



Creating a haystack from a needle

In situ SIMS sulfur isotope analysis

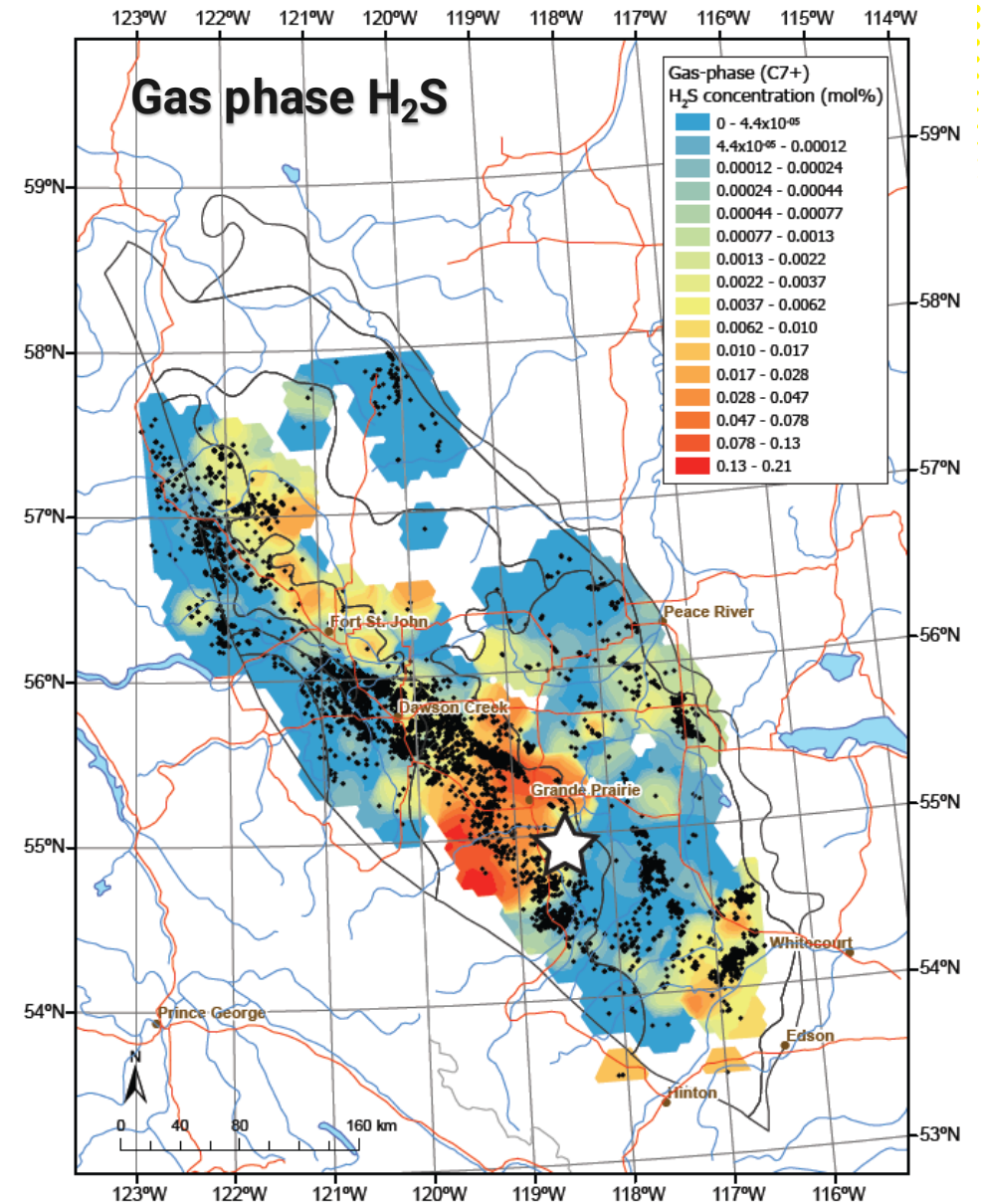
Andrew Kingston & Omid Ardakani

| Traditional Territorial Acknowledgement

I acknowledge that I am working on the traditional territories of the people of the Treaty 7 region in Southern Alberta. These are the Tsuut'ina First Nation, the Stoney Nakoda First Nation (including people of the Chiniki, Bearpaw, and Wesley), and the Blackfoot Confederacy (which includes people of the Siksika, Kainai, and Piikani). This region is also home to Métis Nation of Alberta, Region III.

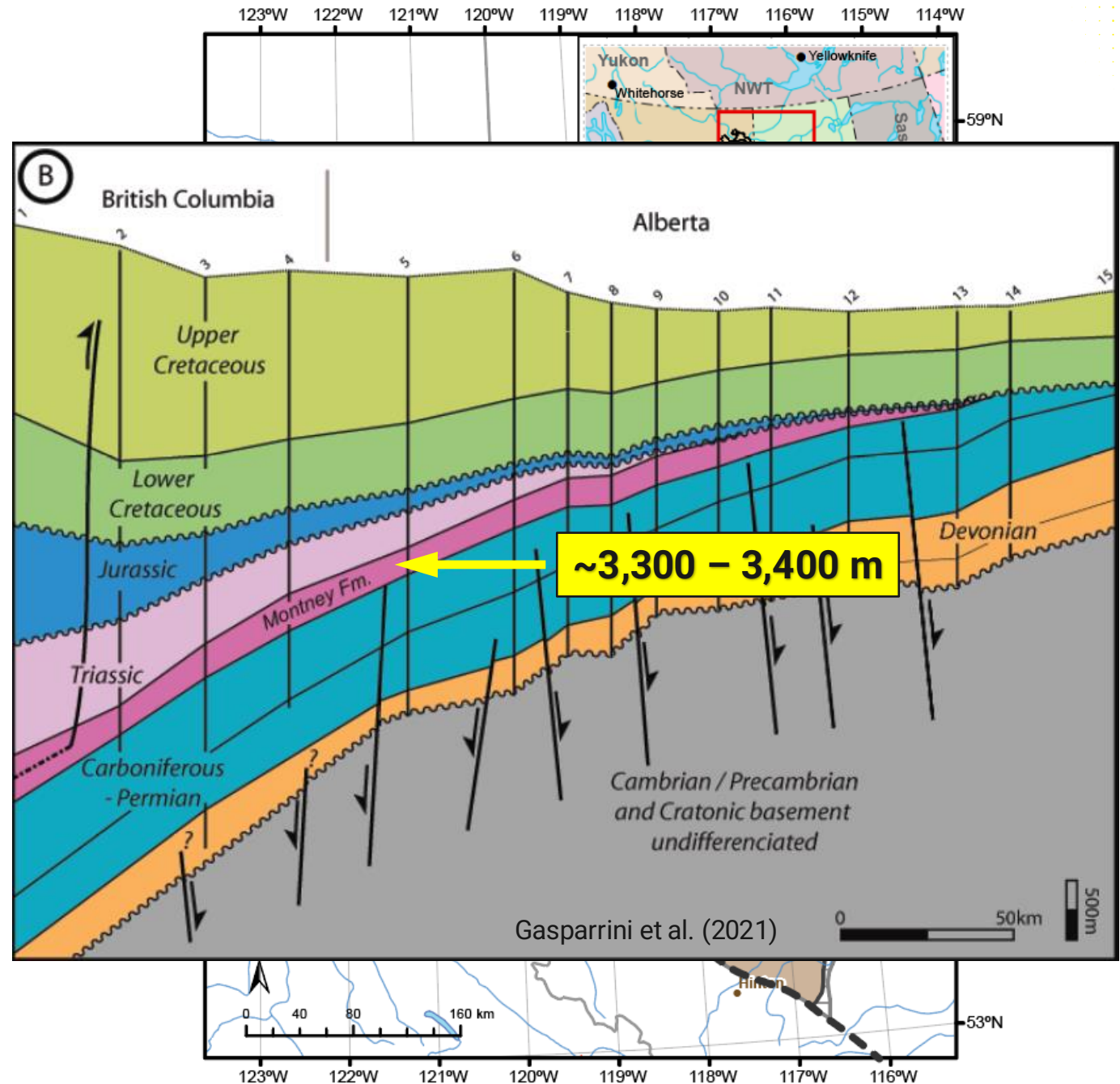
Motivation

- Sour gas makes up $\sim 1/3$ of the gas produced in Alberta
- Montney Formation is Canada's most productive gas reservoir
- Essential to understand H_2S formation processes to protect people and infrastructure in hydrocarbon producing regions



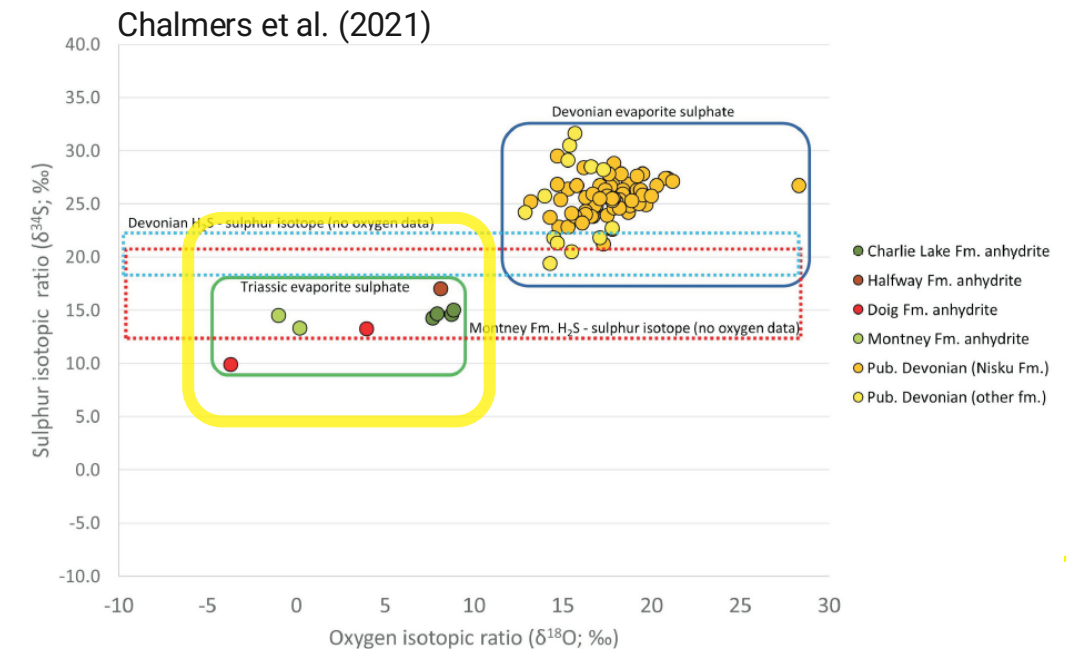
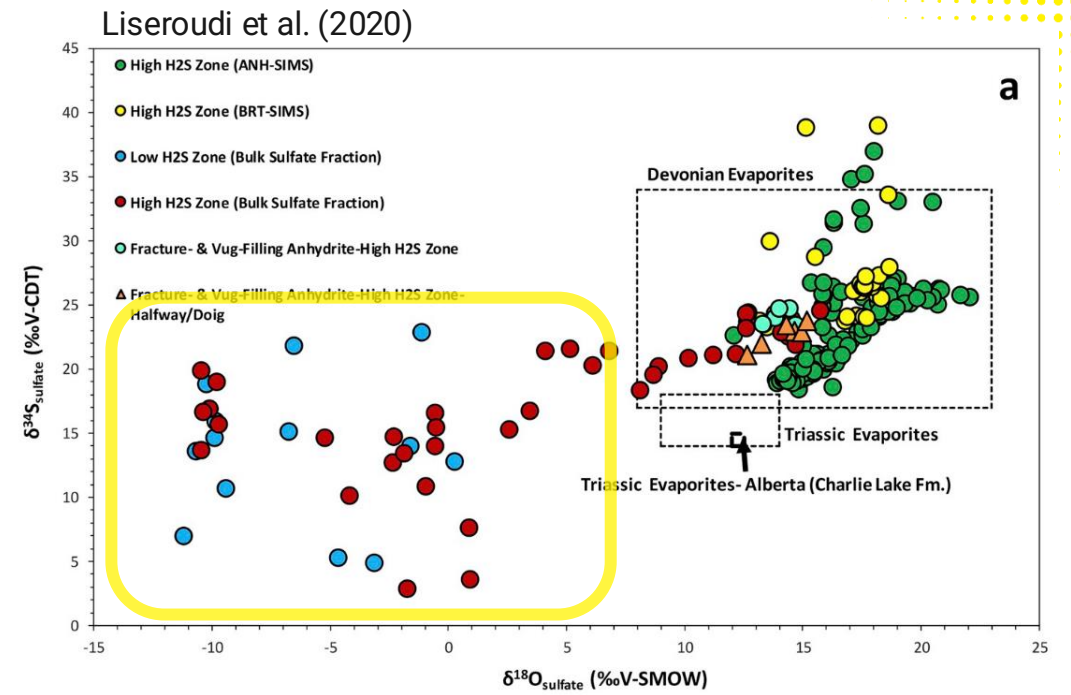
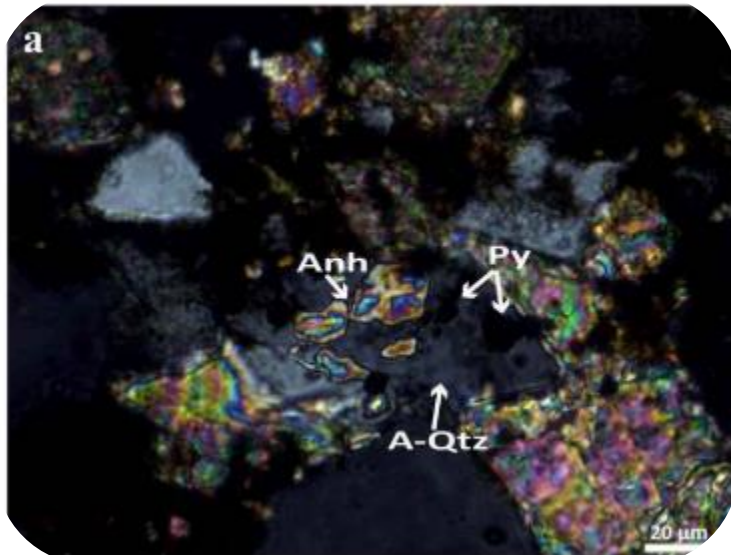
Study Objectives

- **Mineralogical, geochemical, isotopic and paragenetic characterization of sulfur-bearing phases**
 - **Core Material**
 - Fluids
 - Gases
 - Water
- Anthropogenic stimulation of H₂S generation



