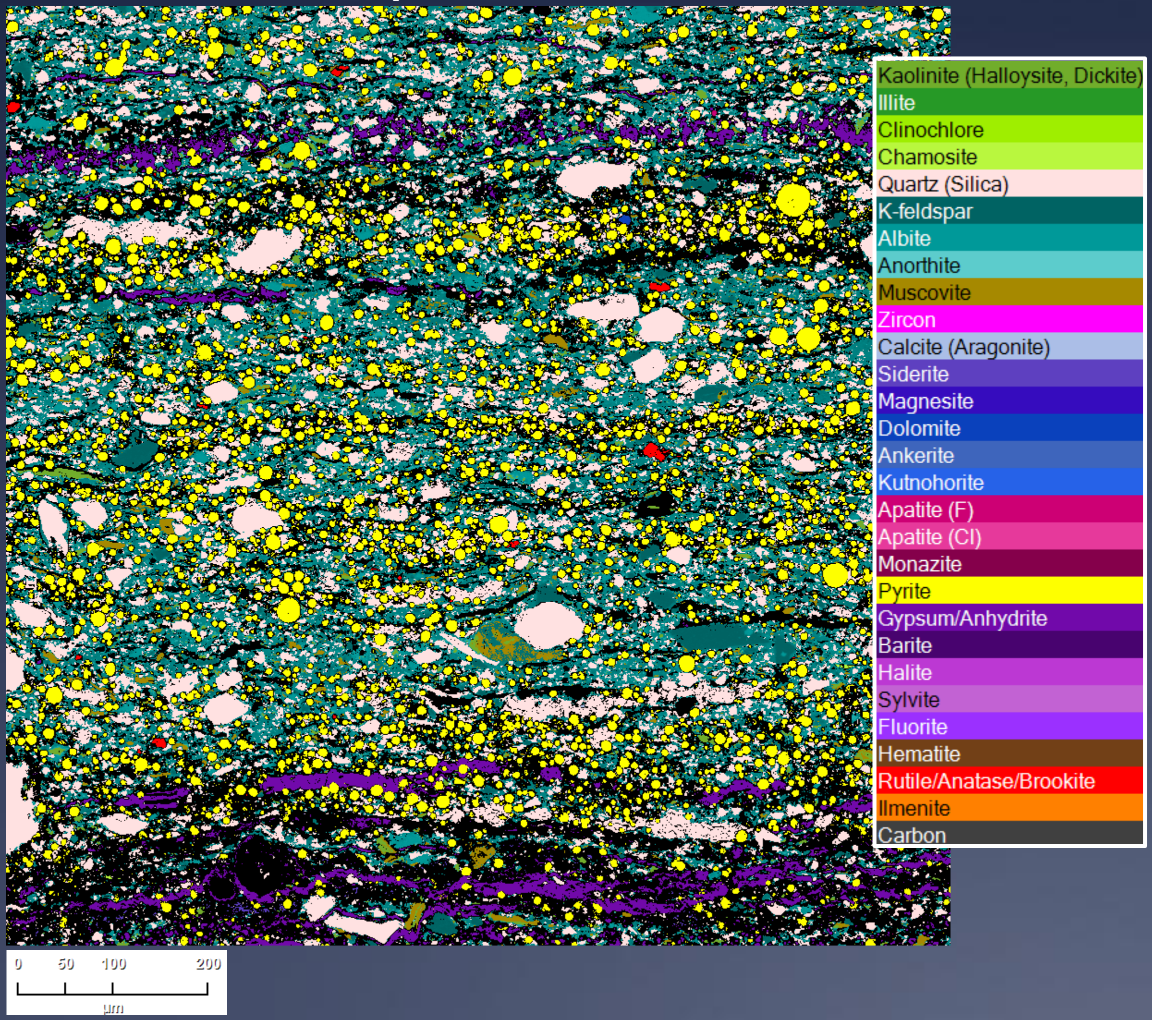
The Ideal Analytical System:

- an automated mineral mapping
- At relevant (sub micron) resolution
- quantification of mineral abundance and particle associations
- Broad scan area *that retains* sub micron resolution



