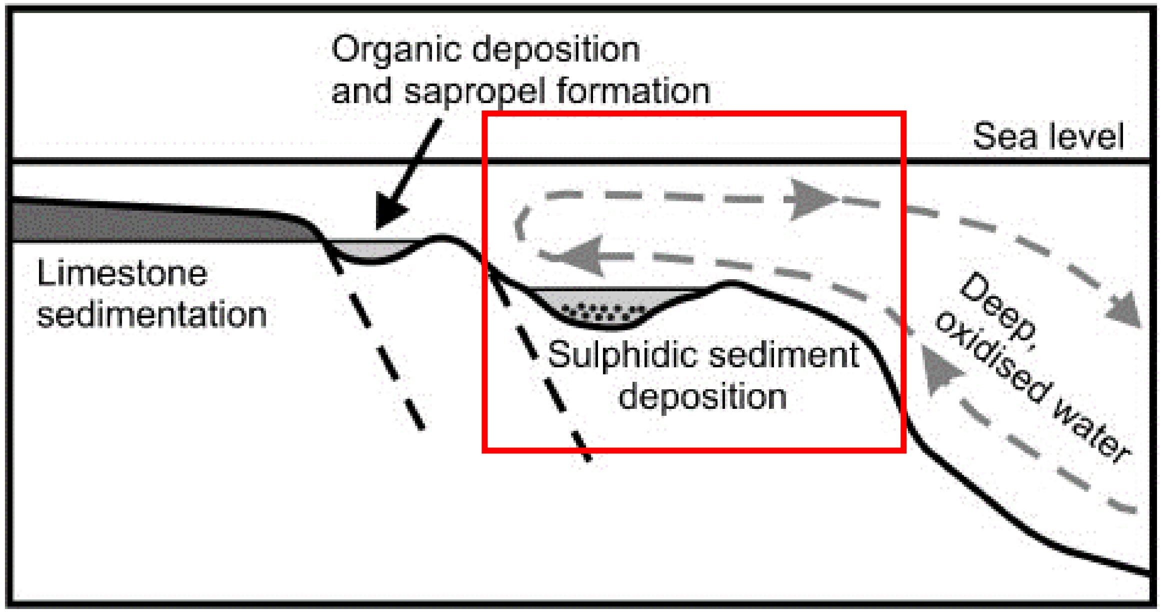
Finding Ni-Mo – Disentangling ore genesis models for metalliferous black shales

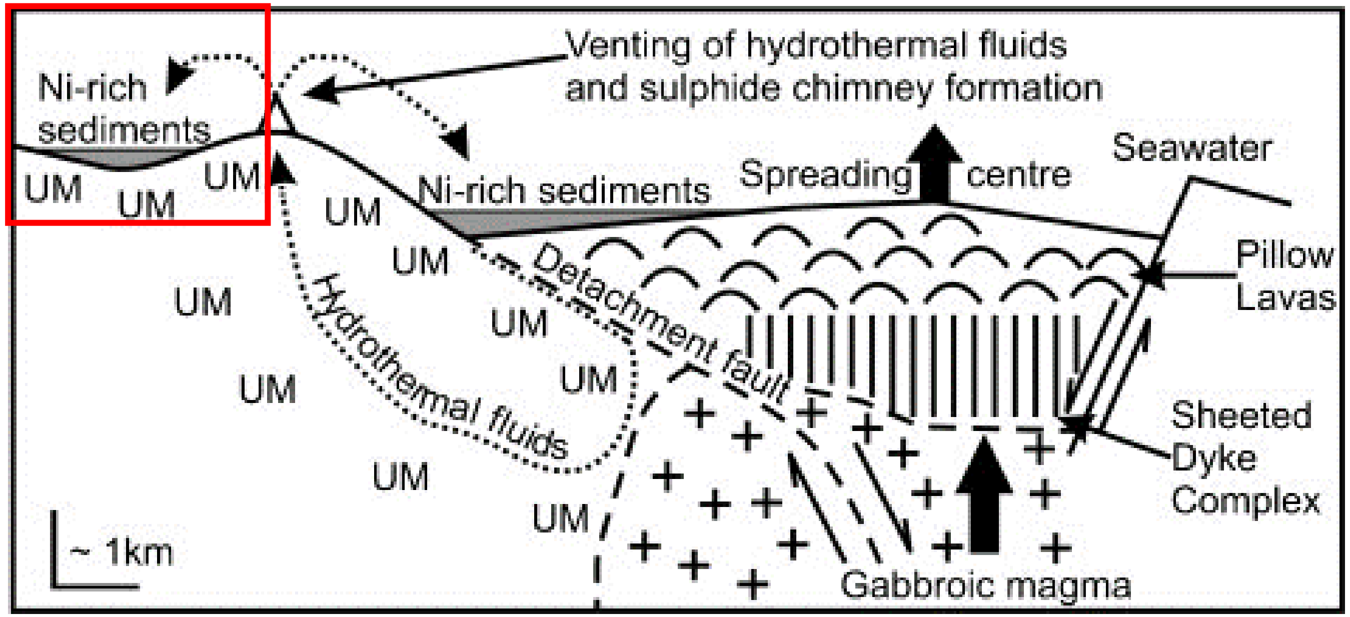
Indrani Mukherjee, Daniel Gregory, Anthony Chappaz and Jennifer Cann