Previous work

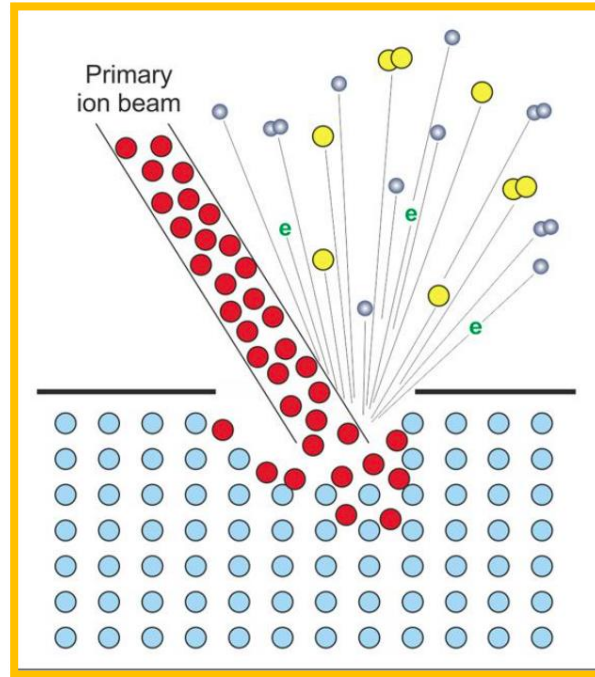
- Previous investigations of sulfur isotope geochemistry of **bulk rock extracts** and **SIMS** indicate *in situ* methods are better suited
- Evidence of sample processing artefacts on extracted sulfate (e.g., Mangalo et al. 2007)



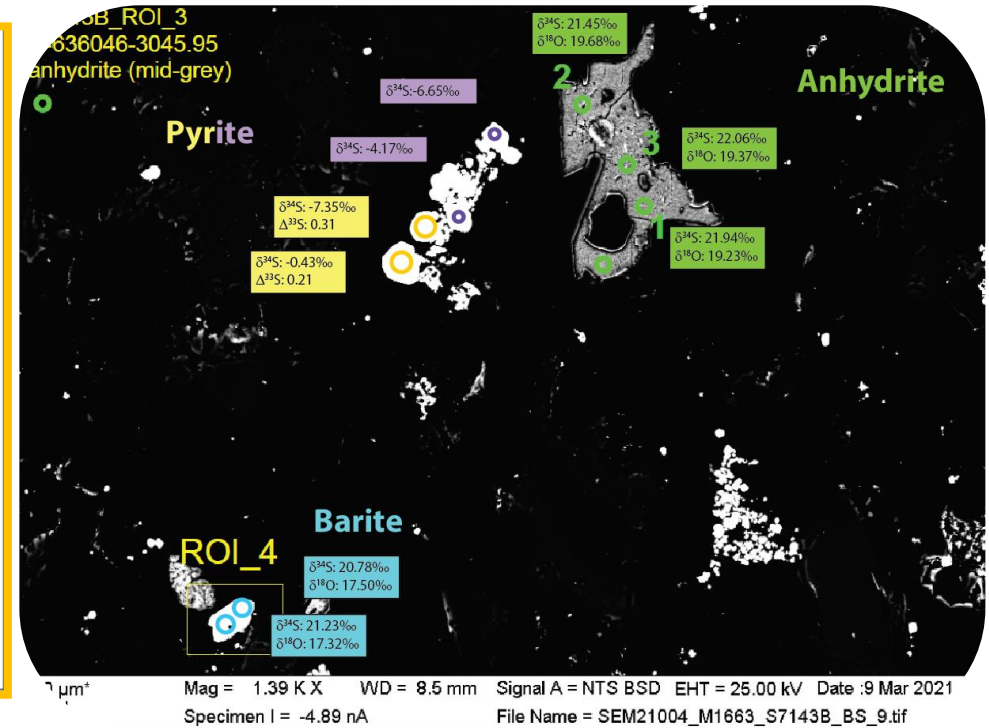
Analytical Techniques



Bulk sampling + CF-IRMS



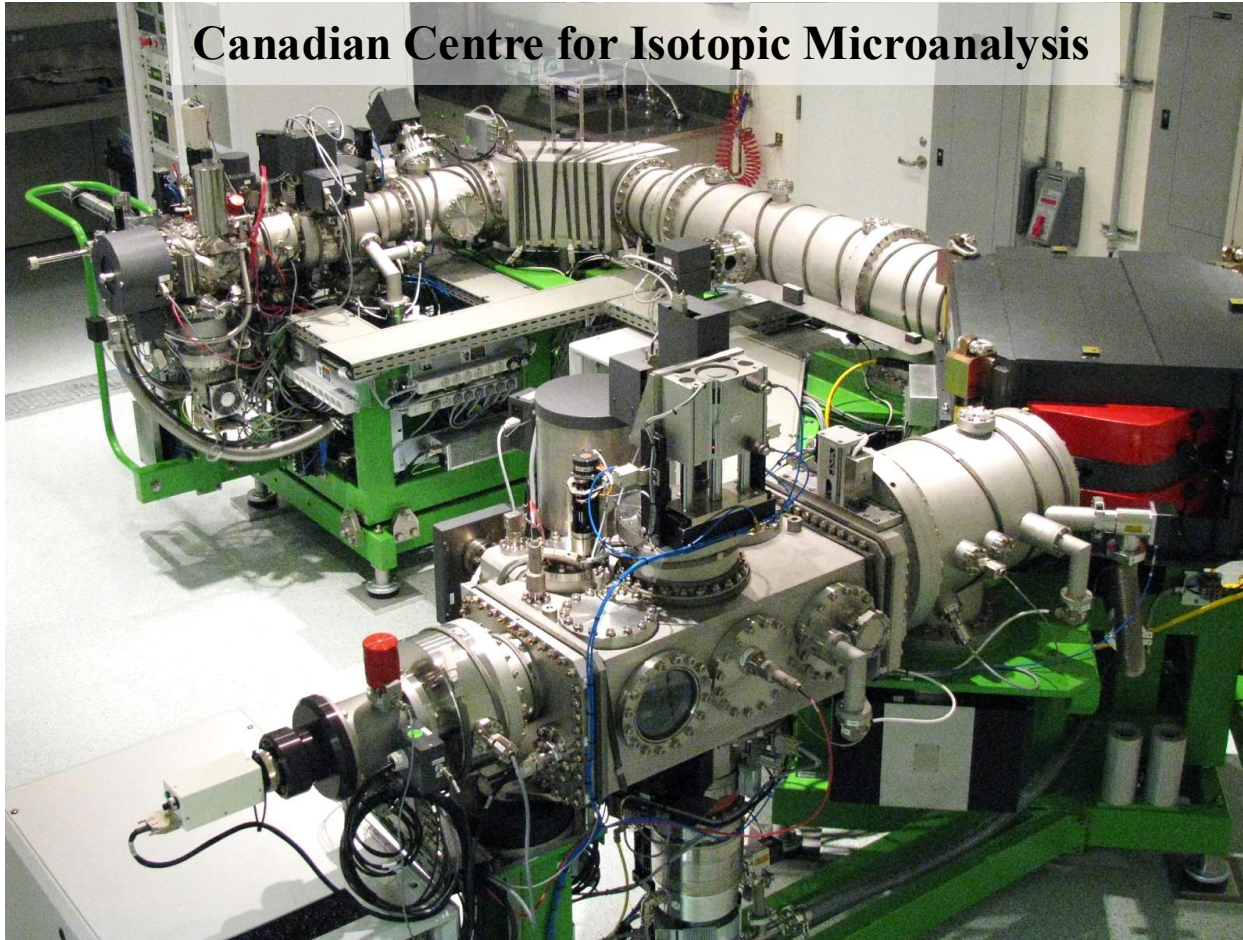
GEOW



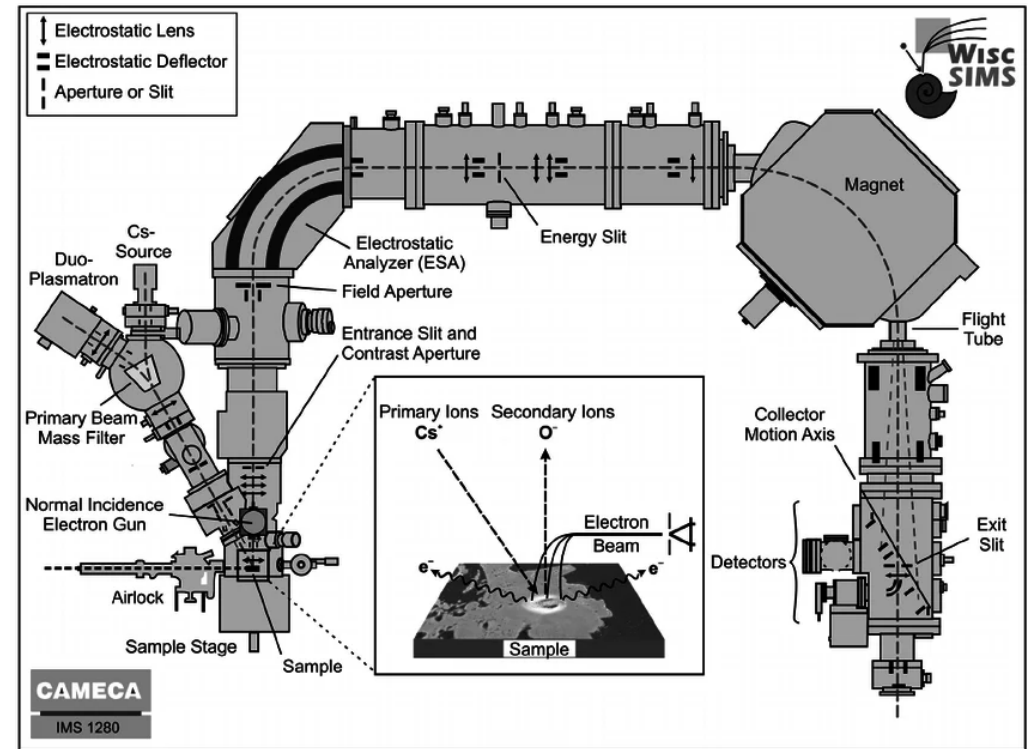
In situ SIMS

Secondary Ion Mass Spectrometry (SIMS)

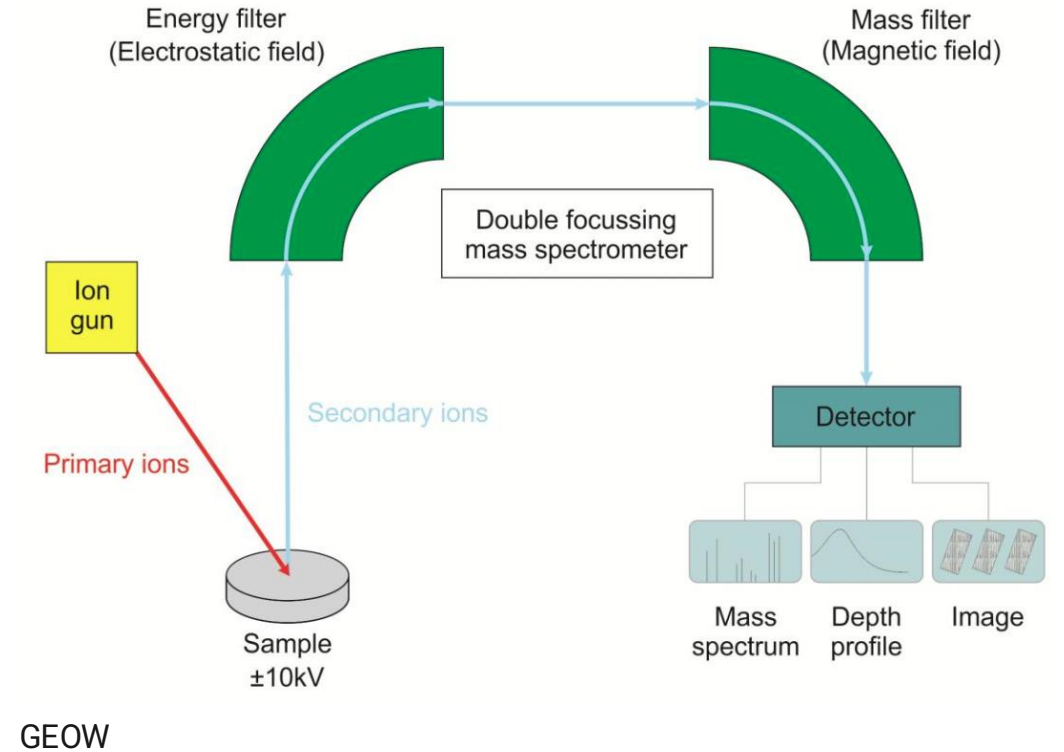
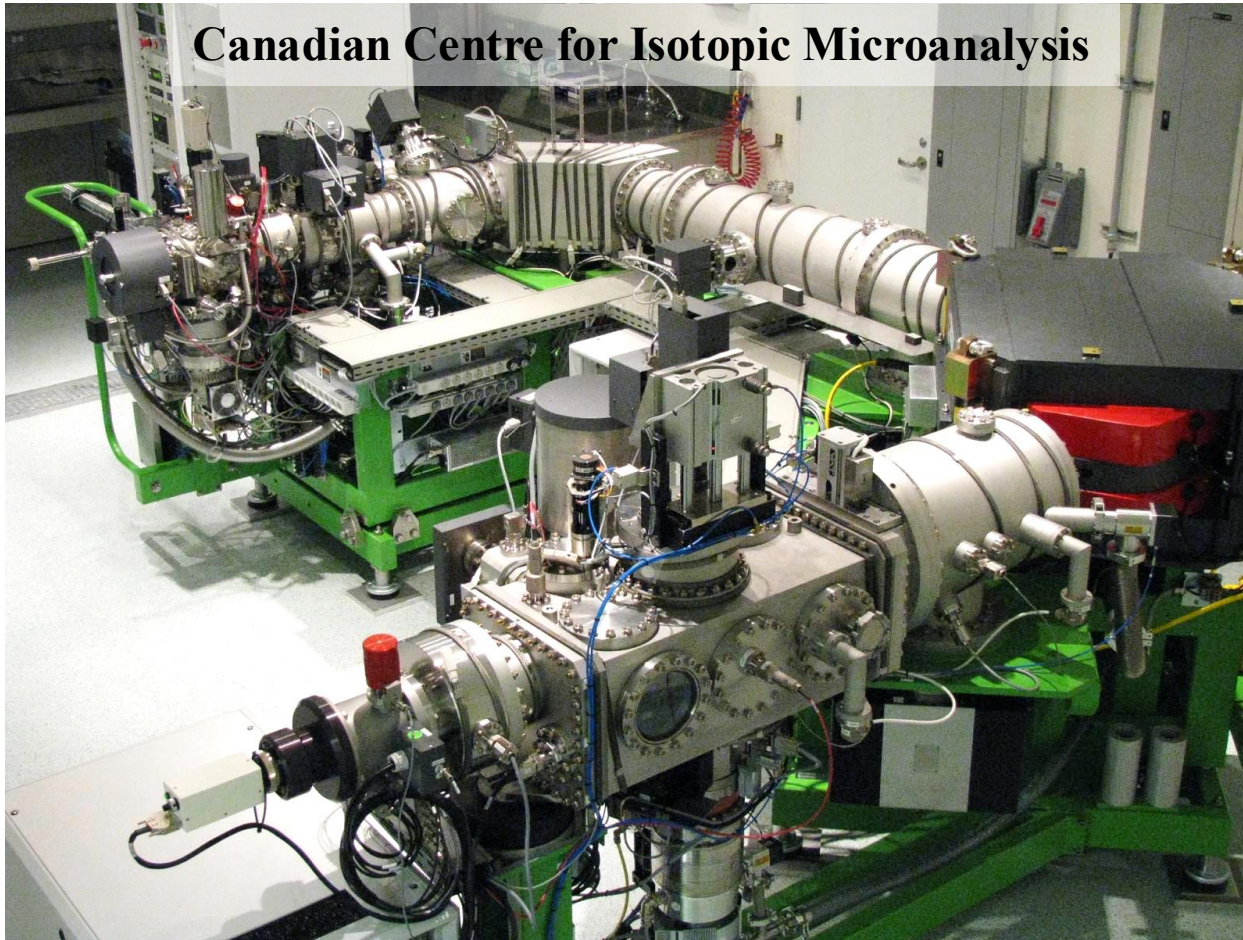
Canadian Centre for Isotopic Microanalysis