QEMSCAN: first generation mineral mapping for geological materials

QEMSCAN

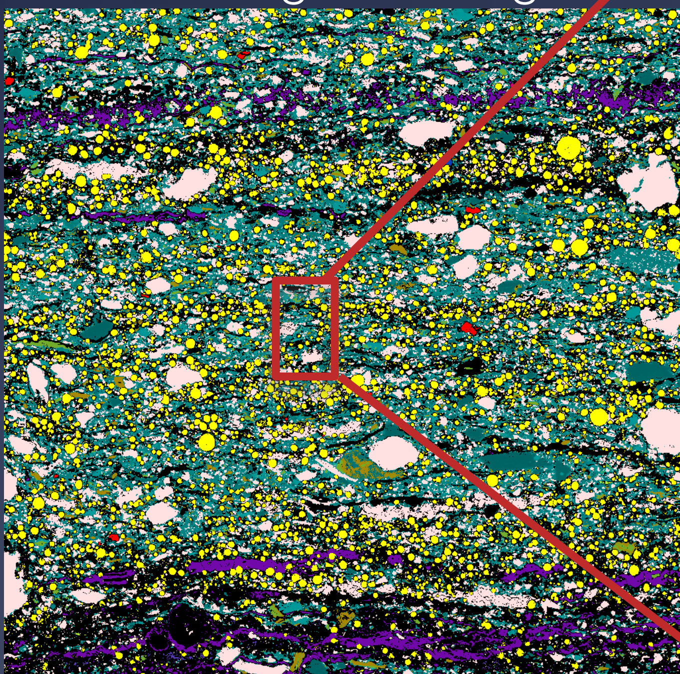


- Interprets EDX spectra and uses mineral data base to assign mineralogy
- Pixel size is >5µm
- Pixels have only one mineral assignment (average value)

- **inaccuracy for shale with grain size < 5µm**

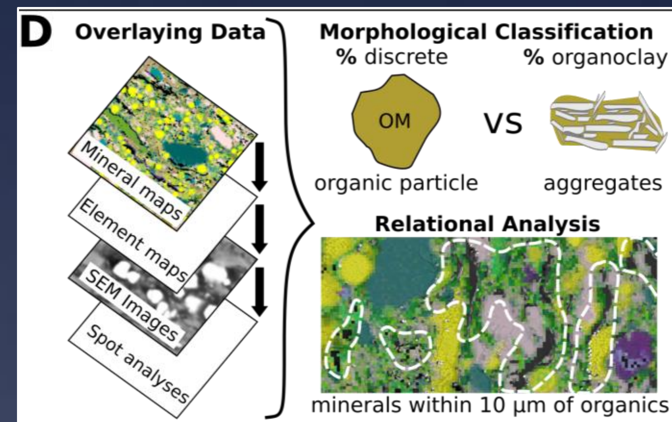
The next generation system: Nanomin at Macquarie University Shale Lab. Specifically designed for shale analysis

- produces multiphase model for each 2 μm pixel
- 500 nm mineral resolution
- BSEM integrated image