Metalliferous black shales ore genesis models

Seawater

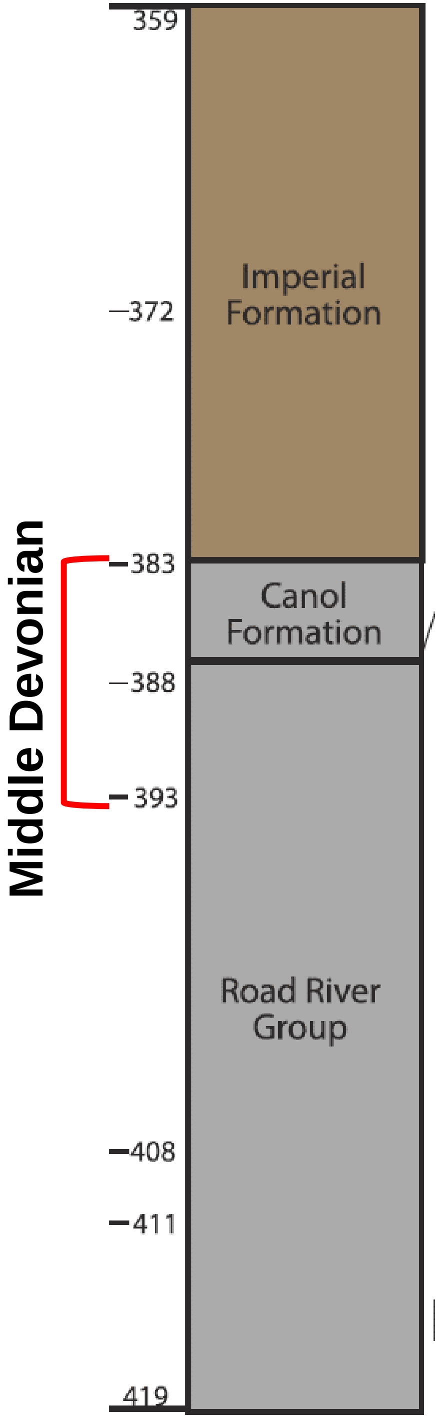


Hydrothermal



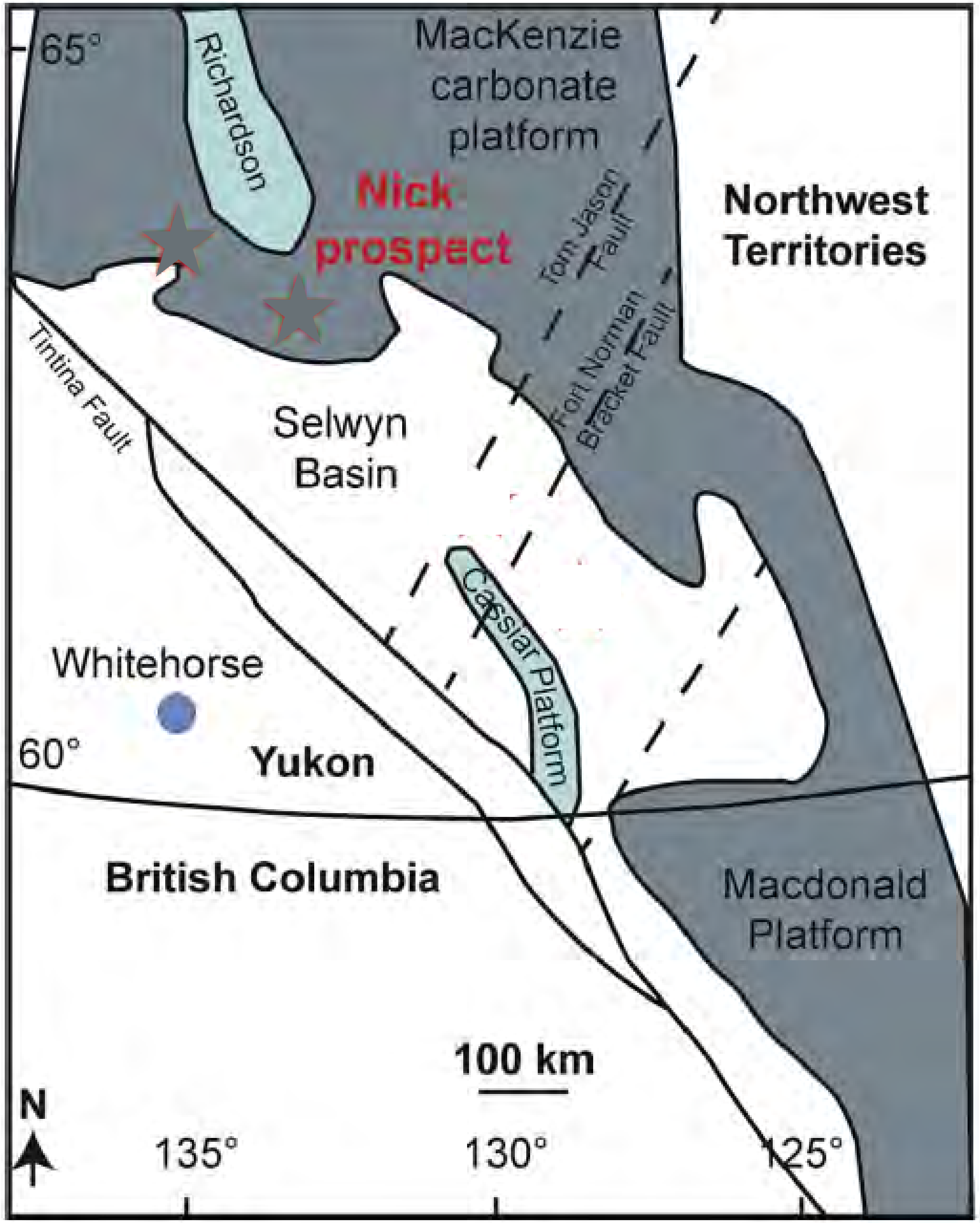
Jowitt and Keays, 2012

"Petrex model (Emsbo 2004)"



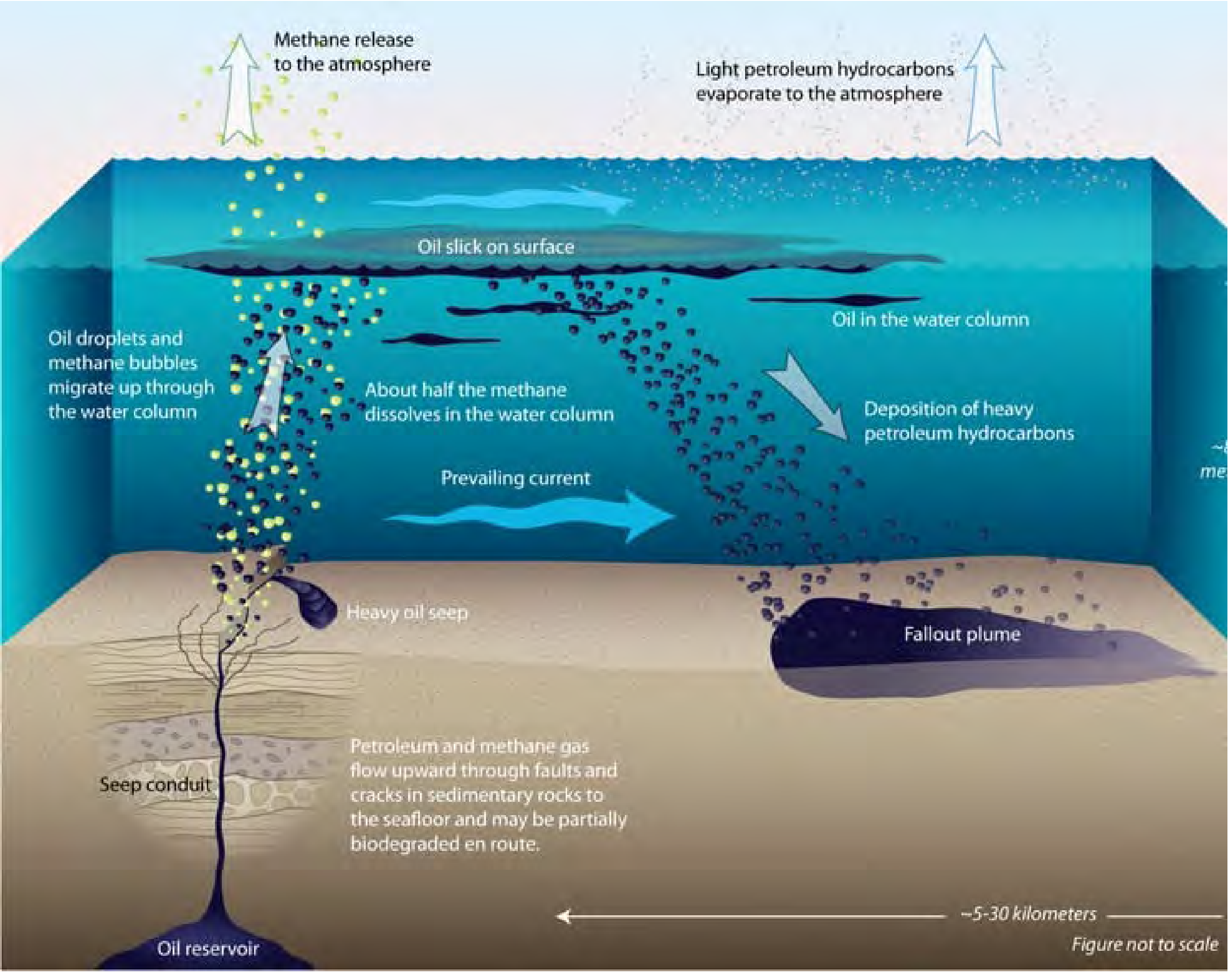
Sample information

Thickness: 5 - 15 cm
Grade: Ni (7.8% Ni), Zn (1.2%), Mo (0.4%) and PGE (up to 1050 ppb).
Minerals: pyrite, vaesite, melnikovite (sulphide “gel” of pyrite and marcasite), wurzite and sphalerite (Hulbert et al., 1992).
The Nick deposit also preserves plant material suggesting an input of terrestrial material.



Modified after Pages et al 2018

Oil-seawater model (step 1)