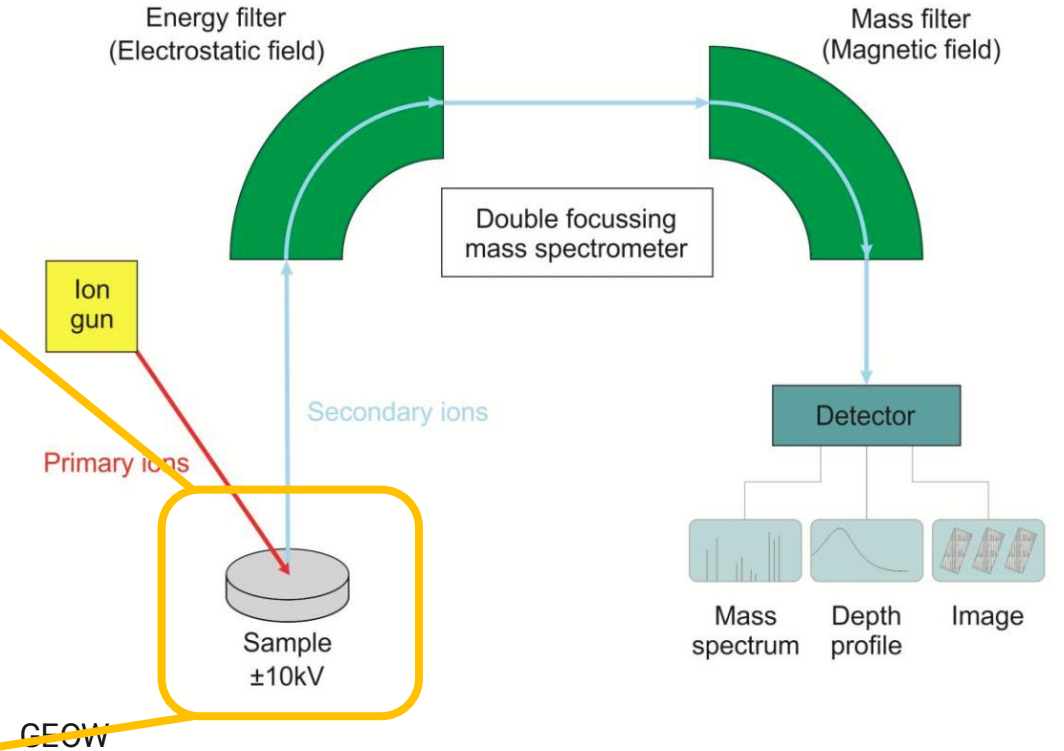
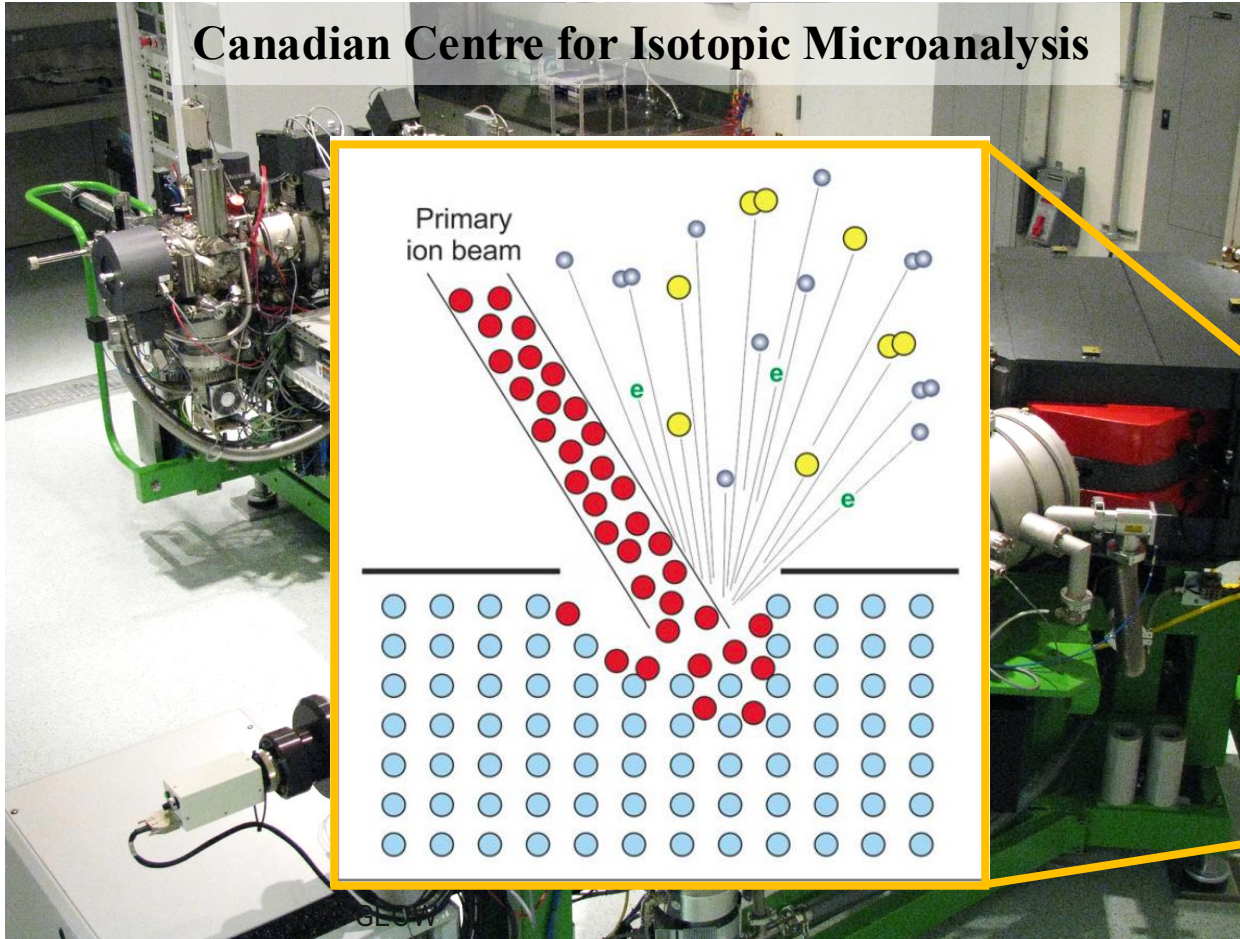
- CAMECA IMS-1280 multi-collector ion microprobe at the CCIM (UofA)



Secondary Ion Mass Spectrometry (SIMS)

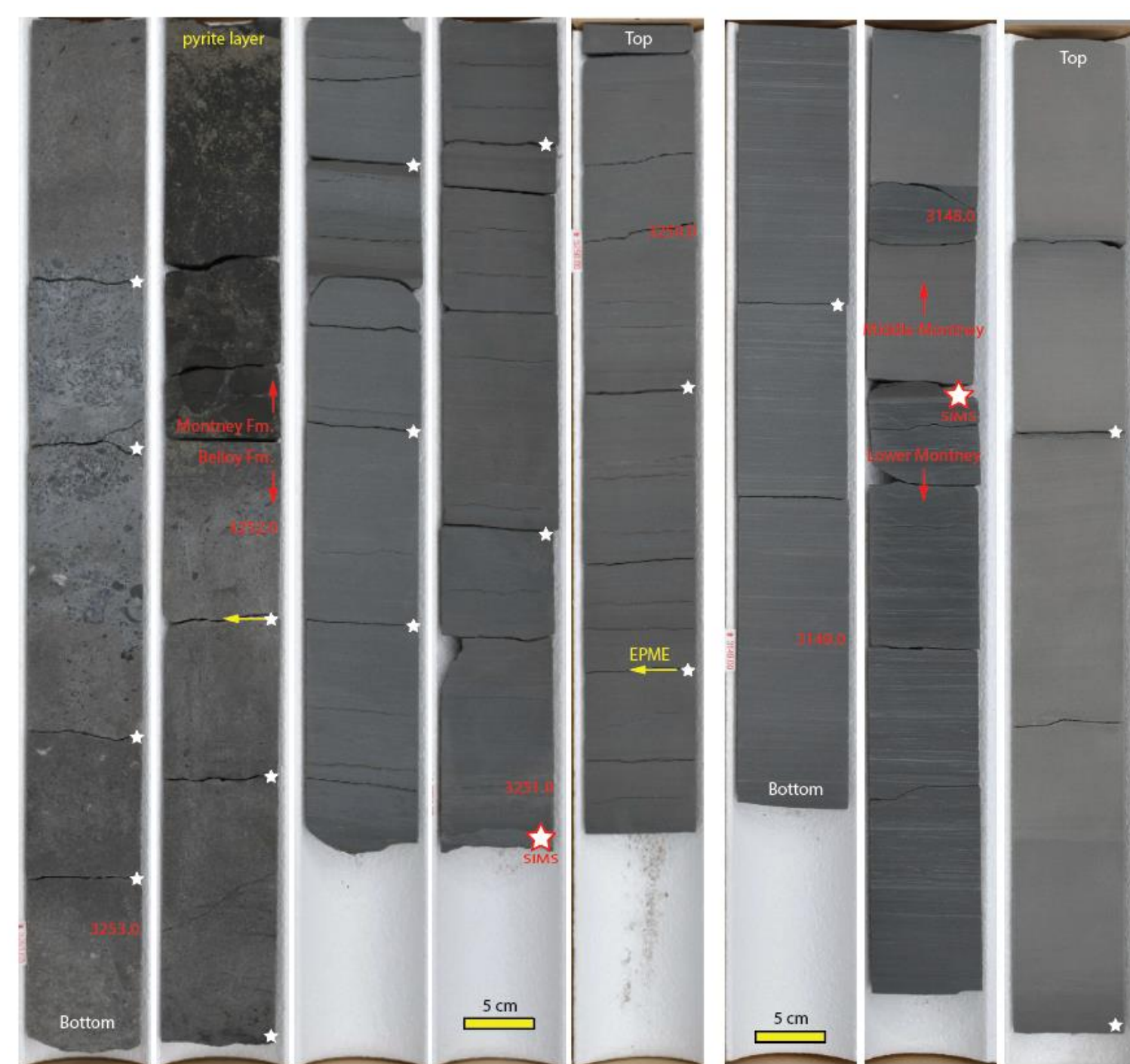


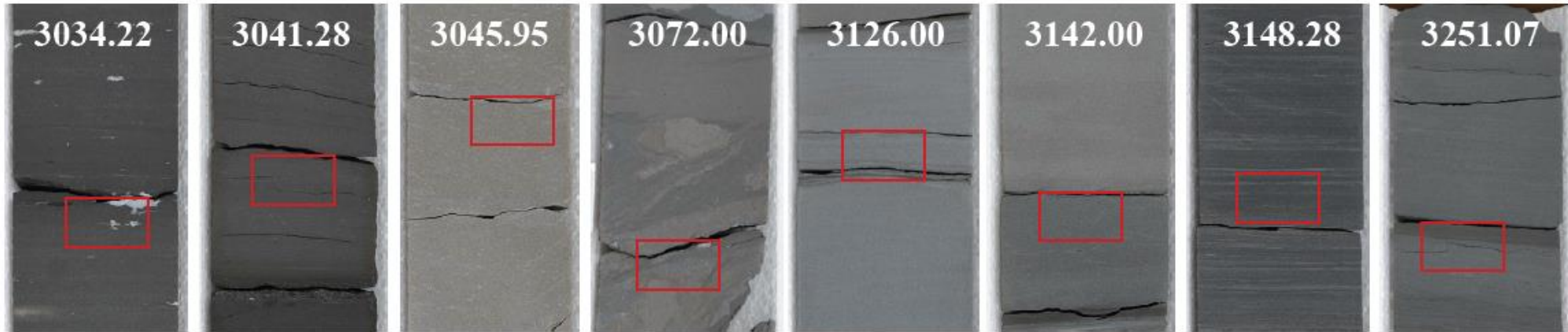
Secondary Ion Mass Spectrometry (SIMS)



Core overview

- 210 m core from the Montney Formation
- Covers the End Permian Mass Extinction (EPME) and the Early Triassic
- Transition from offshore to nearshore environment
- Change in depositional environ results in variations in sulfur-bearing species