Qemscan

Nanomin

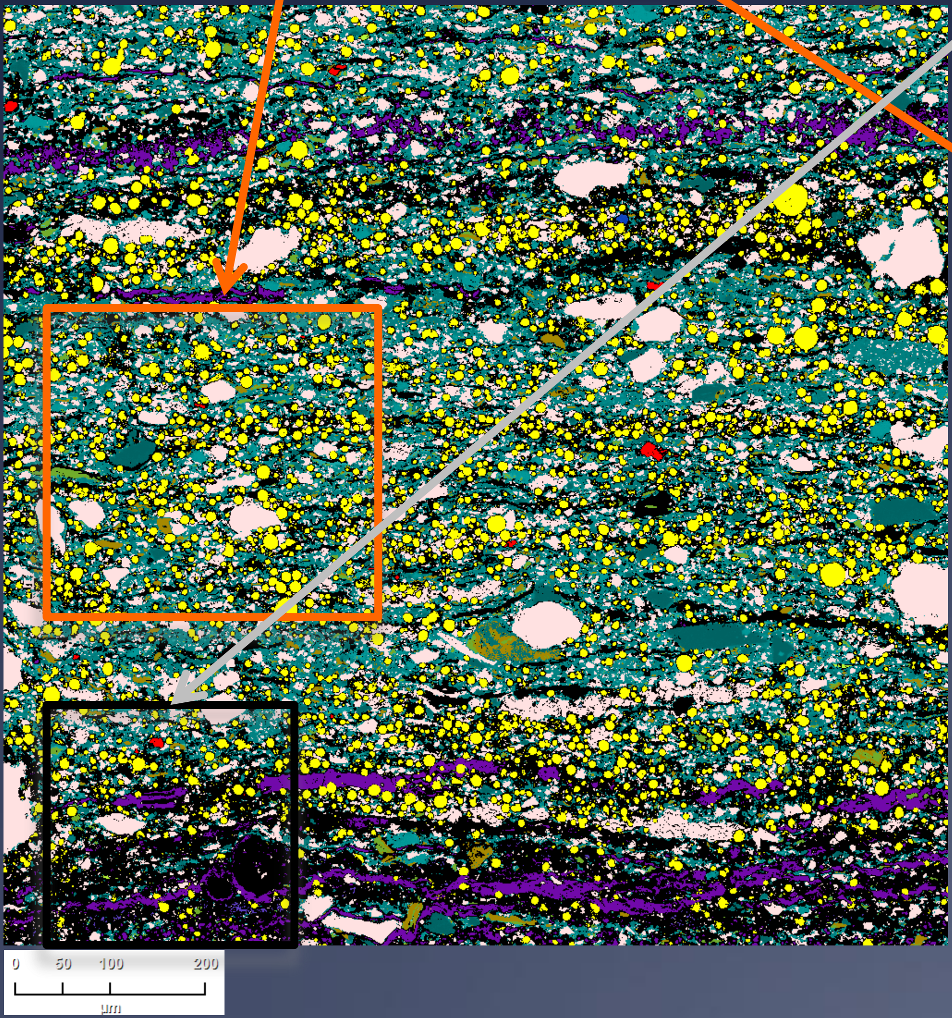


QEMSCAN and Nanomin Compared

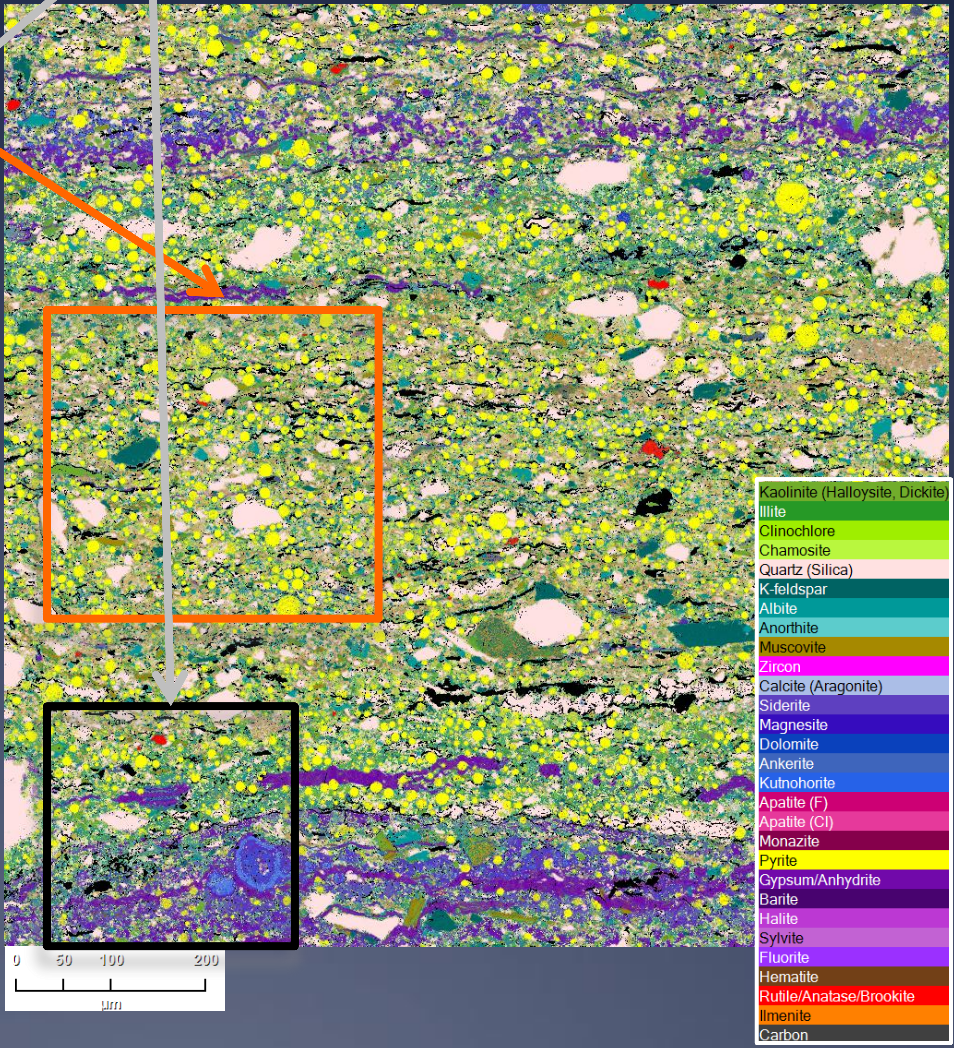
Carbonate not identified, much unclassified