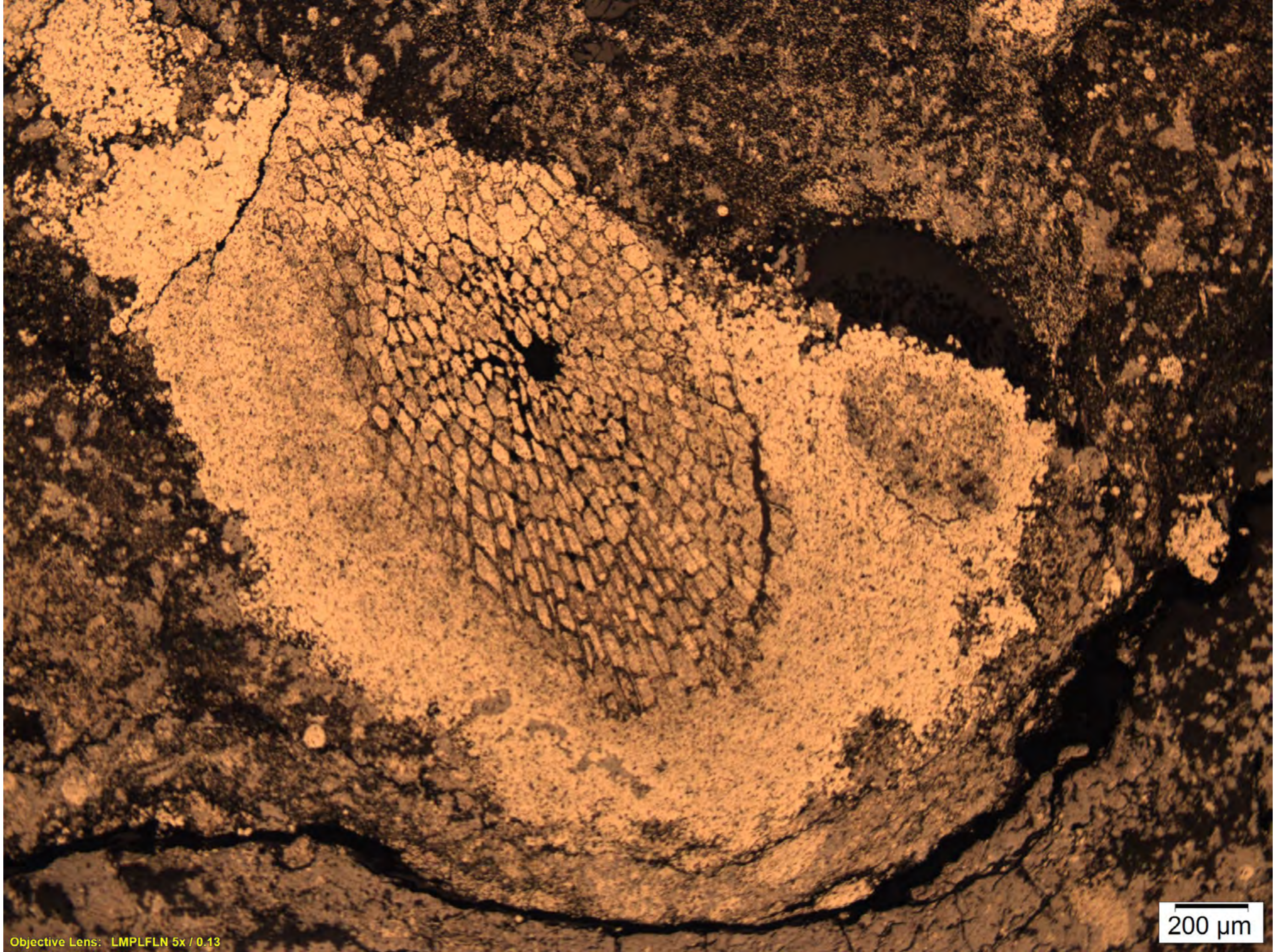


What happens?

Oil discharge into the water column/sediments triggering the formation of framboidal minerals. The process (i.e., formation framboidal minerals (magnetite - not sulphides) has been observed in the La Victoria Oil field in SW Venezuela (Aldana et al., 1999).

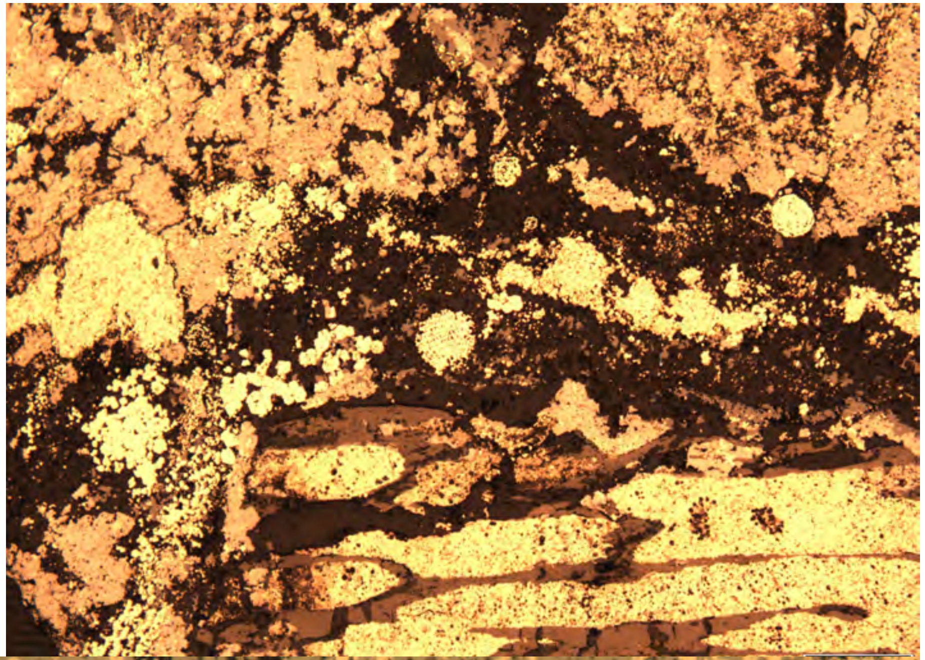
Cavalazzi et al., 2012 – iron framboids in the hydrocarbon related Middle Devonian Hollard Mound.

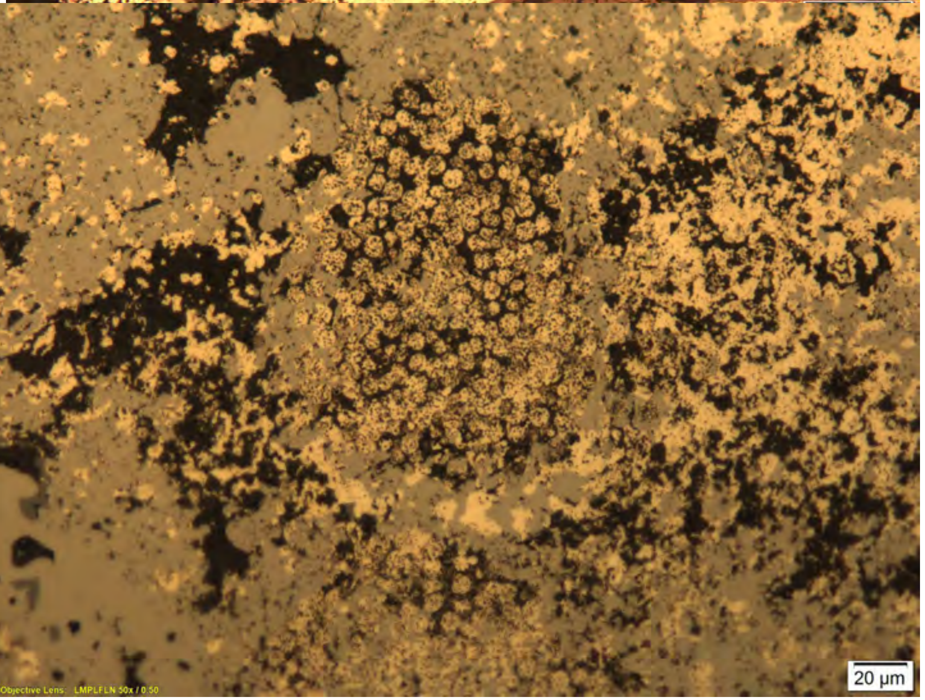
(Illustration by Jack Cook, Woods Hole Oceanographic Institution; https://www2.whoi.edu/site/chrisreddylab/oil-spill-research/while-oil-gently-seeps-from-the-seafloor/)