Doig Fm.
fine grain
OM-rich,
abundant
anhydrite
pyrite

Doig -
Montney
transition,
fine grained,
pyrite-rich

Anhydrite
cement
(spotting),
coarser silt-
stone, upper
shoreface

Soft sedi-
ment defor-
mation,
uppers hore-
face

Transition
shoreface to
lower sho

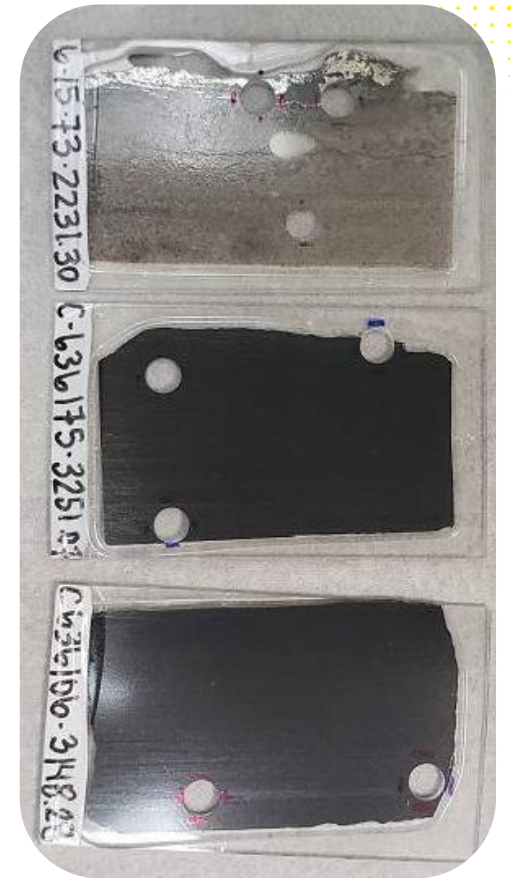
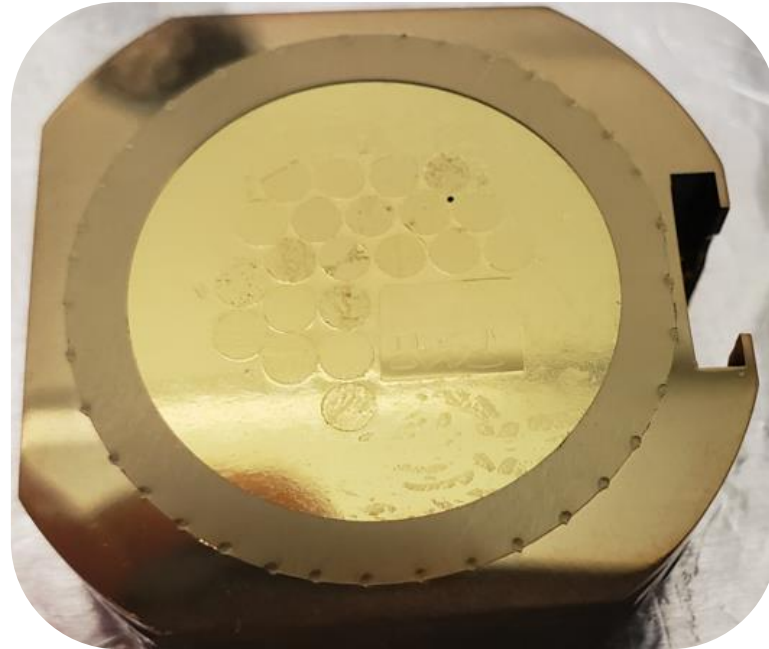
Sediment
gravity
flows

Deeper off-
shore thin
bedded silt-
stone

Near base of
Montney,
anoxic envi-
ronment

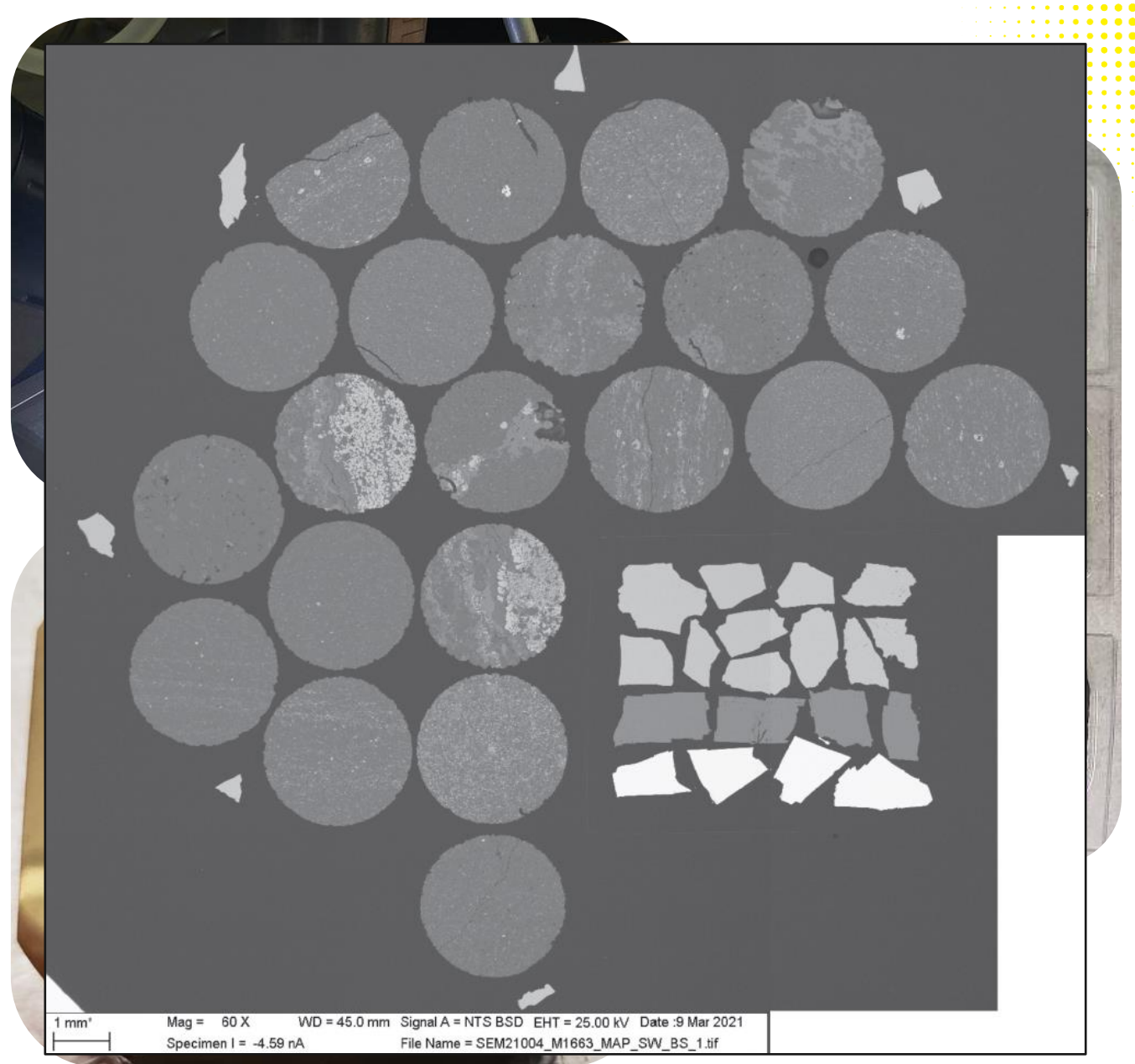
SIMS Sample preparation

- Thick section prep (100 μm)
- ROI selection
- Coring ROIs from thick sections
- Mounting alongside reference materials, sputter coating
- SEM imaging

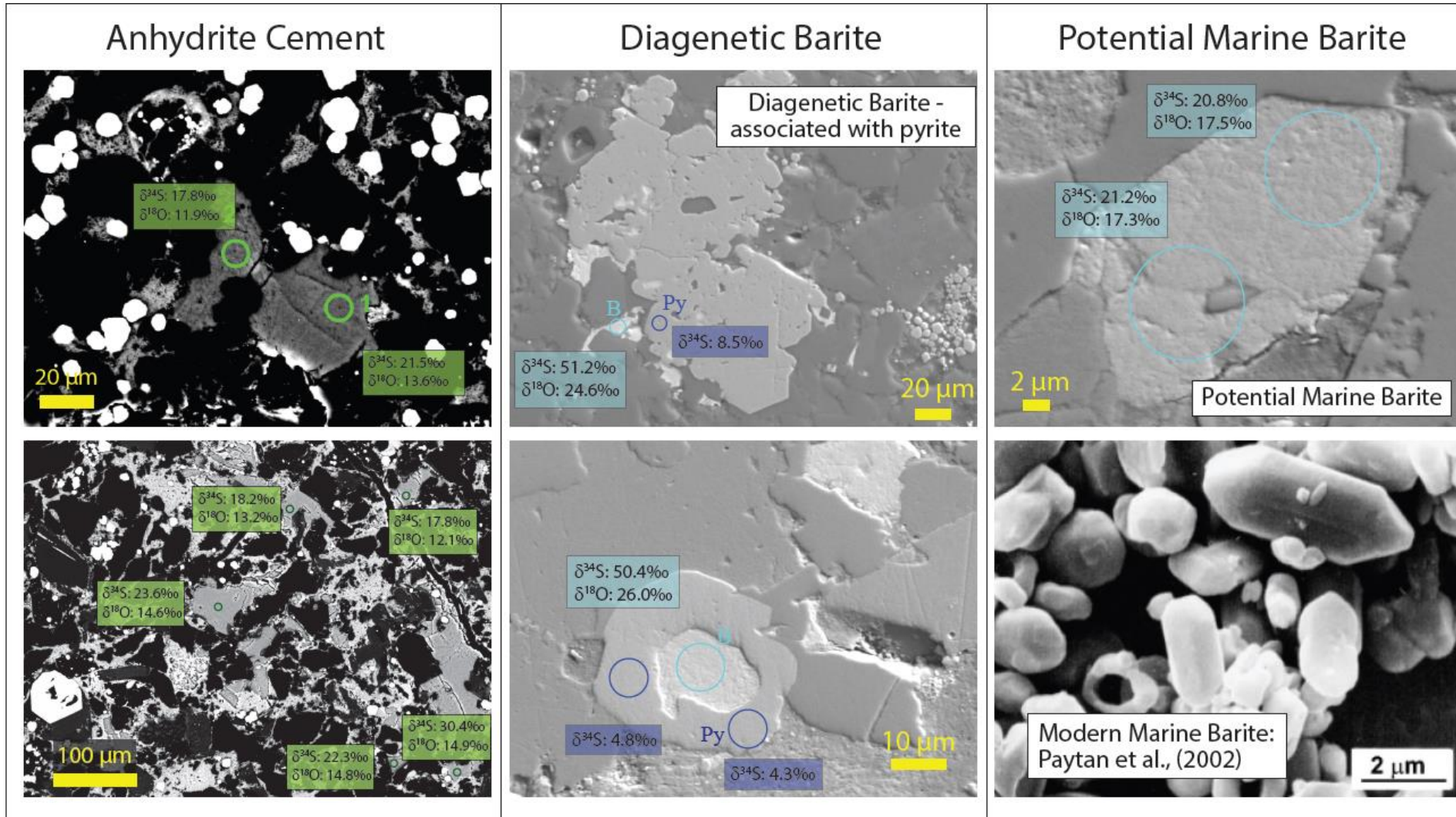


SIMS Sample preparation

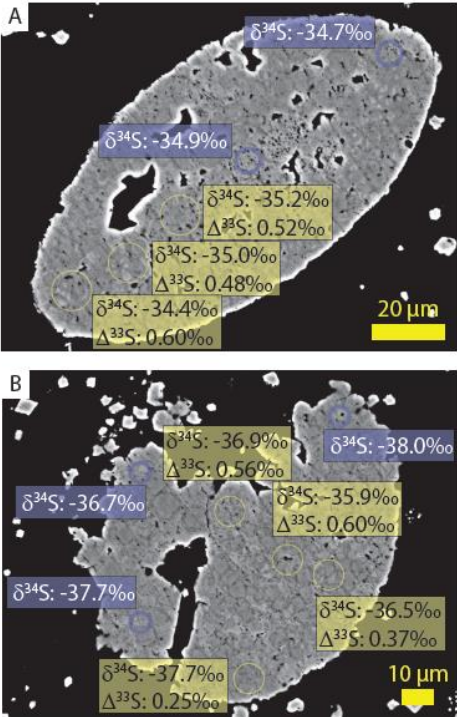
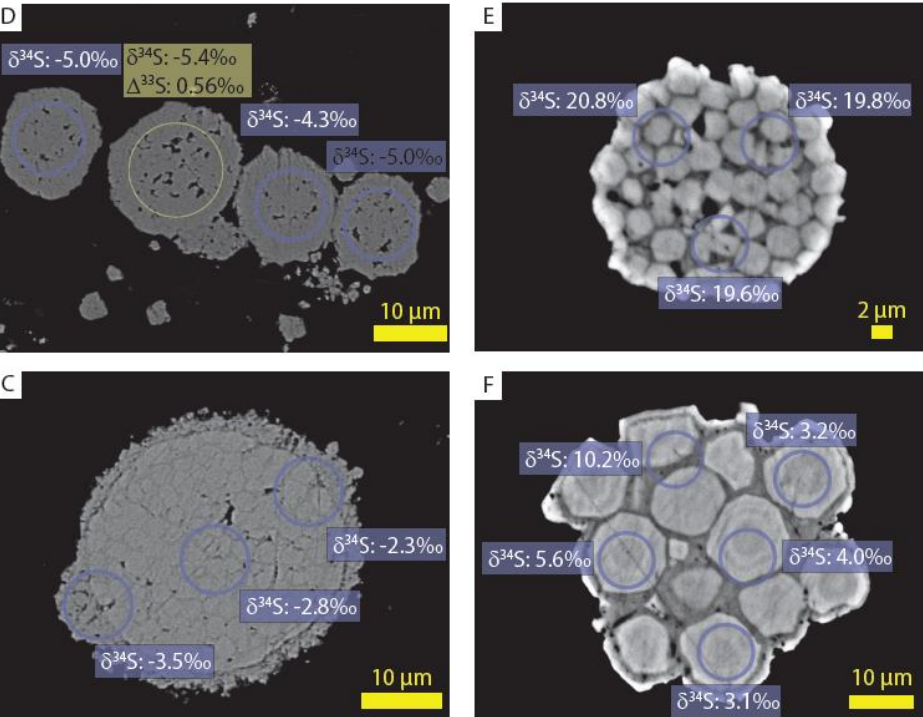
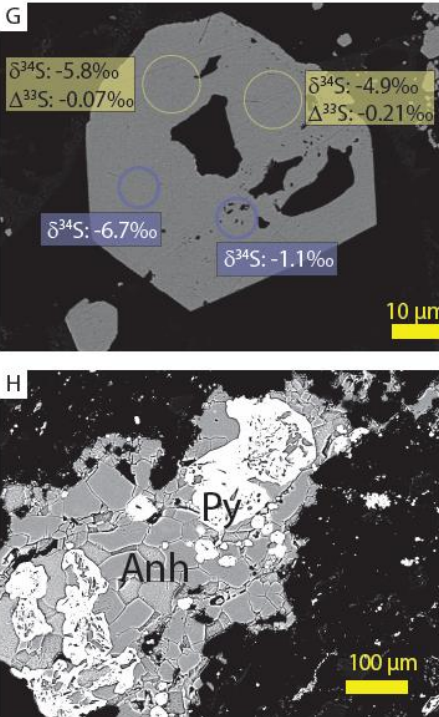
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Sulfate Phases