Clay matrix misclassified as feldspar

QEMSCAN



NanoMin



Quantitative Mineralogy QEMSCAN vs NanoMin

Mineral	QEMSCAN - Area %	NanoMin - Area %
Quartz	18.53	26.15
Alkali Feldspar	25.48	15.17
Plagioclase	0.76	0.81
Muscovite	1.46	8
Kaolinite	1.14	4.31
Illite	0	2.1
Chlorite	0.02	3.99
Siderite	0.05	4.17
Mn Carbonate	0	4.05
Pyrite	11.07	15.84
Gypsum	3.21	5.64
Unclassified	32.32	0.88
Porosity	5.85	5.85

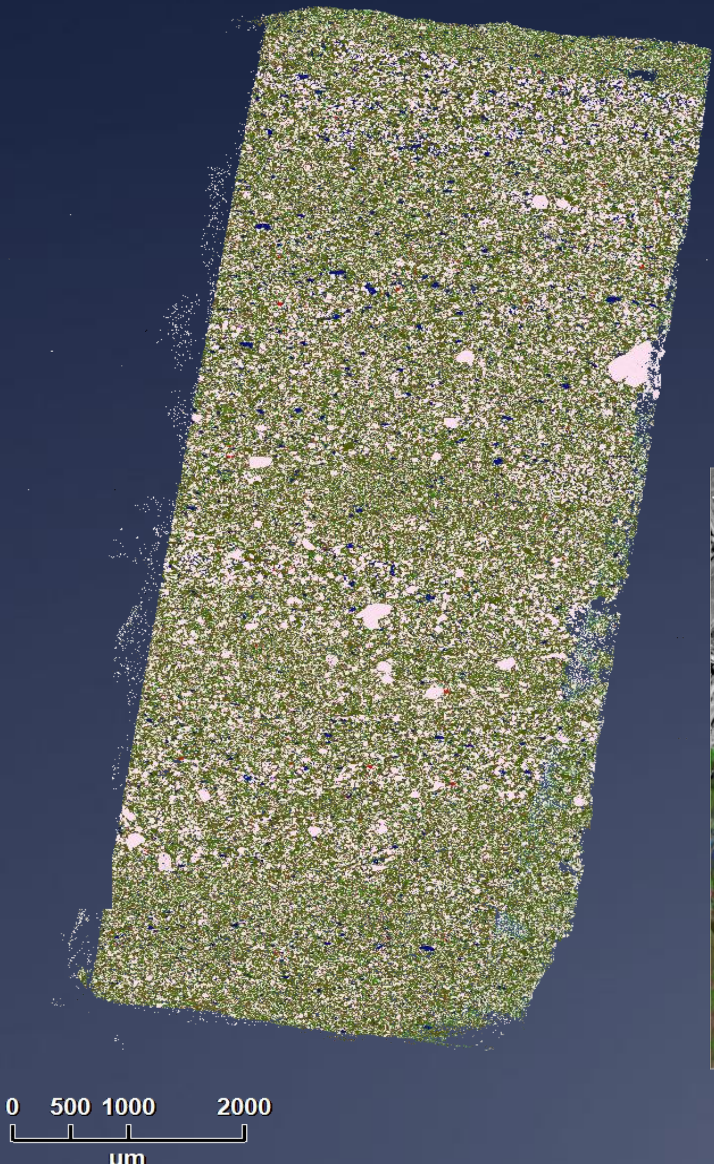
Quartz silt under-reported

Clays and mixed minerals misreported as feldspar