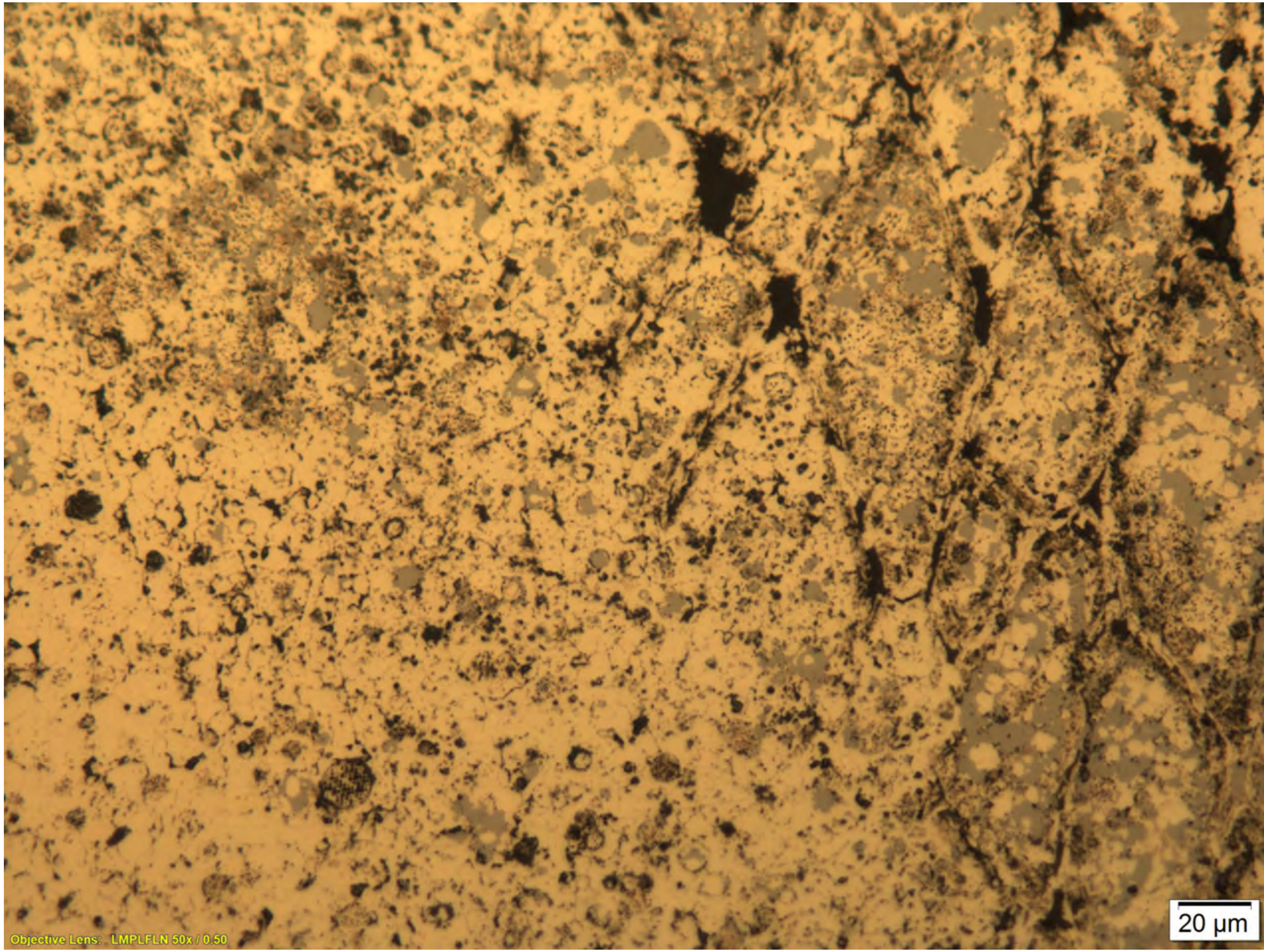


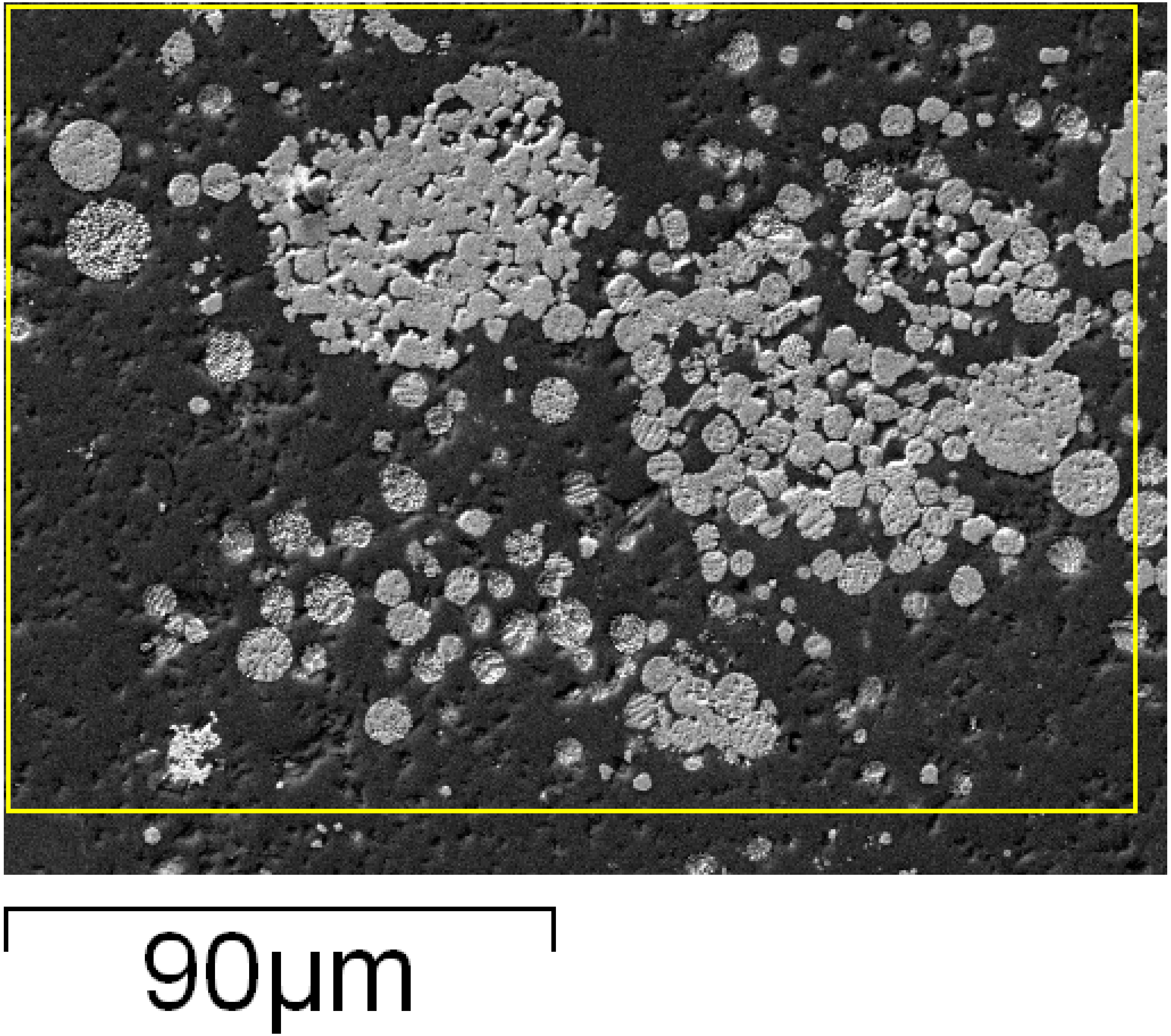
200 µm
Objective Lens: LMPLFLN 5x / 0.13