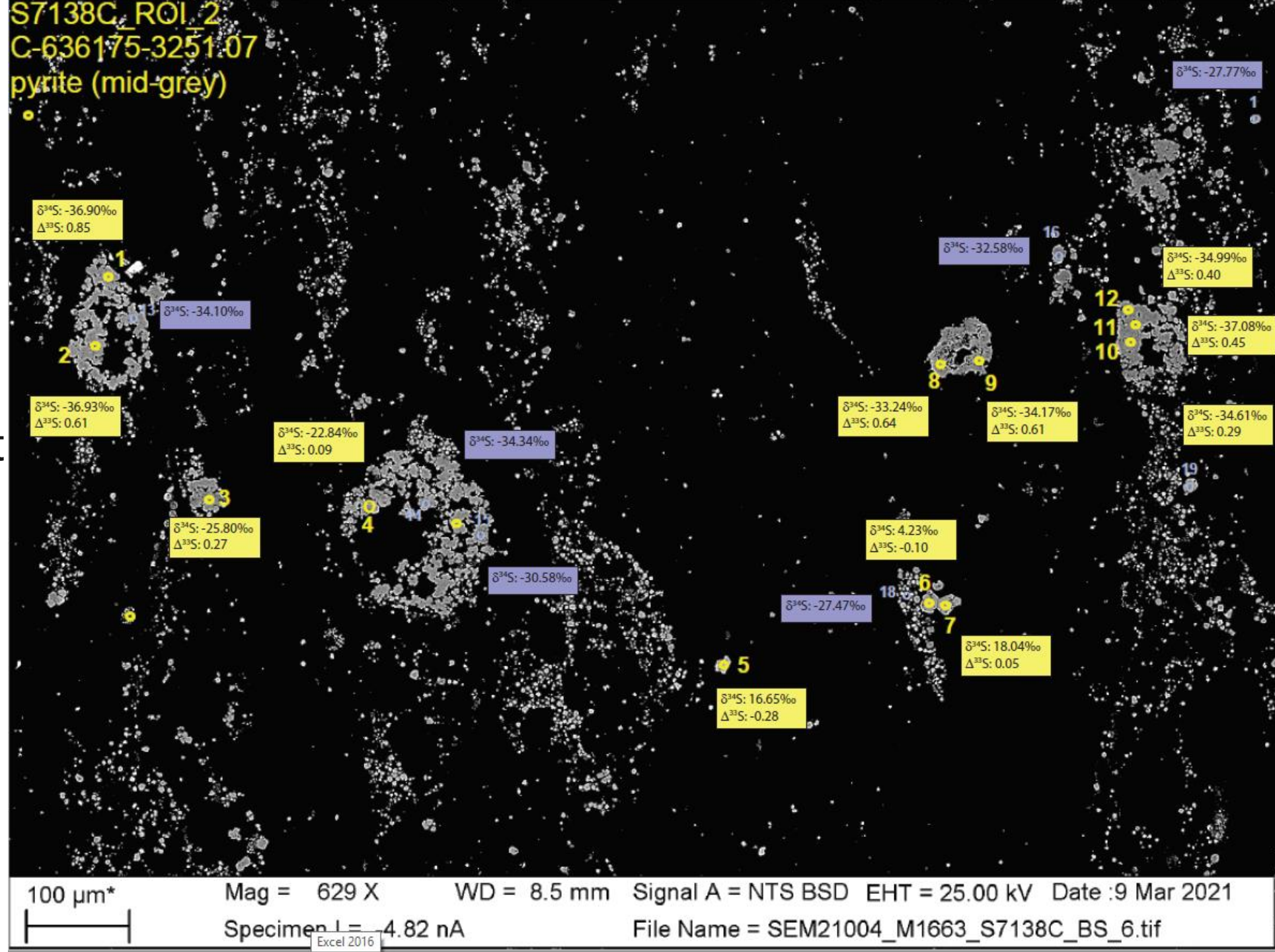


Pyrite Phases

Pyritized Microfossils	Framboids and Recrystallized Framboids	Euhedral and Crystalline
 <p>A</p> <p>$\delta^{34}\text{S}$: -34.7‰ $\delta^{34}\text{S}$: -34.9‰ $\delta^{34}\text{S}$: -35.2‰ $\delta^{34}\text{S}$: -35.0‰ $\delta^{34}\text{S}$: -34.4‰ $\Delta^{33}\text{S}$: 0.52‰ $\Delta^{33}\text{S}$: 0.48‰ $\Delta^{33}\text{S}$: 0.60‰</p> <p>B</p> <p>$\delta^{34}\text{S}$: -36.9‰ $\delta^{34}\text{S}$: -38.0‰ $\delta^{34}\text{S}$: -36.7‰ $\delta^{34}\text{S}$: -35.9‰ $\delta^{34}\text{S}$: -37.7‰ $\delta^{34}\text{S}$: -36.5‰ $\delta^{34}\text{S}$: -37.7‰ $\Delta^{33}\text{S}$: 0.56‰ $\Delta^{33}\text{S}$: 0.60‰ $\Delta^{33}\text{S}$: 0.25‰</p> <p>20 μm 10 μm</p>	 <p>D</p> <p>$\delta^{34}\text{S}$: -5.0‰ $\delta^{34}\text{S}$: -5.4‰ $\Delta^{33}\text{S}$: 0.56‰ $\delta^{34}\text{S}$: -4.3‰ $\delta^{34}\text{S}$: -5.0‰</p> <p>E</p> <p>$\delta^{34}\text{S}$: 20.8‰ $\delta^{34}\text{S}$: 19.8‰ $\delta^{34}\text{S}$: 19.6‰</p> <p>F</p> <p>$\delta^{34}\text{S}$: 10.2‰ $\delta^{34}\text{S}$: 3.2‰ $\delta^{34}\text{S}$: 5.6‰ $\delta^{34}\text{S}$: 4.0‰ $\delta^{34}\text{S}$: 3.1‰</p> <p>C</p> <p>$\delta^{34}\text{S}$: -3.5‰ $\delta^{34}\text{S}$: -2.3‰ $\delta^{34}\text{S}$: -2.8‰</p> <p>10 μm 2 μm 10 μm 10 μm</p>	 <p>G</p> <p>$\delta^{34}\text{S}$: -5.8‰ $\Delta^{33}\text{S}$: -0.07‰ $\delta^{34}\text{S}$: -4.9‰ $\Delta^{33}\text{S}$: -0.21‰ $\delta^{34}\text{S}$: -6.7‰ $\delta^{34}\text{S}$: -1.1‰</p> <p>H</p> <p>Py Anh</p> <p>10 μm 100 μm</p>
<ul style="list-style-type: none"> • Found at base of core • Fine-grain pyrite replacement of skeletal material, sometimes with framboidal cores • Early diagenesis in an anoxic environment. 	<ul style="list-style-type: none"> • Found throughout the core • Often display evidence of recrystallization on pyrite cementation • Vary in size from ~2 μm to 50 μm, multiple phases of growth • Small size makes SIMS $\Delta^{33}\text{S}$ isotope analysis difficult, prone to analytical issues, see below 	<ul style="list-style-type: none"> • Found throughout the core, larger more abundant at core top • Variable in size, ~2 μm to mm • Often associated with anhydrite (Anh) at top of core • Formed during later diagenesis

High $\delta^{34}\text{S}_{\text{pyr}}$ variability

- Extremely high small-scale variability
- Two forms of pyrite with distinct morphology, $\delta^{34}\text{S}_{\text{pyr}} + \Delta^{33}\text{S}_{\text{pyr}}$ values
 - Low $\delta^{34}\text{S}_{\text{pyr}}$ early biogenic
 - High $\delta^{34}\text{S}_{\text{pyr}}$ late stage diagenetic



High $\delta^{34}\text{S}_{\text{pyr}}$ variability

S7138C_ROI_2
C-636175-3251.07
pyrite (mid-grey)