Minor carbonate phases not identified

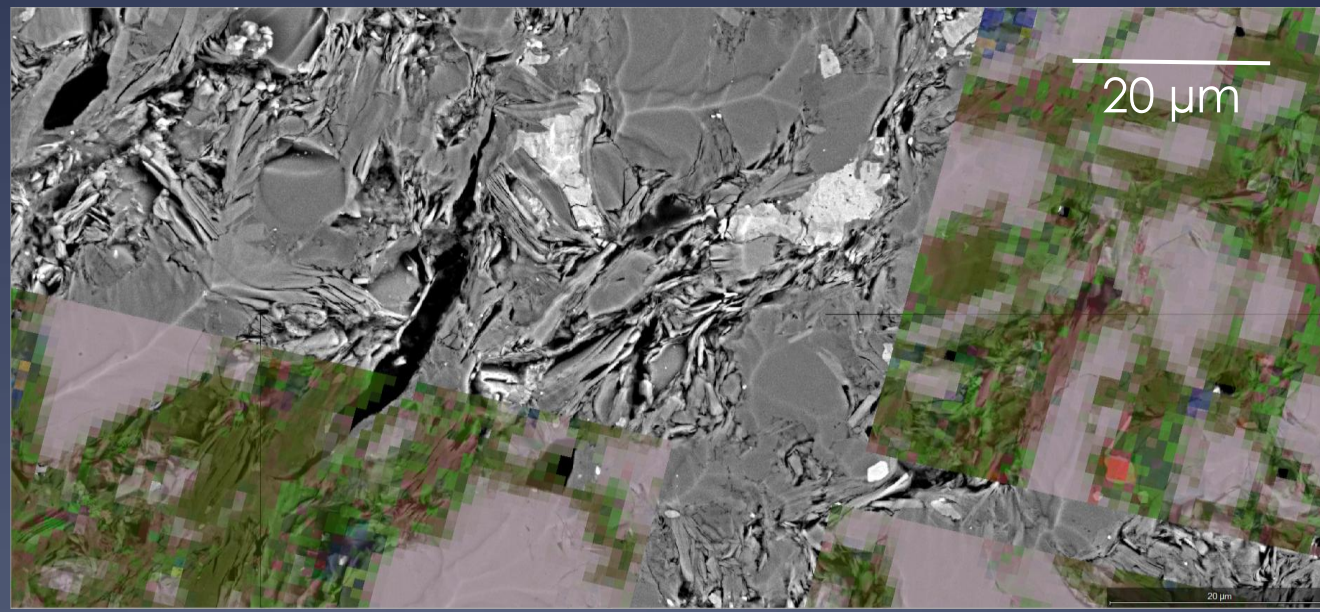
Unclassified

Nanomin mineral mapping



- Quartz
- K-feldspar
- Albite
- Anorthite
- Muscovite
- Zircon
- Kaolinite/Halloysite/Dickite
- Illite
- Calcite/Aragonite
- Siderite
- Magnesite
- Rutile/Anatase/Brookite

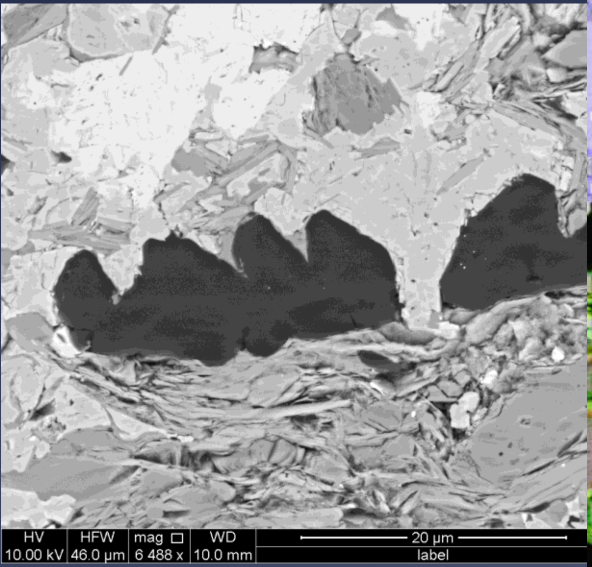
- Whole thin section scan
- µm mineral detail
- Feldspar has resolved in to illite, kaolinite and muscovitite with finer scale analysis of Nanomin