Pyritised samples from Canada

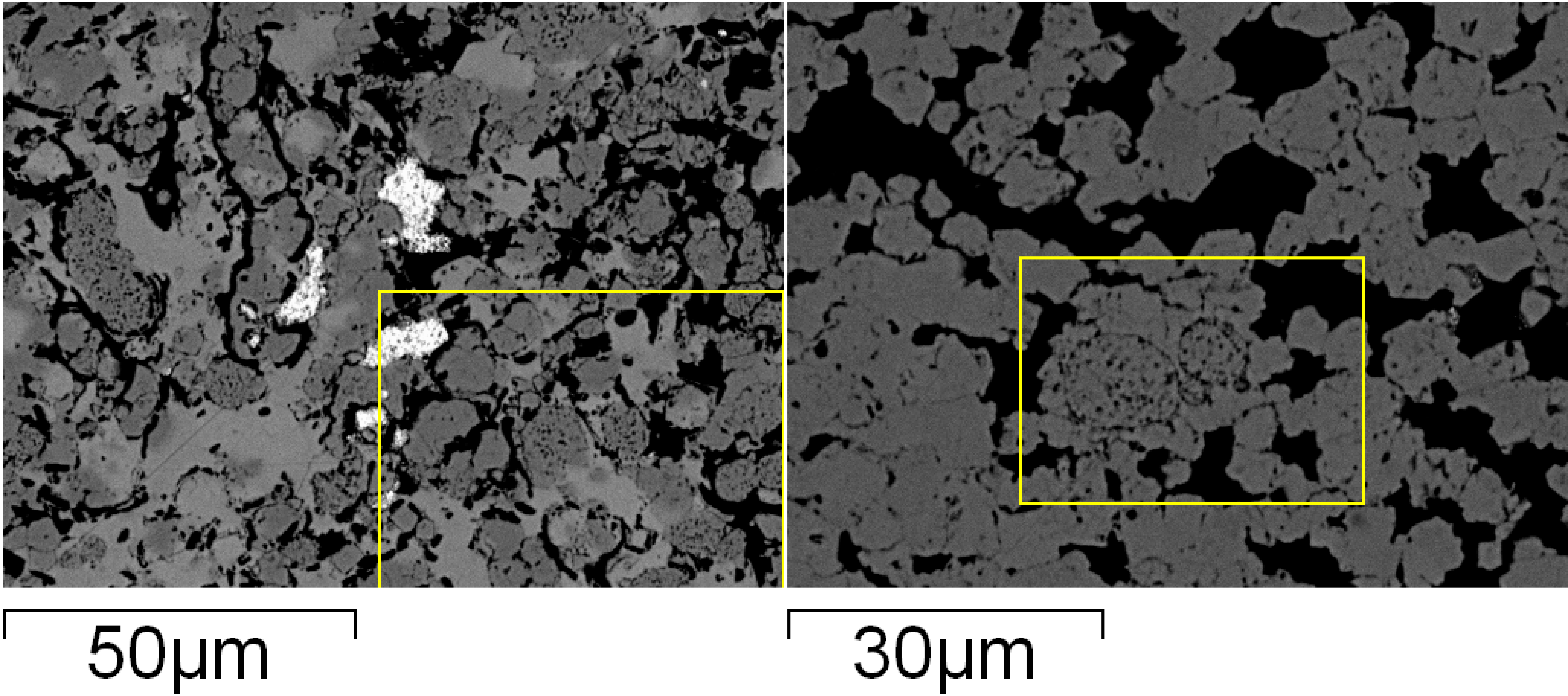




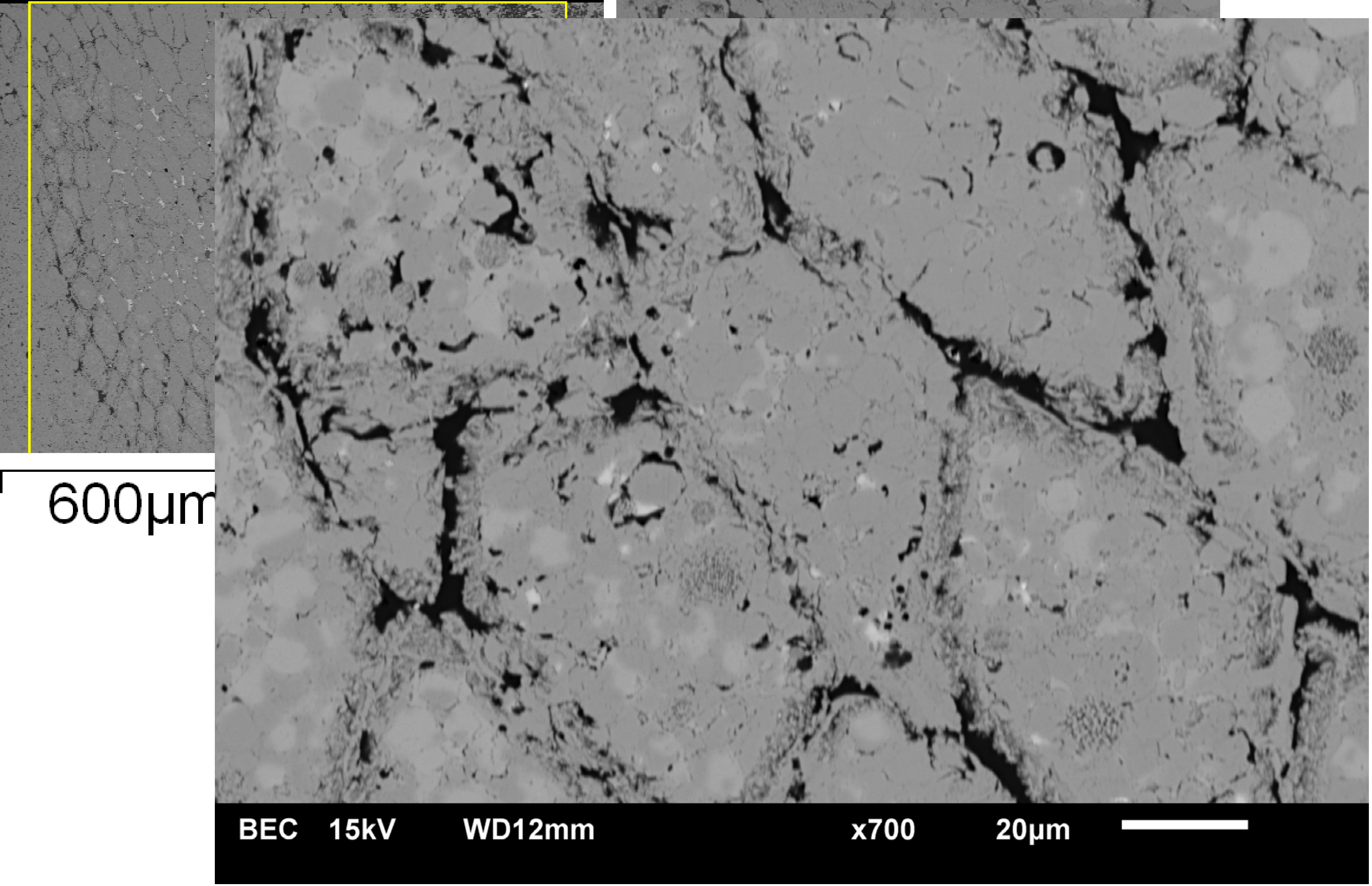




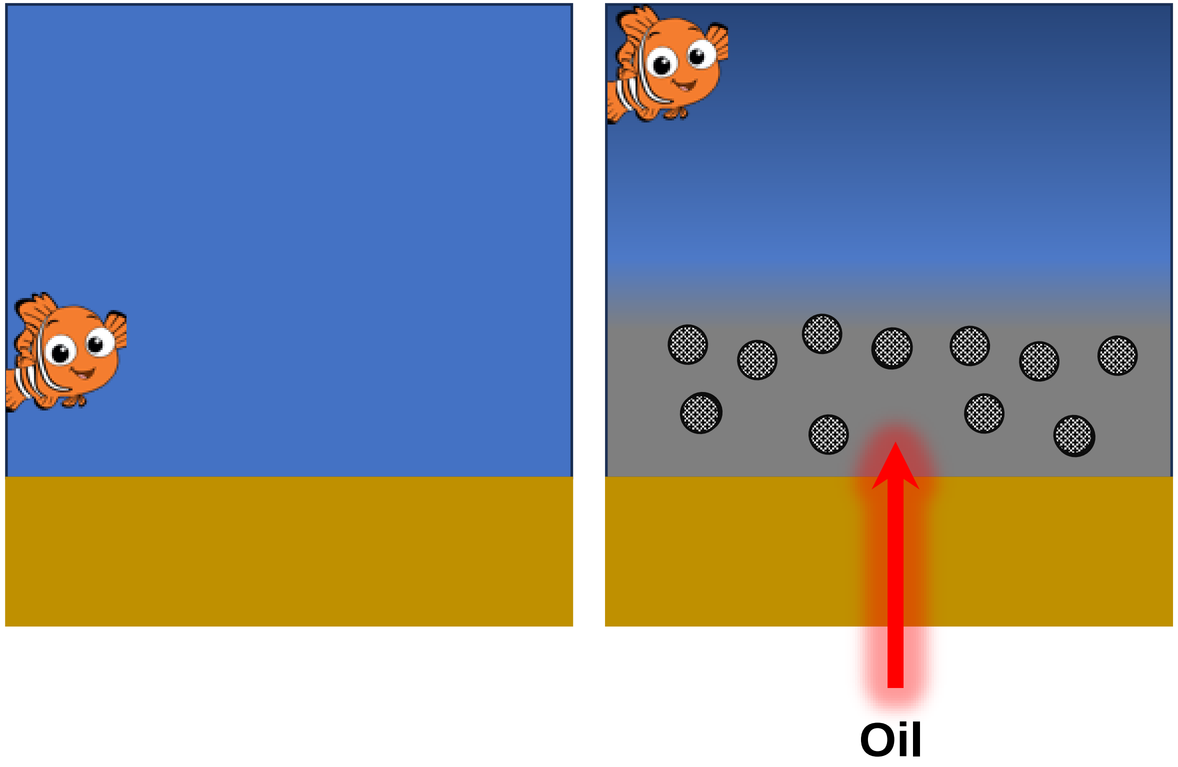
Abundance of framboidal pyrite textures in the Nick Prospect samples



Abundance of framboidal pyrite textures in the Nick Prospect samples


600µm
BEC 15kV WD12mm x700 20µm

Oil-seawater model (step 2)



- If discharge was into the water column – oil-mineral aggregates may have formed as well. Formation of such aggregates is common and have been studied widely at sites of marine oil spills (Cui et al., 2021; Boglaienko and Tansel, 2018; Zhong et al, 2022; Cai et al., 2017).
- Therefore, oil discharge will have caused the formation of spherical aggregates including oil-mineral aggregates.

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JGR Biogeosciences

RESEARCH ARTICLE
10.1029/2021JG006560

Microbially Induced Anaerobic Oxidation of Magnetite to Maghemite in a Hydrocarbon-Contaminated Aquifer