$\delta^{34}\text{S}$: -36.90‰
 $\Delta^{33}\text{S}$: 0.85

$\delta^{34}\text{S}$: 4.23‰
 $\Delta^{33}\text{S}$: -0.10

$\delta^{34}\text{S}$: -27.47‰

$\delta^{34}\text{S}$: 16.65‰
 $\Delta^{33}\text{S}$: -0.28

$\delta^{34}\text{S}$: 18.04‰
 $\Delta^{33}\text{S}$: 0.05

$\delta^{34}\text{S}$: -34.34‰

$\delta^{34}\text{S}$: -30.58‰

$\delta^{34}\text{S}$: -32.58‰

$\delta^{34}\text{S}$: -33.24‰
 $\Delta^{33}\text{S}$: 0.64

$\delta^{34}\text{S}$: -34.17‰
 $\Delta^{33}\text{S}$: 0.61

$\delta^{34}\text{S}$: -34.99‰
 $\Delta^{33}\text{S}$: 0.40

$\delta^{34}\text{S}$: -37.08‰
 $\Delta^{33}\text{S}$: 0.45

$\delta^{34}\text{S}$: -34.61‰
 $\Delta^{33}\text{S}$: 0.29

$\delta^{34}\text{S}$: -27.77‰

WD = 8.5 mm Signal A = NTS BSD EHT = 25.00 kV Date :9 Mar 2021

File Name = SEM21004_M1663_S7138C_BS_6.tif

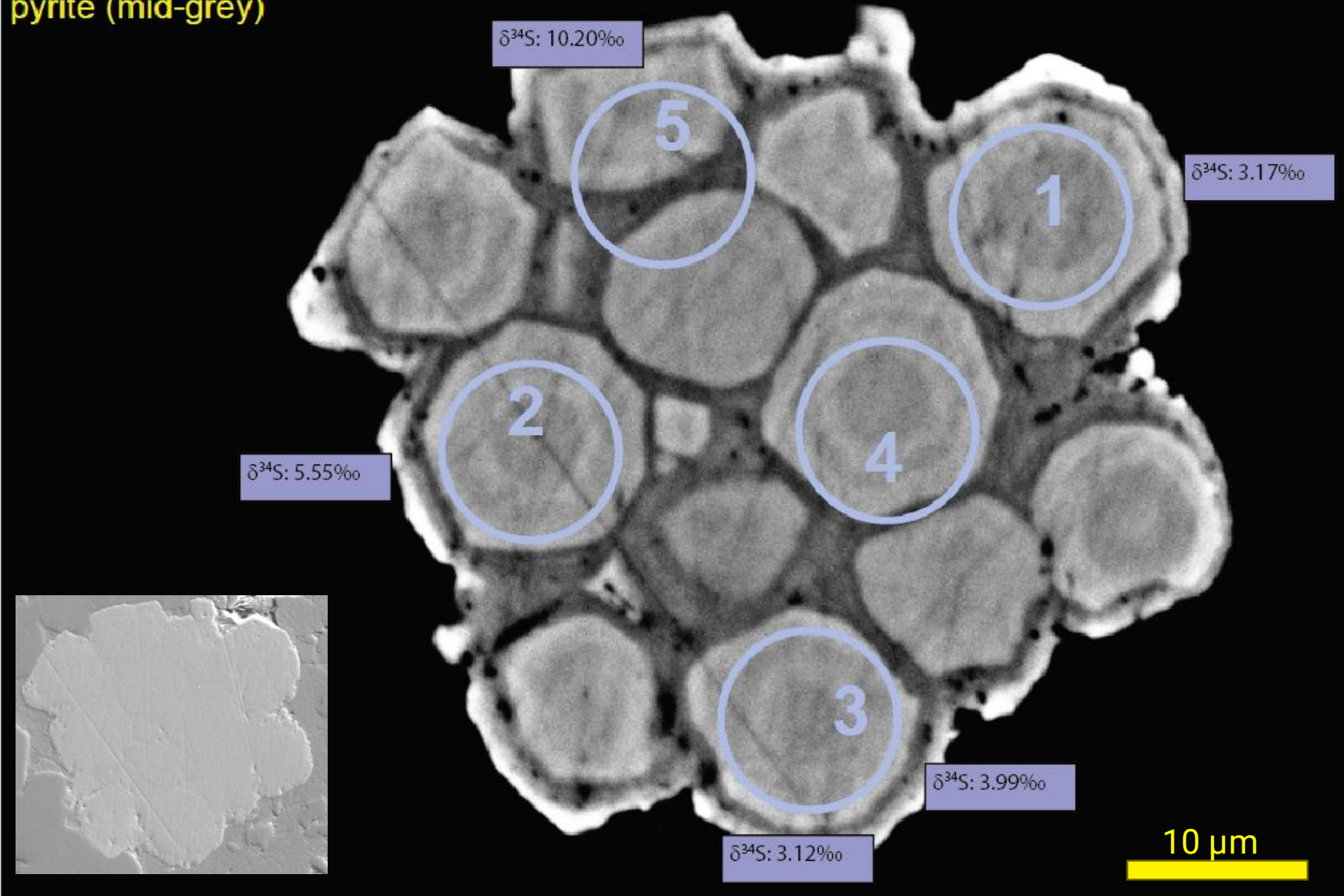
Specimen I = 4.82 nA

Excel 2016

Intra-grain variability

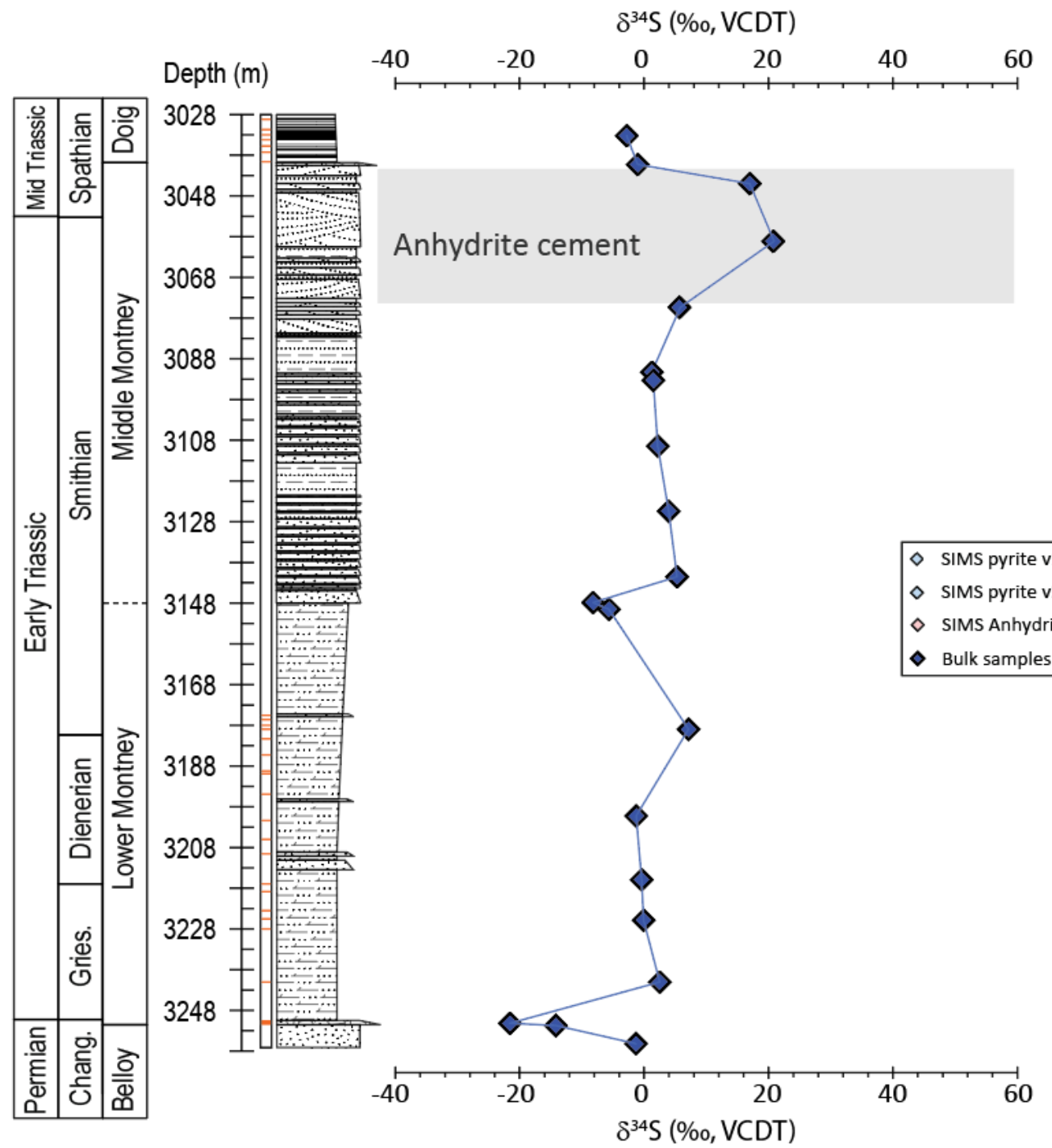
- Coalesced grains of pyrite observed via BSE imaging
- Infill has higher $\delta^{34}\text{S}_{\text{pyr}}$
- Late-stage overgrowth
- Importance of textural relationship

S7141B_ROI_4
C-636090-3126.00
pyrite (mid-grey)



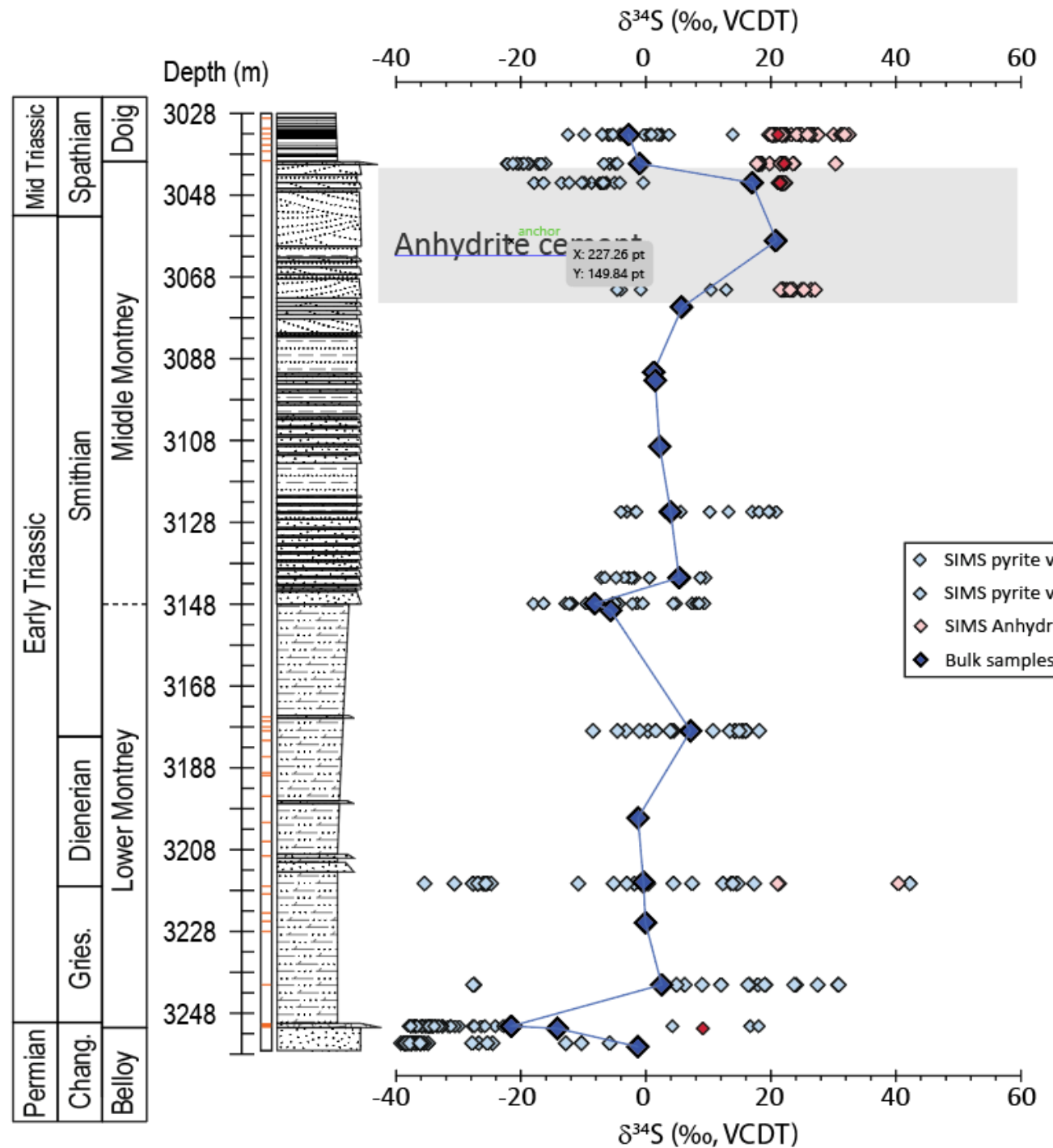
Bulk Isotope Results

- Negative excursion at the base (EPME)
- Another potential excursion at the Lower-Middle boundary
- Values increase in the upper anhydrite (sulfate) rich zone



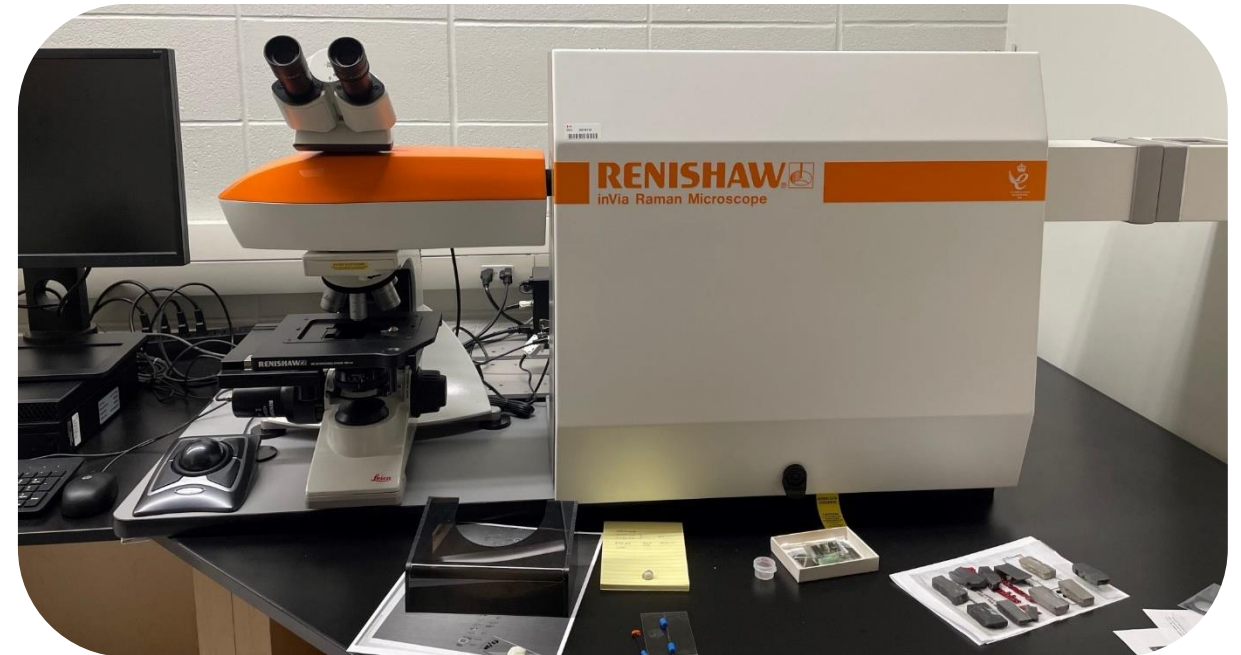
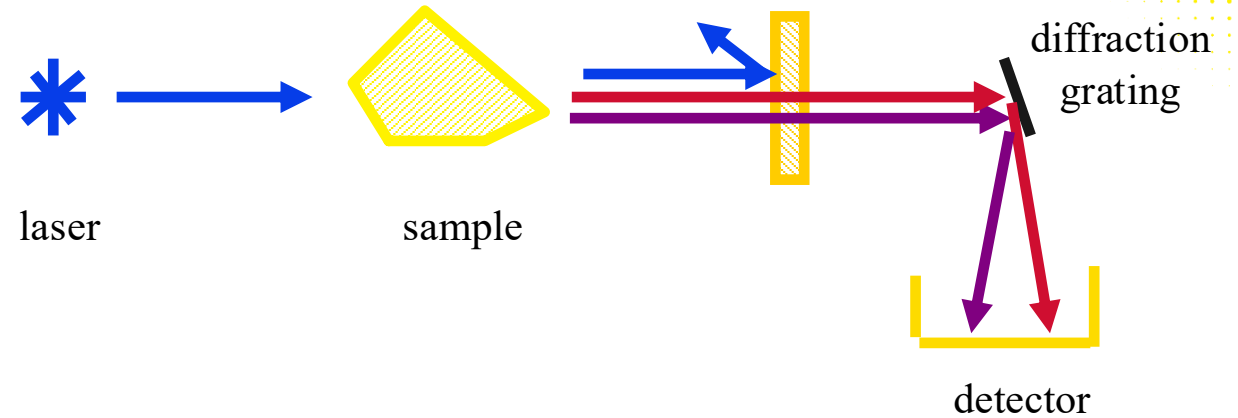
SIMS Isotope Results

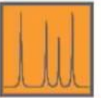

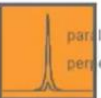
- Mixing of sulfates and sulfides in the upper zone
- Averaging effect
- Paragenetic Obscurity



Raman Spectroscopy

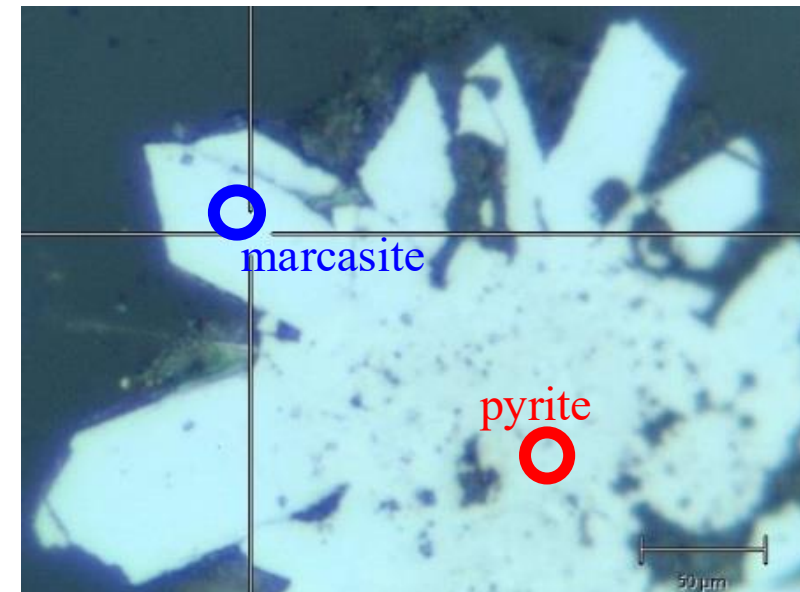
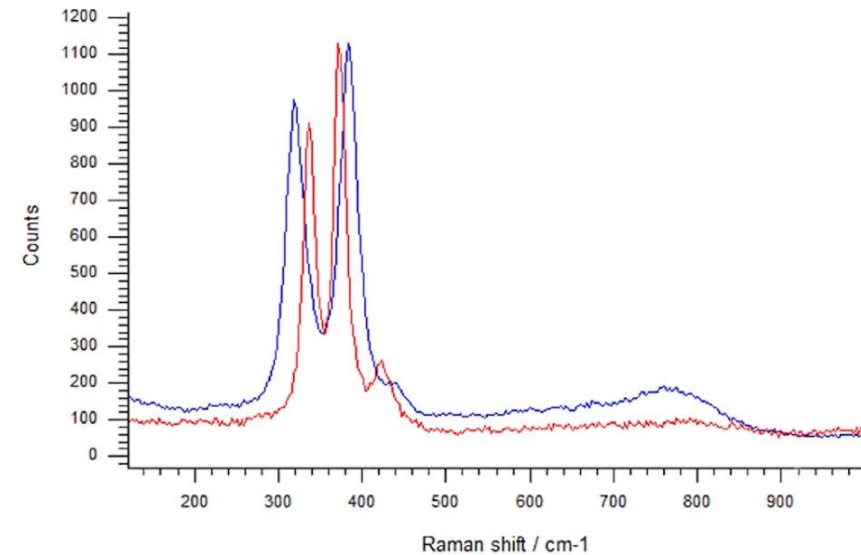
- Illuminate a sample with a LASER
- Block the original wavelength (blue)
- Measure the relative intensity and frequency shift of the inelastically scattered light