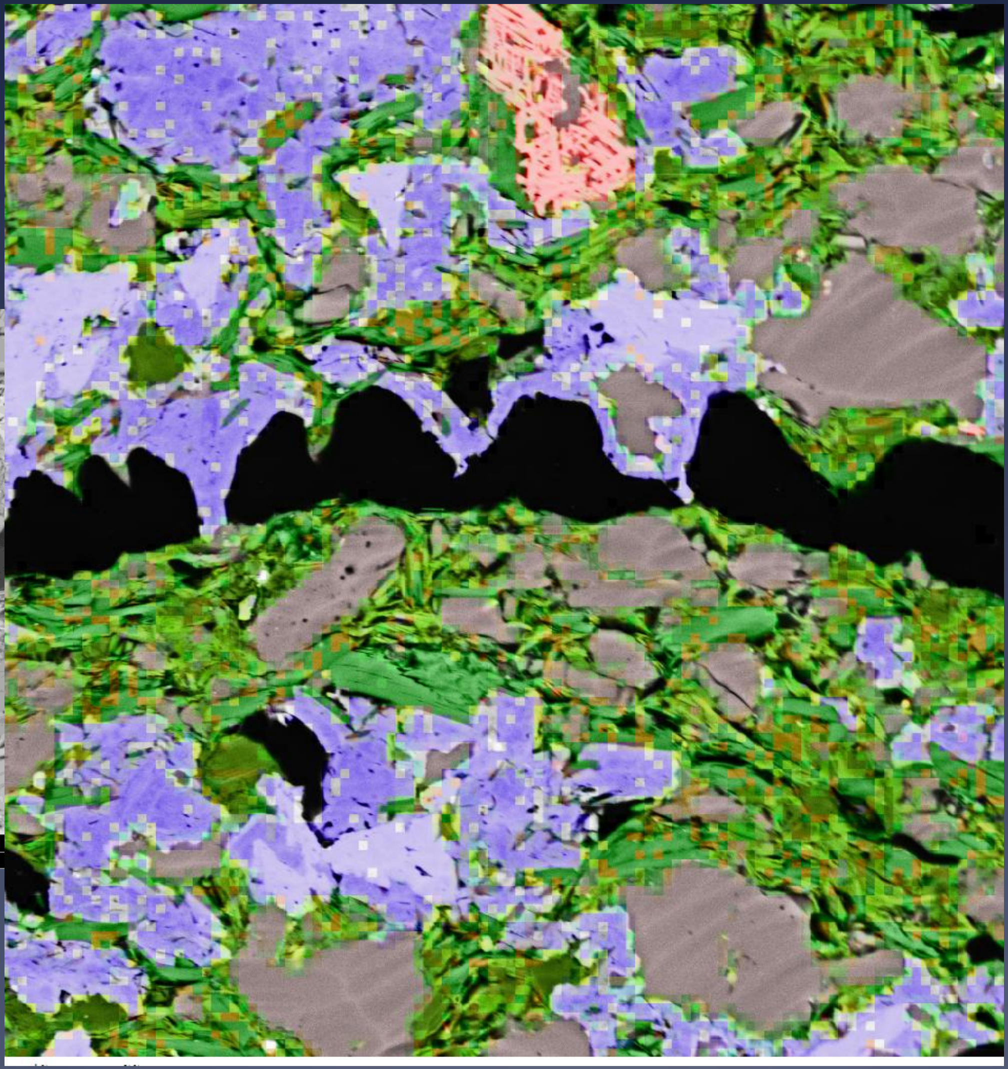


Cooper Basin, Murteree Shale

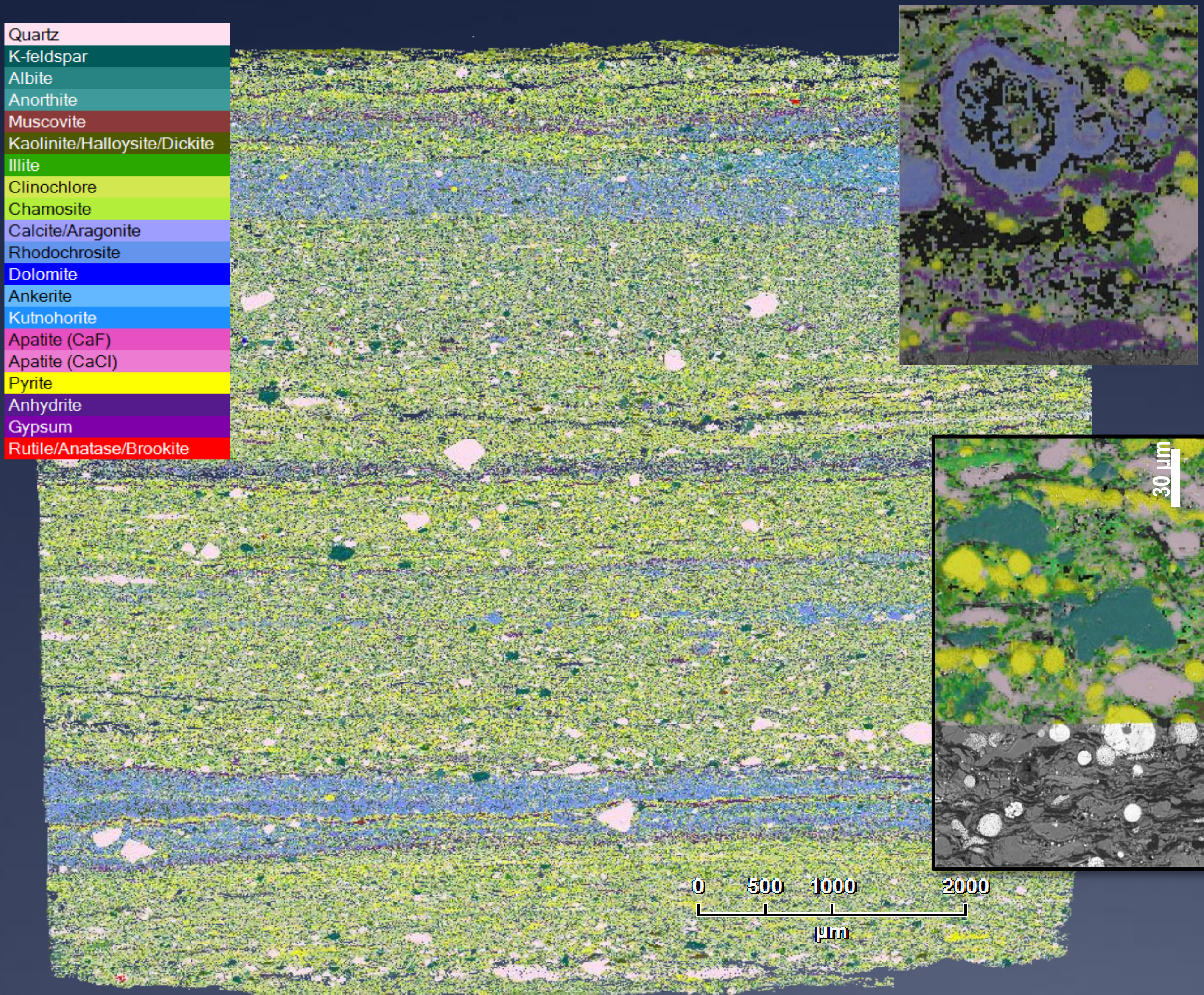
Details of Siderite distribution Cooper Basin