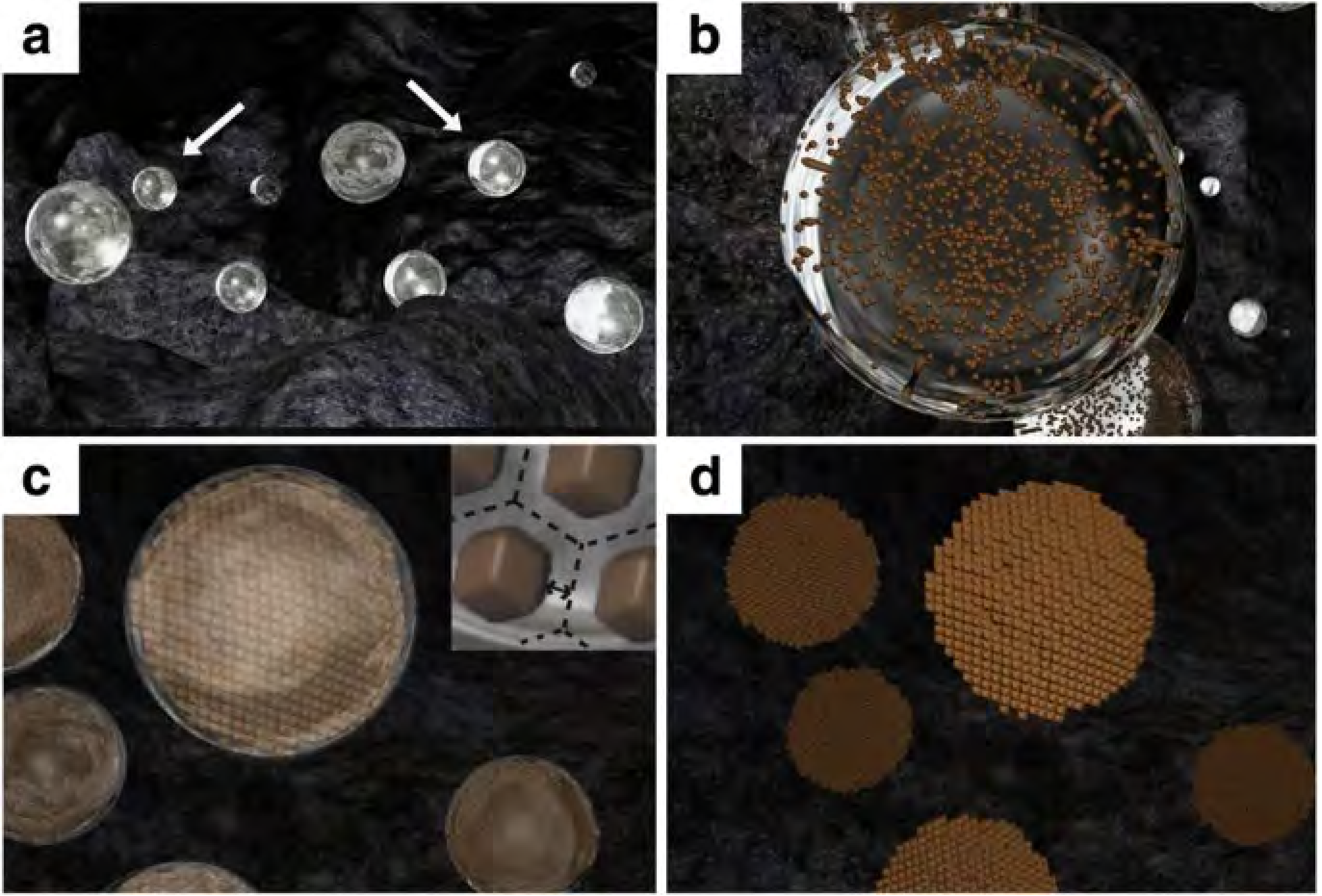
Leonard O. Ohenhen[1,2], Joshua M. Feinberg[3], Lee D. Slater[4], Dimitrios Ntarlagiannis[4], Isabelle M. Cozzarelli[5], Miriam Rios-Sanchez[6], Carl W. Isaacson[6], Alexis Stricker[3], and Estella A. Atekwana[1,7]

[1]Department of Earth Sciences, University of Delaware, Newark, DE, USA, [2]Now at Department of Geosciences, Virginia Tech, Blacksburg, VA, USA, [3]Department of Earth & Environmental Sciences, Institute for Rock Magnetism, University of Minnesota, Minneapolis, MN, USA, [4]Department of Earth and Environmental Sciences, Rutgers University Newark, Newark, NJ, USA, [5]Geology, Energy & Minerals Science Center, U.S. Geological Survey, Reston, VA, USA, [6]Center for Sustainability Studies, Bemidji State University, Bemidji, MN, USA, [7]Now at Department of Earth and Planetary Sciences, University of California Davis, Davis, CA, USA

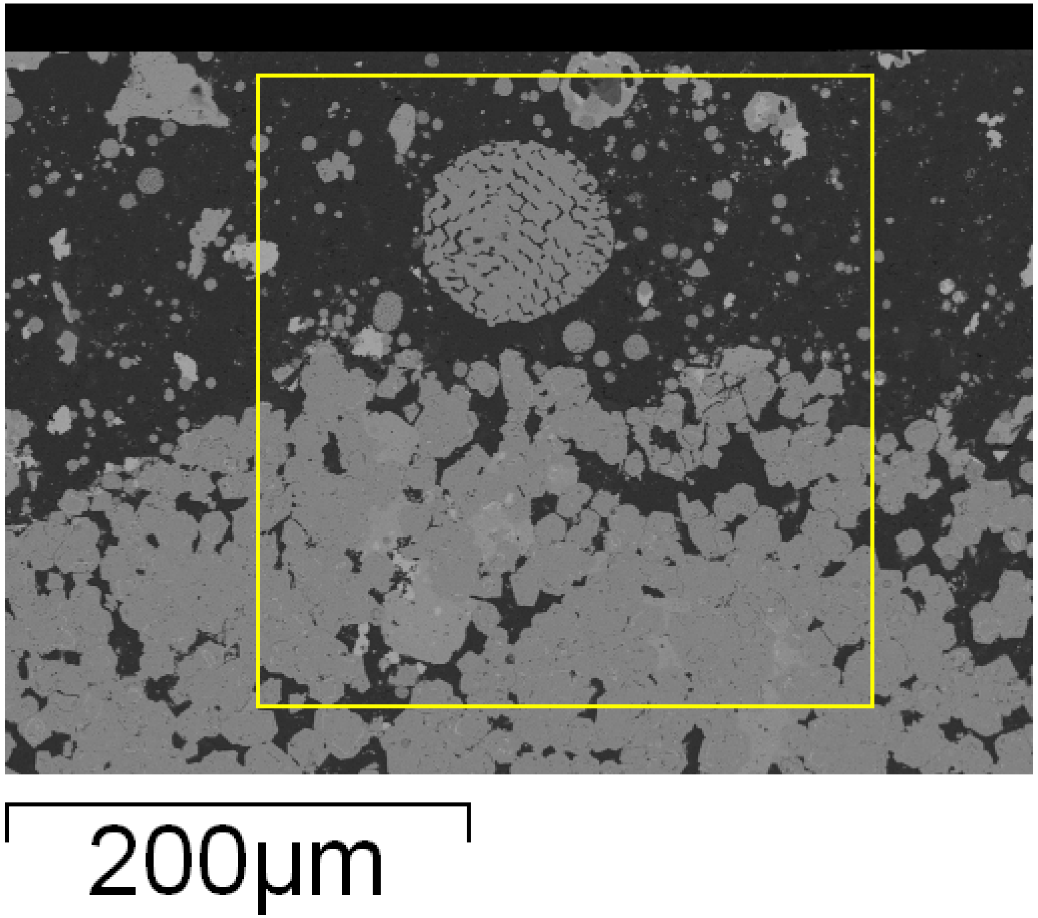
Key Points:

- Fluctuations in magnetization may occur due to microbially induced iron mineral transformation in hydrocarbon-contaminated aquifers
- Loss of magnetization is due to maghemitization (oxidation) and dissolution of magnetite grains
- Within the anoxic portions of the hydrocarbon plume, maghemitization occurs through anaerobic oxidation induced by microorganisms

“*Magnetite transformation to maghemite typically occurs under oxic conditions, here, we propose that maghemitization occurs within the anoxic portions of the plume via microbially mediated anaerobic oxidation.*”



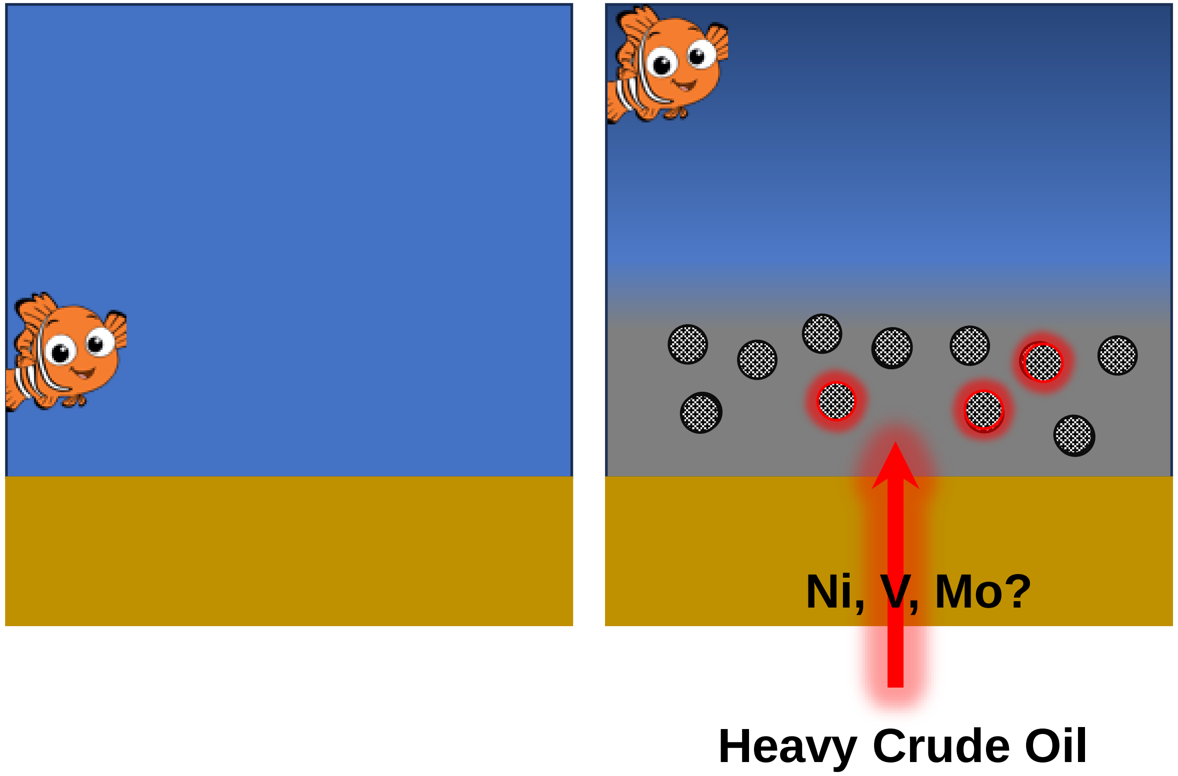
Kimura 2013



- **Remanence in authigenic magnetite: Testing the hydrocarbon-magnetite hypothesis (Elmore and Crawford, 1990)**