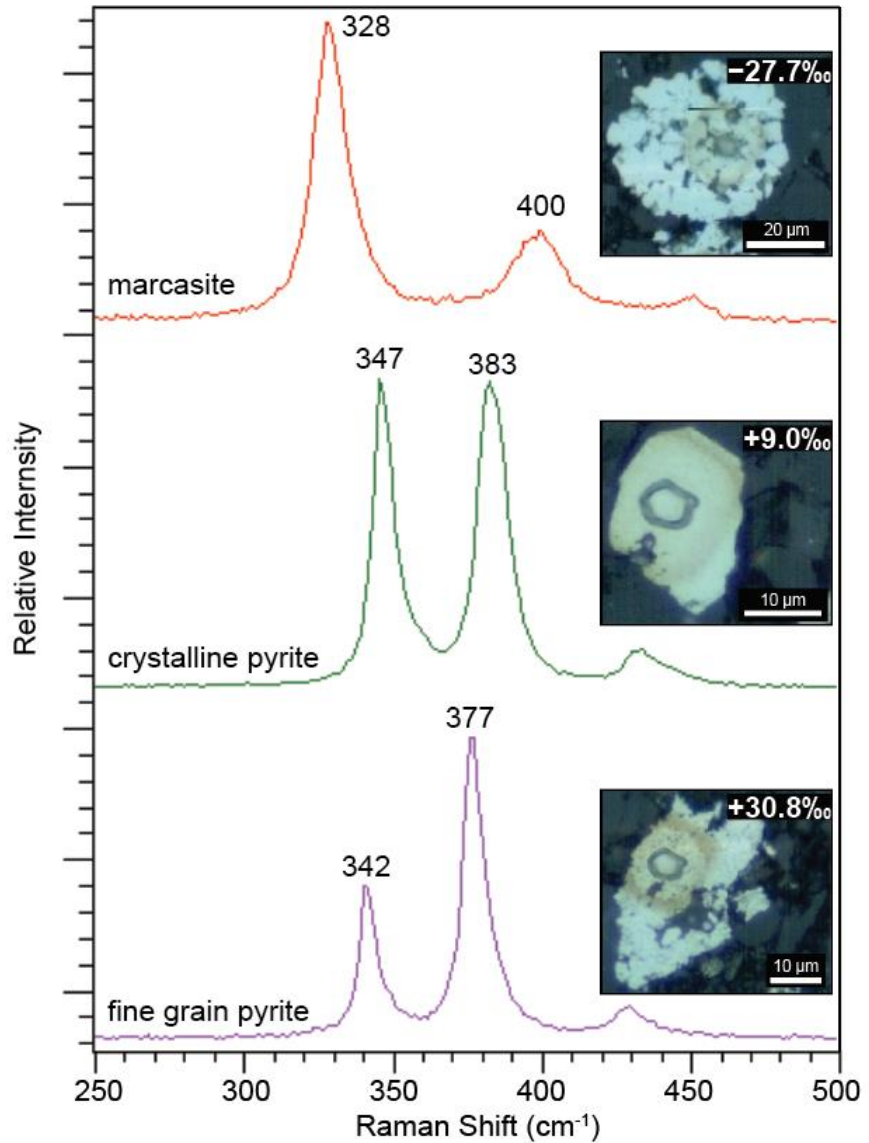
Raman band parameter	Information
 Characteristic frequencies	Chemical / structural identification
 Variation in absolute / relative intensity	Absolute / relative concentration
 Intensity variation with changing polarisation	Crystallographic orientation

Sulfide mineral species: Pyrite vs Marcasite

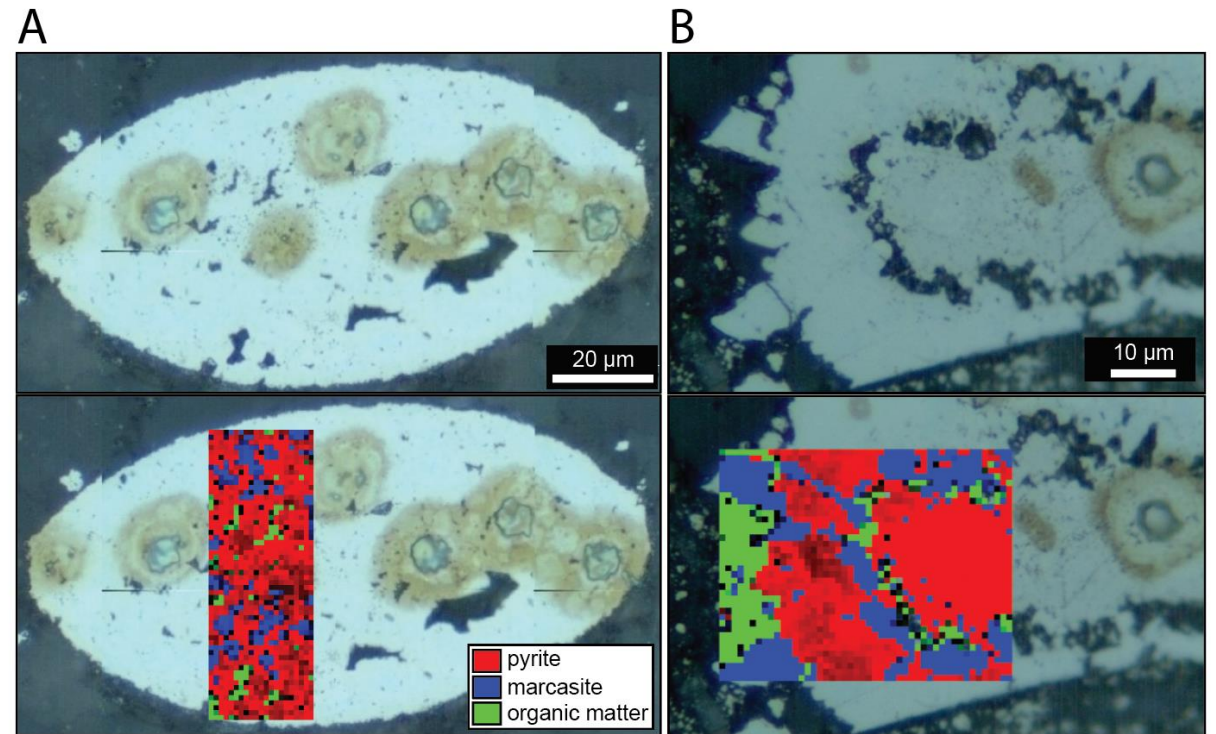
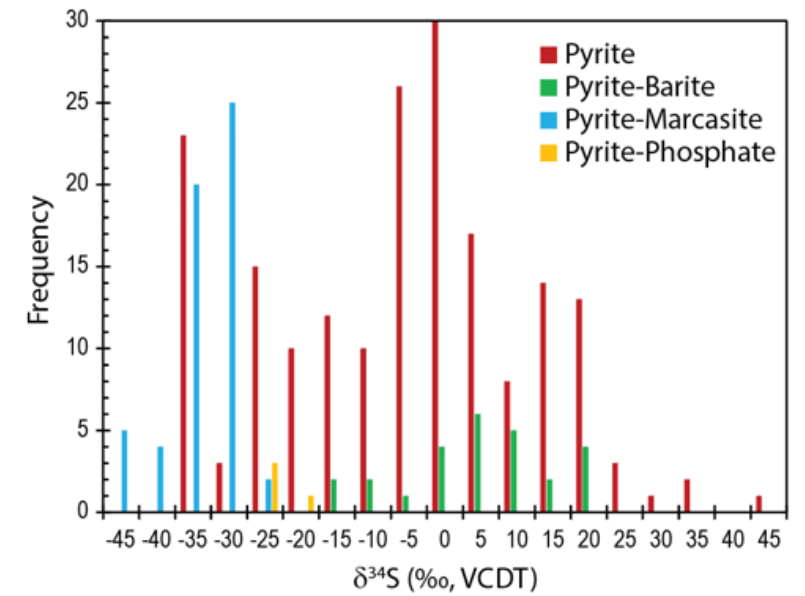
- Pyrite – Cubic/isometric
- Marcasite – orthorhombic
 - Forms at low temperatures and more acidic environments (pH <5)
 - Closely linked to progressive degradation of OM
 - Forms in highly reducing conditions – indicator of acidic or sulfidic waters
 - Metastable - Reacts with moisture/oxygen



Sulfide mineral species

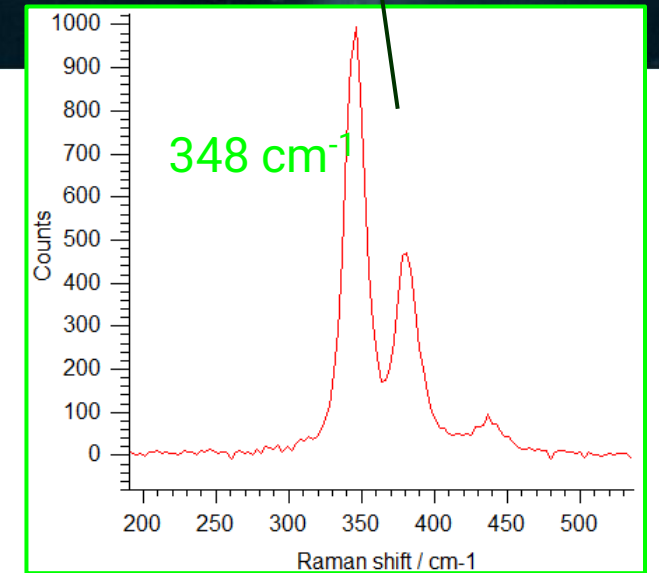
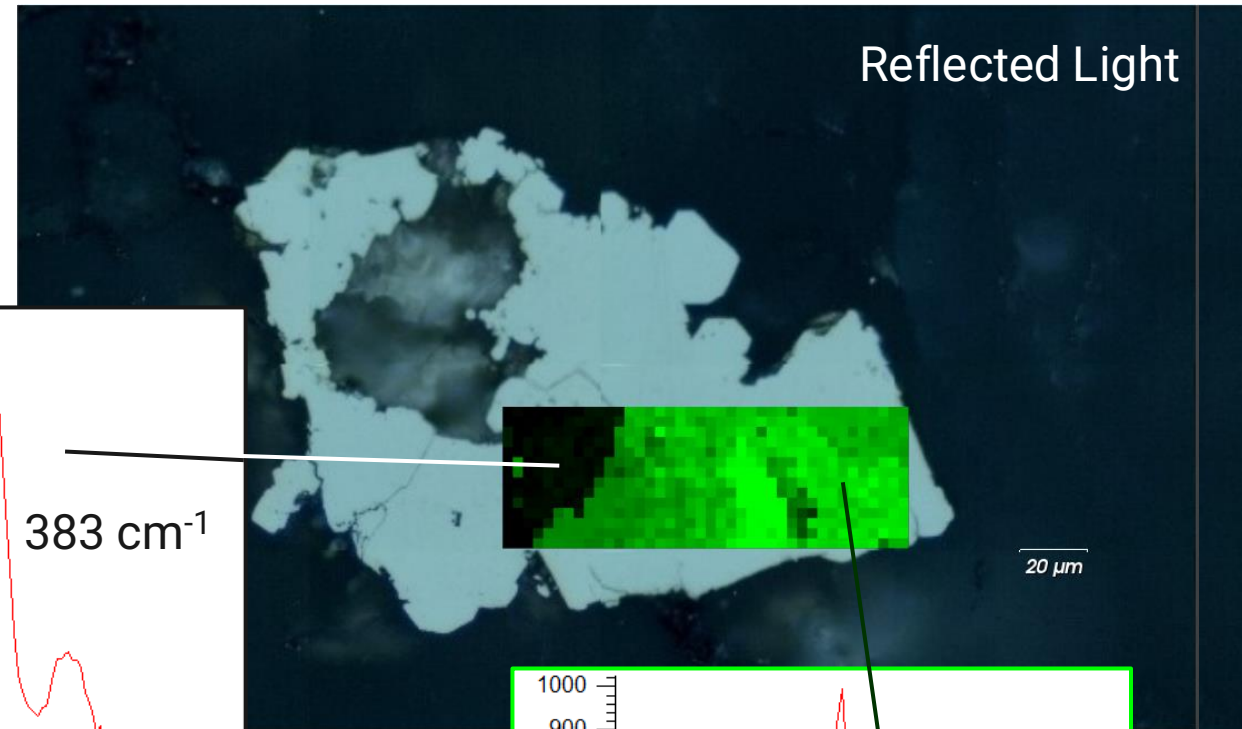
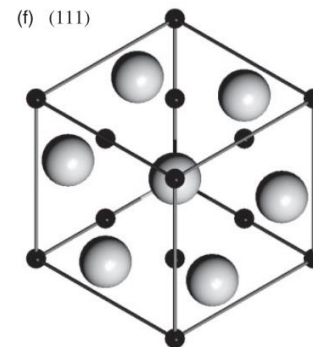
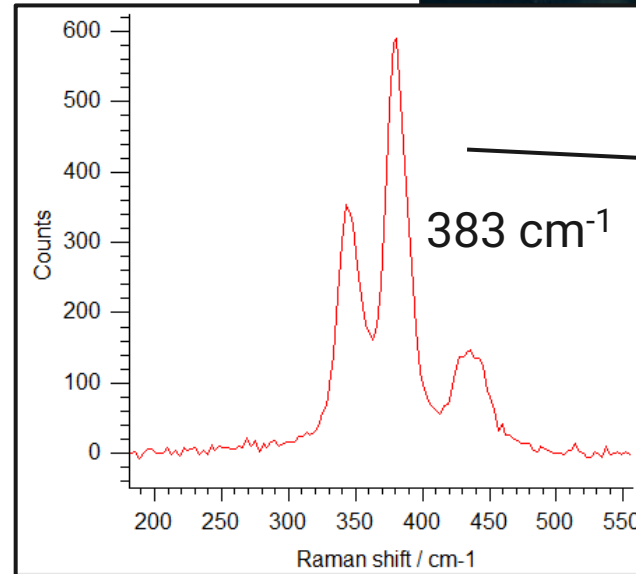
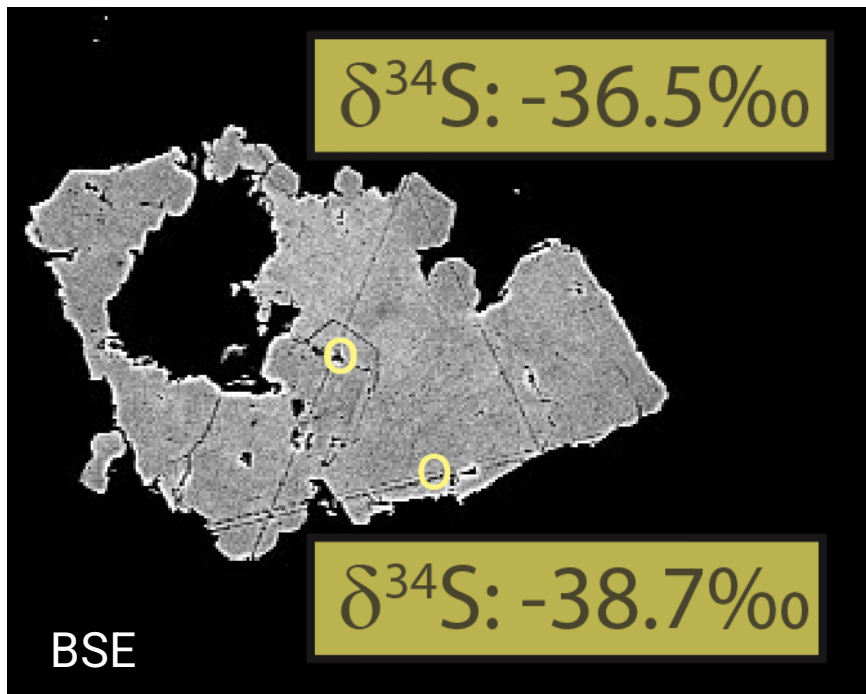