- Displacive groth
- Close association with illite and organic particles





Trace Minerals are Key to interpretation

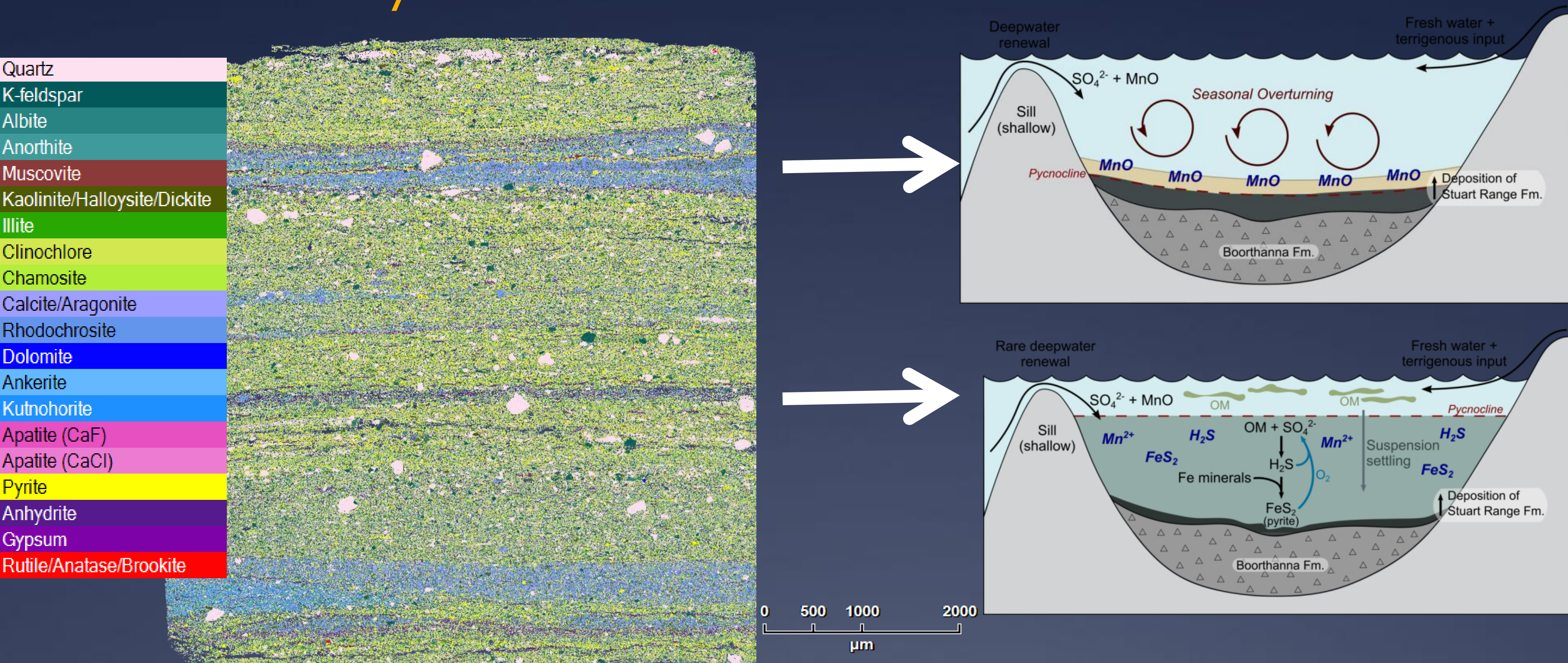


Stuart Range Fm, Arckaringa Basin

- Alternation of kutnohorite (Mn carbonate) and pyrite
- Kutnohorite not recorded in XRD analysis
- Associated with oxidizing conditions
- Pyrite (20%)= reducing conditions and sulfur bonded OM