- **Occurrence of secondary magnetite within biodegraded oil (McCabe et al., 1987)**

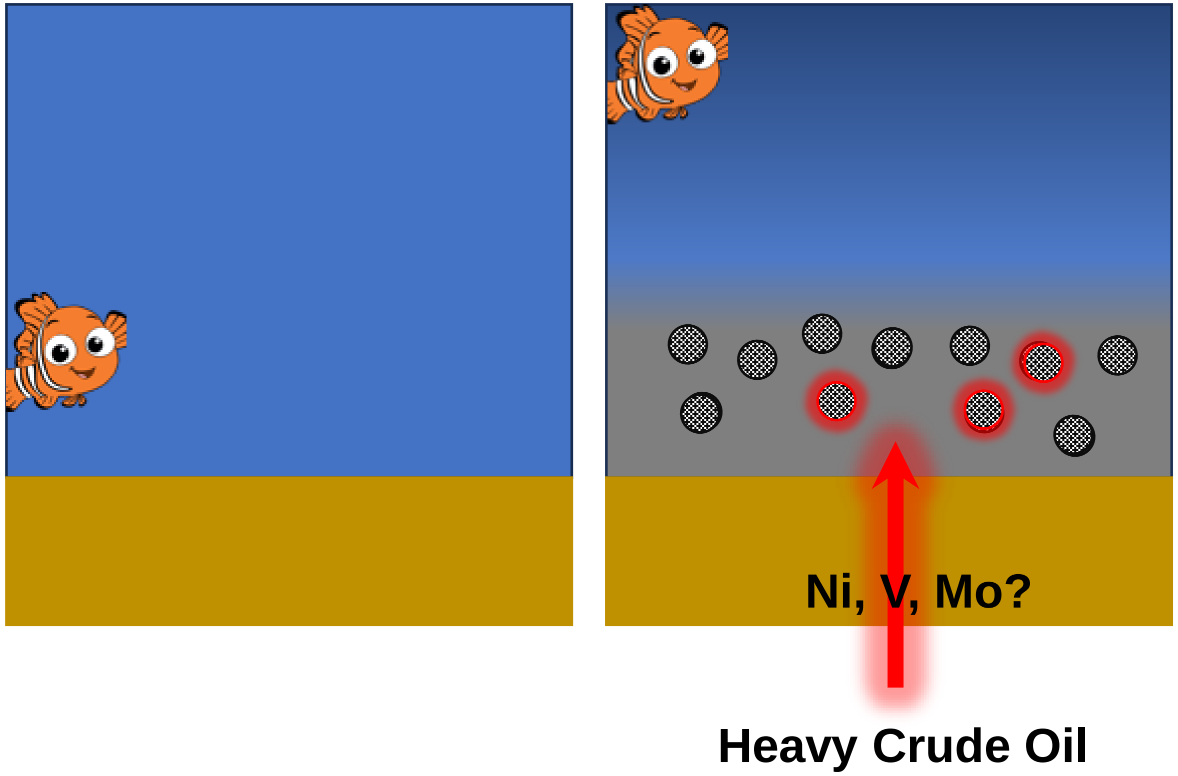
Oil-seawater model (step 2)



What kind of oil?

The oil is likely to be heavy crude oil – with high in impurities like Ni, V etc. with concentrations ranging from 1000 ppm to a few wt % (Babalola and Susu, 2019) and Mo to a lesser extent.

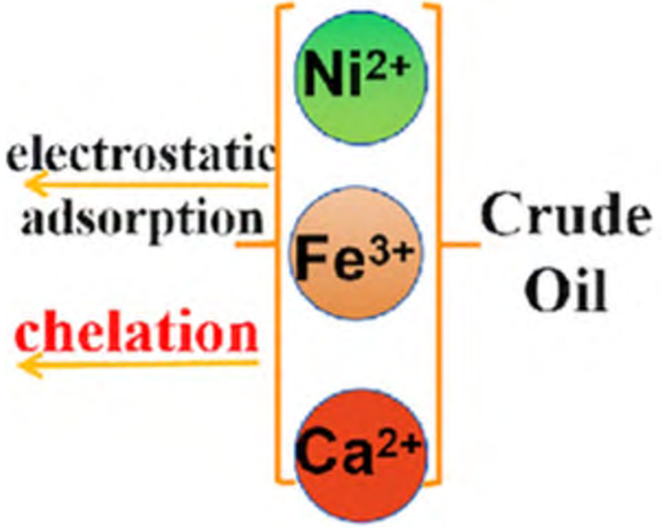
Oil-seawater model (step 3)



Presence of metals in oil do not necessarily imply their direct availability to form their sulphides. A series of chemical reactions and transformations will have to occur for the metals to be released from the oil and be available for subsequent steps for mineralisation.

•If our assumption is true – that is, the oil discharged into the sediment/water was high in metals like (Ni, Co, V etc.) then next steps will have to be **de-metallisation of the oil**.

Oil-seawater model (step 3)



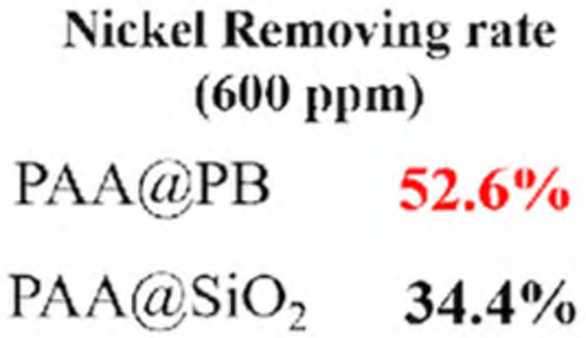
- The process is highly efficient and results in at least 51% V and 65% Ni recovery (Babalola and Susu, 2019). Most metals combine with organic acids to form complex organometallic compounds or oil-soluble metalloporphyrins.

- By a sequence of two mechanisms, the porphyrins are first dehydrogenated to form precursor species which thereafter undergo ring-cleavage reactions leading to metal deposition on the catalyst surface.
  - $(MP)+H2 \rightleftharpoons (MPH2) \longrightarrow M+PH2$

- where MP is the metalloporphyrin, MPH_2 is the intermediate hydrogenated metalloporphyrin, M is the deposited metal, and PH_2 is the resulting hydrocarbon. Using chemical methods, metalloporphyrins react with an acid as given in Eq. (2):
  - $MP+HX \rightleftharpoons MX+PH$

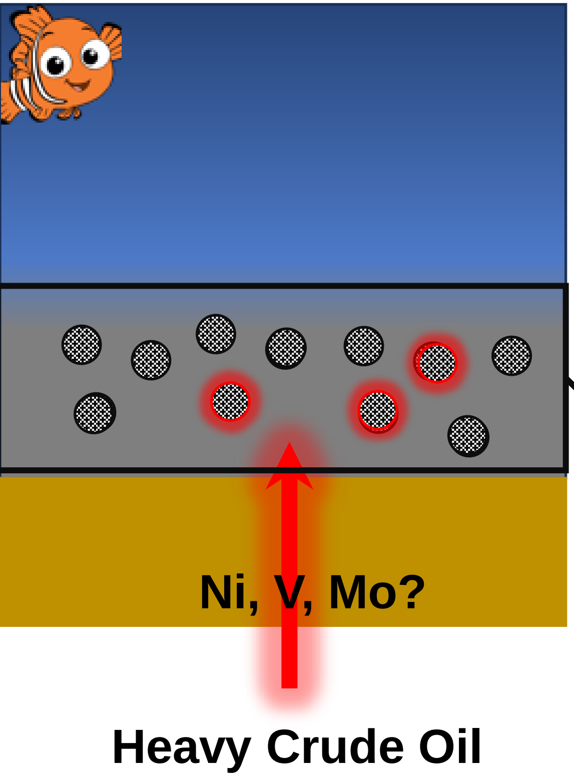
- where MP is the metalloporphyrin, HX is the acid, MX is the metal-acid complex, and PH is the resulting hydrocarbon [28].

The equations mentioned above may have easily occurred in reducing sediments with high contents of organic matter – characteristic of such deposits.