- Mapping sulfide species and associated minerals
- Early vs. late-stage diagenesis



Crystallographic orientation

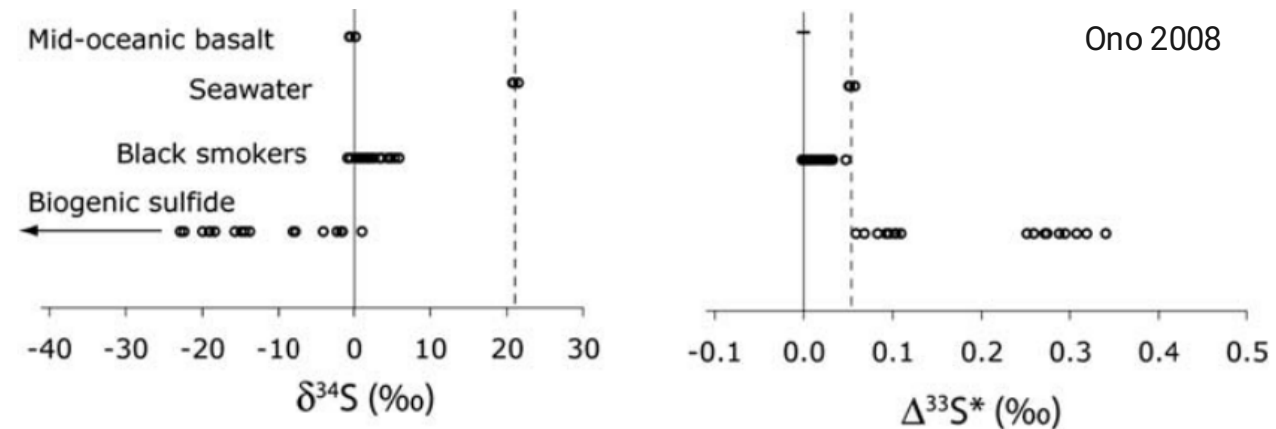
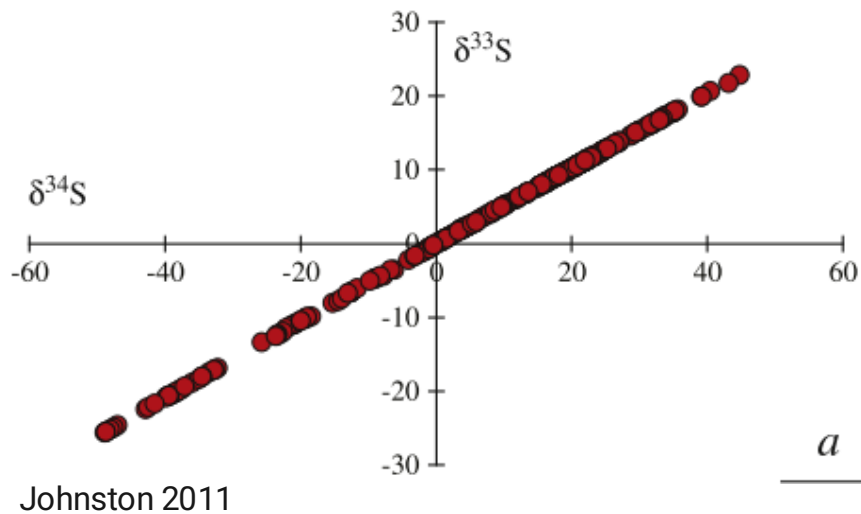
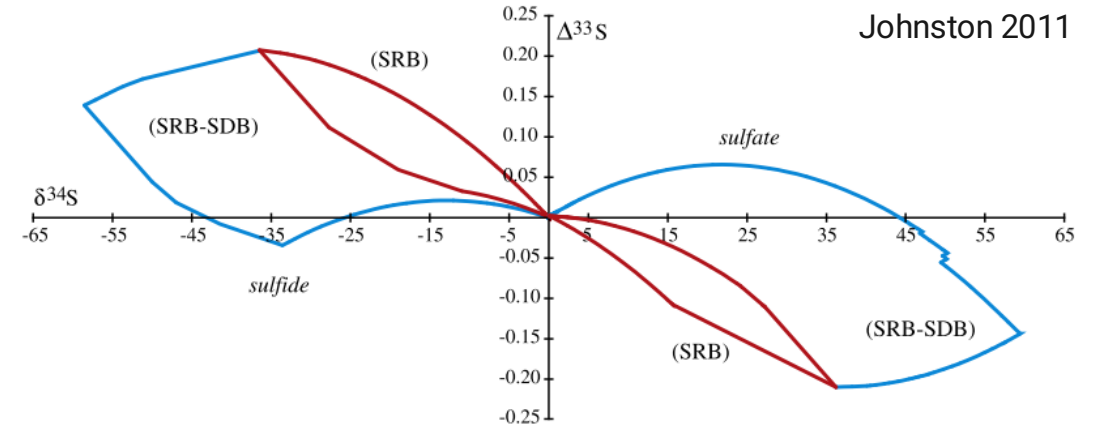
- Variations in band intensity ratios
- Define growth structures



Multiple Sulfur Isotope Analysis

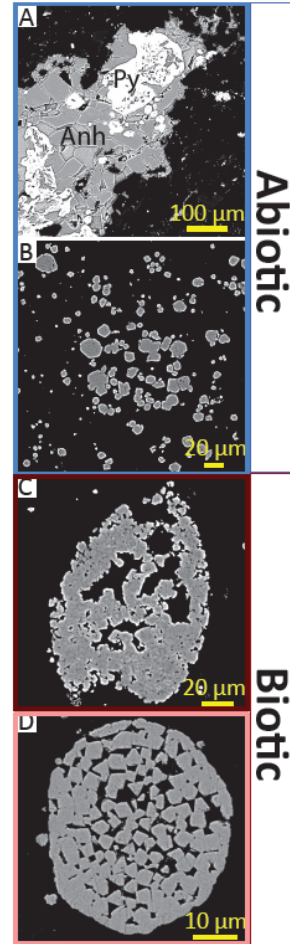
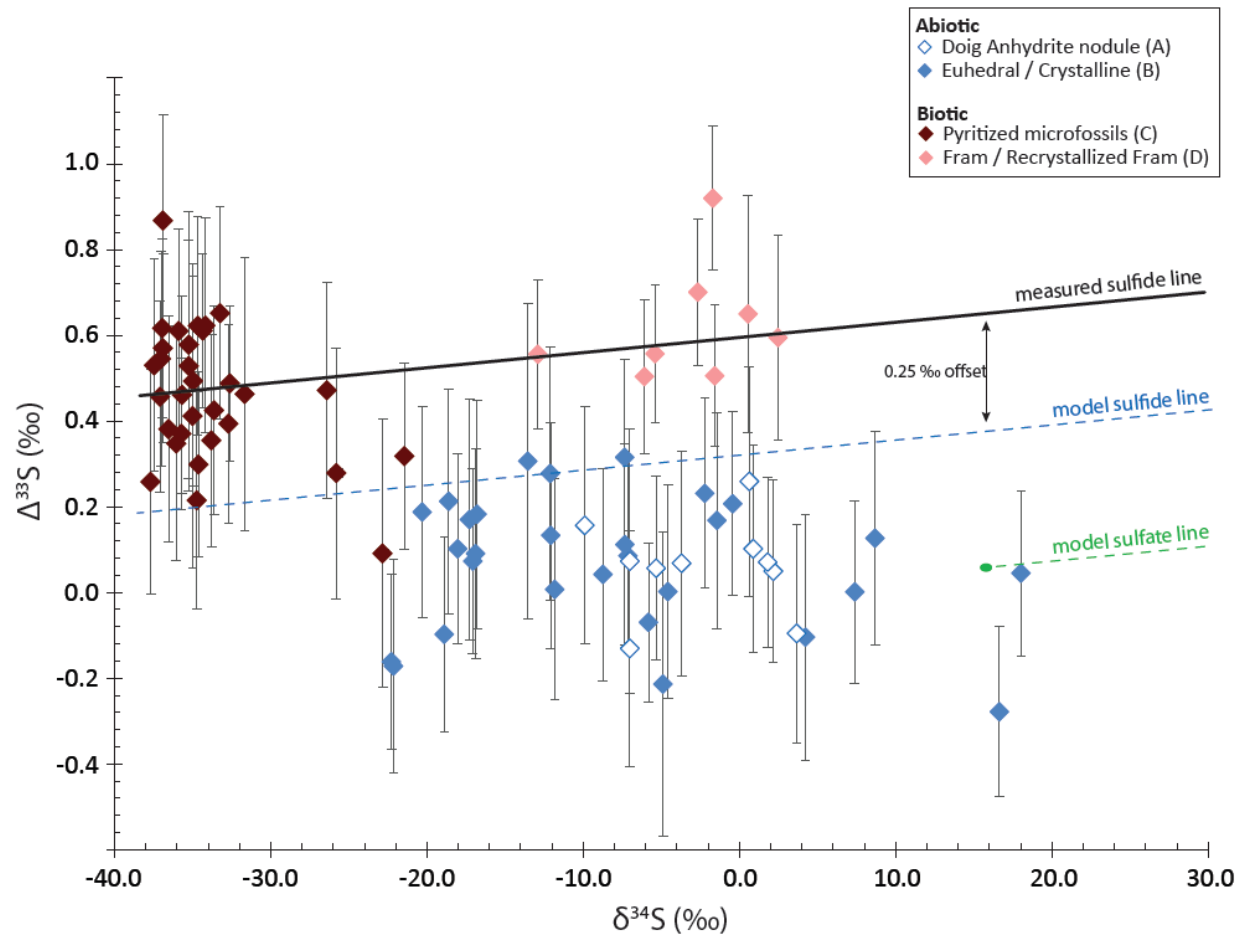
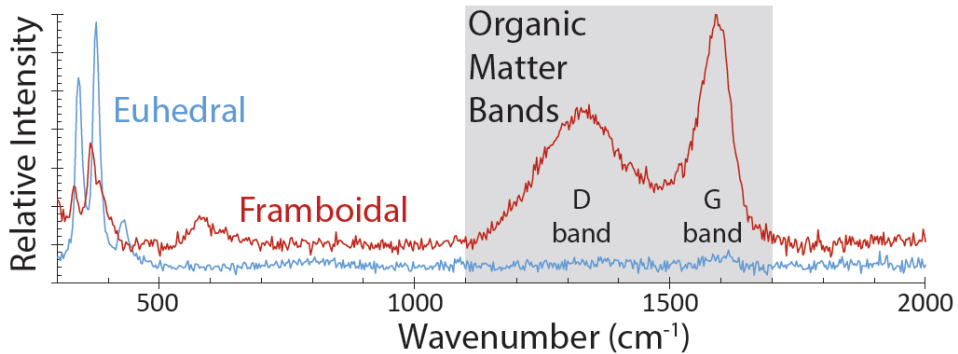
- $\delta^{34}\text{S}_{\text{pyr}}$ vs. $\delta^{33}\text{S}_{\text{pyr}}$ should follow Mass Dependant Line (MDL)
- Deviations from this line defined as $\Delta^{33}\text{S}_{\text{pyr}}$
- Biological reactions leave $\Delta^{33}\text{S}_{\text{pyr}}$ signature
- Traditionally use fluorination lines to generate SF_6 for analysis

Isotope	Atomic Mass ¹	Mole Fraction ²
³² S	31.972 070 73(15)	0.950 3957(90)
³³ S	32.971 458 54(15)	0.007 4865(12)
³⁴ S	33.967 866 87(14)	0.041 9719(87)
³⁶ S	35.967 080 88(25)	0.000 1459(21)



Hydride formation and implications for SIMS $\Delta^{33}\text{S}_{\text{pyr}}$

- Raman analysis indicates OM trapped in biogenic pyrite (e.g., framboids)
- Hydrogen-bearing phases can form hydrides during ion bombardment
- SH ions isobaric with ^{33}S



Model Inputs	$\delta^{34}\text{S}$ of Triassic SW	$\delta^{34}\text{S}$ of Triassic pyrite	$\delta^{33}\text{S}$ of Triassic SW	$\delta^{33}\text{S}$ of Triassic pyrite	$\delta^{33}\text{S}'$ of Triassic SW	$\delta^{33}\text{S}'$ of Triassic pyrite	$^{34}\alpha$	$^{33}\theta$	$^{33}\theta_{\text{net}}$
	19.2	-34.8176	0.0220	0.1389	9.8012	-17.9487	0.947	0.5117	0.515
	9.7535	-35.4382	19.0180	-18.1117					

Conclusions

- The deeper you dive the more complex – especially in sulfur world
 - Beware of sampling processing artefacts when doing extracts
 - Combination of multiple analytical methods is important – SEM, Raman
 - Different mineral polymorphs – pyrite vs. marcasite
 - Different phases of deposition in coalesced grains
 - Crystallographic orientation (growth structures)
 - Beware of instrumental artefacts – if its weird it might not be ground-breaking
 - Formation of hydrides – impacts minor isotopes
-

Acknowledgements



- Funded by a Geoscience for New Energy Supply (GNES) grant at NRCan
 - Richard Stern at CCIM for SIMS work
 - Bernhard Mayer, Steve Taylor, and Veith Becker from U of C for bulk isotopes
 - Andy Hublely and team from ARC Resources for sharing core material
 - AER for core access and sampling
 - AGAT Labs for sampling and support
-