How does this information help us understand the geology:

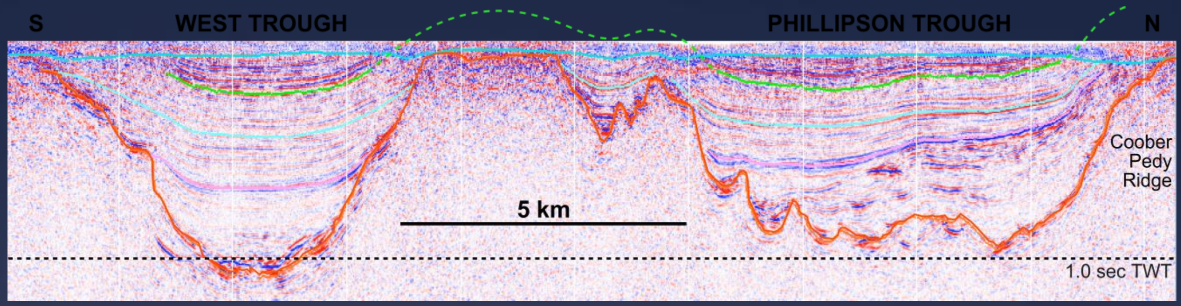
Cycles=water column influence



- Kutnohorite cycles= oxidizing basinal conditions, Type III, OM lean
- Pyrite cycles= water column HS-, Type II, OM rich sulfur bonds
- S from marine connection, no S or S bonding for lacustrine Cooper

Basin Scale Depositional controls of Stuart Range Fm in Arckaringa Basin

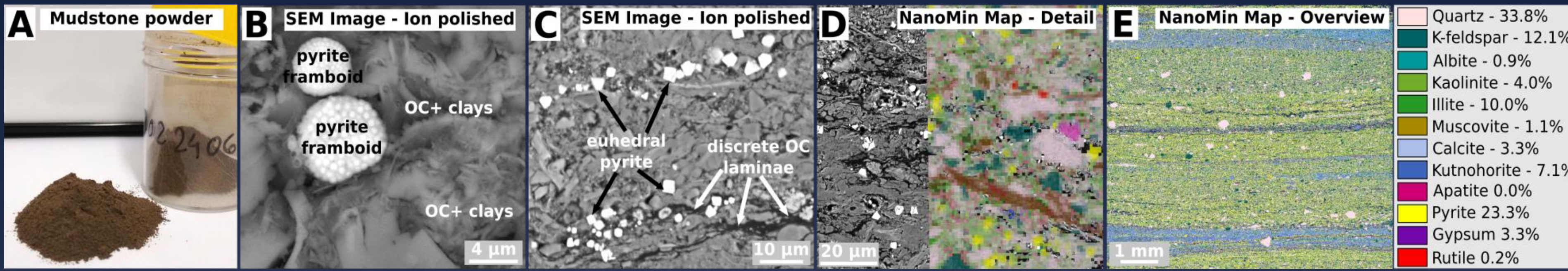
- Basin troughs = glacial erosional features (fjords)
- End-moraines formed sills controlling marine inflow, restriction and stratification leading to euxinic cycles
- Cyclical overturn resulted in varves of S rich and Mn rich composition
- Mn rich (Kutnohorite) cycles record overturn and oxidizing phases as in Baltic Sea (e.g. Huckriede and Meischner 1996)



(Menpes 2010)

Mitre Peak, Milford Sound, NZ (pocruises.com 2014)

What was added by this approach?



Cooper Basin:

- Siderite cement, early diagenetic- predated migration
- High TOC samples are from migrated phase
- Parsed reservoir contributing to overpressure
- S poor (lacustrine setting) no S bonding leading to poor OM preservation resulting and low hydrogen index

Arckaringa Basin

- Kutnohorite intervals record oxic cycles in restricted basin that host only terrigenous OM with low hydrogen index
- OM preserved in pyritic intervals and show OM- S bonding that preserve labile OM