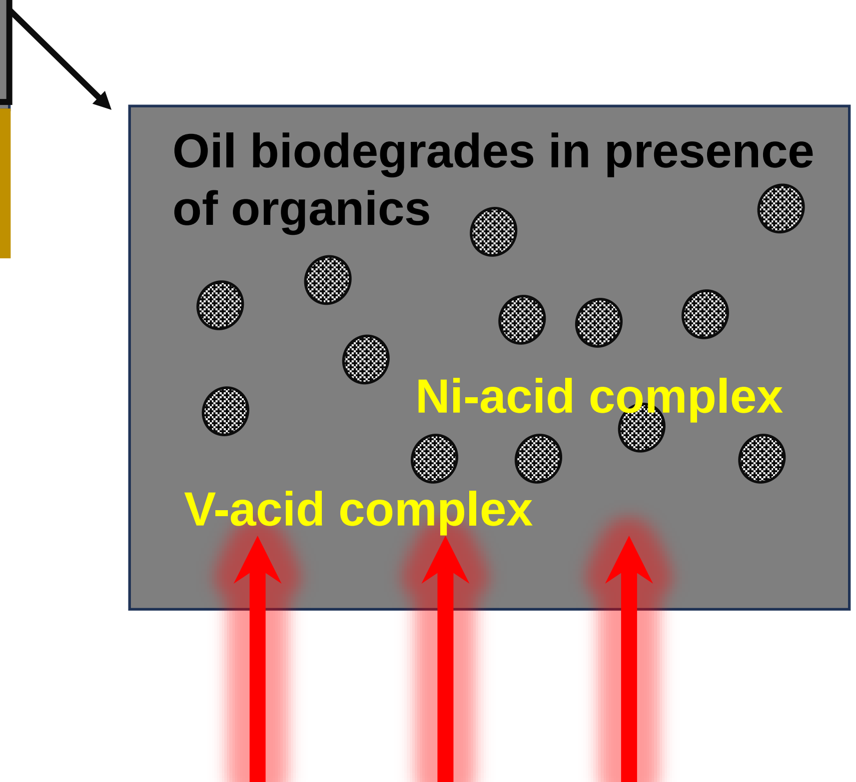


https://doi.org/10.1002/app.52709

Oil-seawater model (step 3)



If our assumption is true – that is, the oil discharged into the sediment/water was high in metals like (Ni, Co, V etc.) then next steps will have to be **de-metallisation of the oil**.



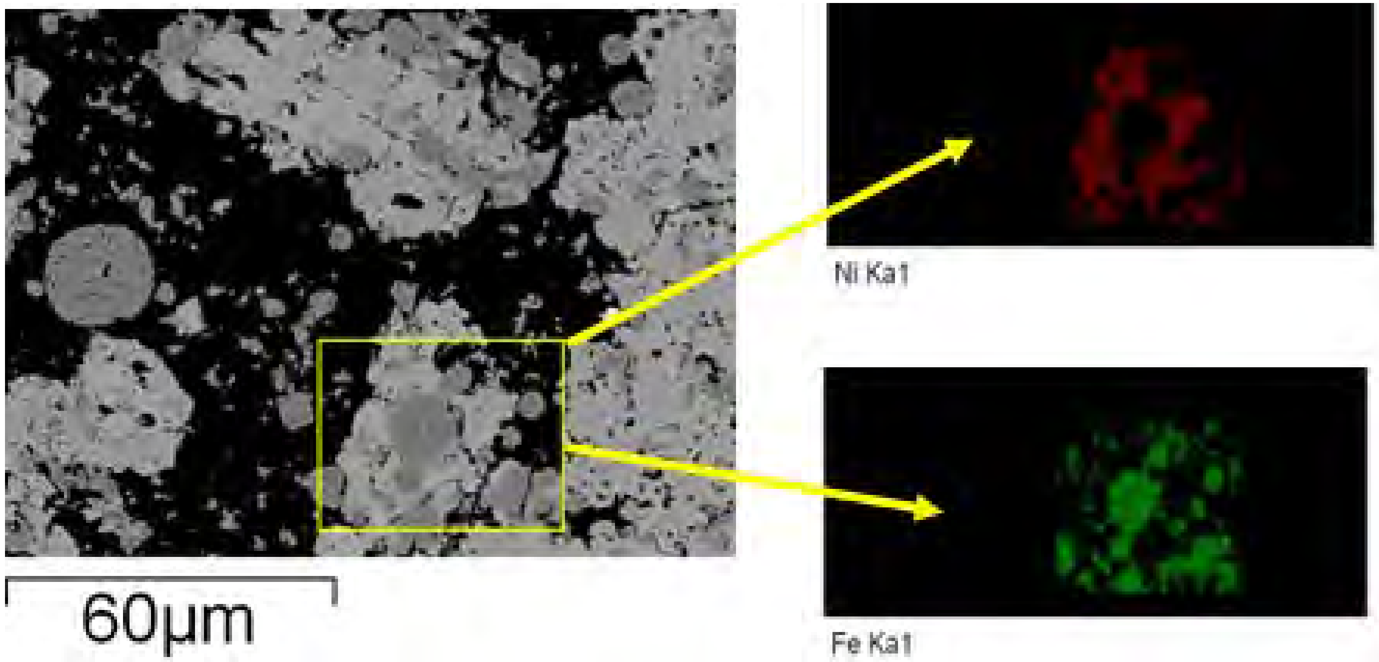
Oil-seawater model (step 4)

A series of chemical reactions may have occurred to extract the metals from the oil and be made available as metals/ metal acid complexes to

a) form their own sulphides (probably not reducing enough)

Or

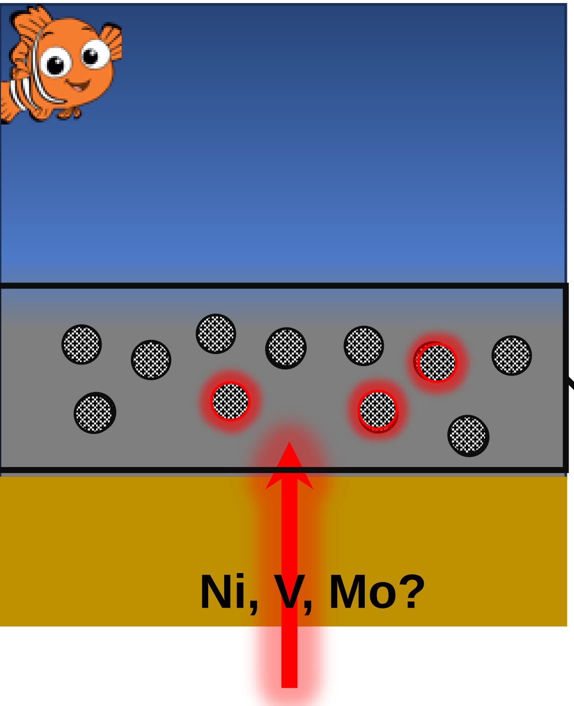
b) be incorporated into other minerals such as pyrite/magnetite/greigite



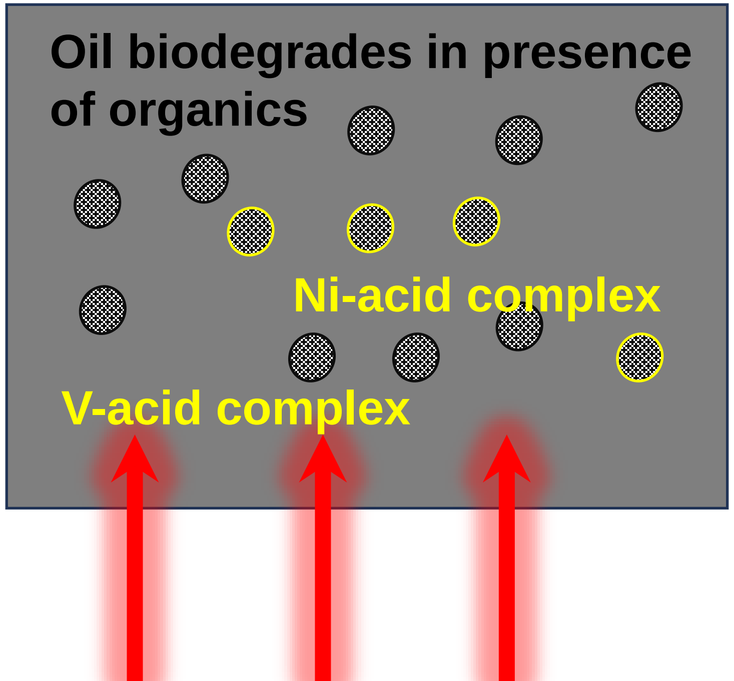
Oil-seawater model (step 5)

- Ni and other metals were perhaps being adsorbed onto magnetite framboids – this is chemically feasible. In fact, it is a highly efficient process – and used in wastewater management process (Adeli et al., 2017). Magnetite nanoparticles efficiently remove Ni, Cu, Zn etc. from wastewaters.

- In our case, the framboidal texture (higher surface area to volume) and magnetite may have also acted as important hosts. Important to note here is that magnetite framboids or aggregates formed first and then acted as adsorbers (much like the wastewater scenario).

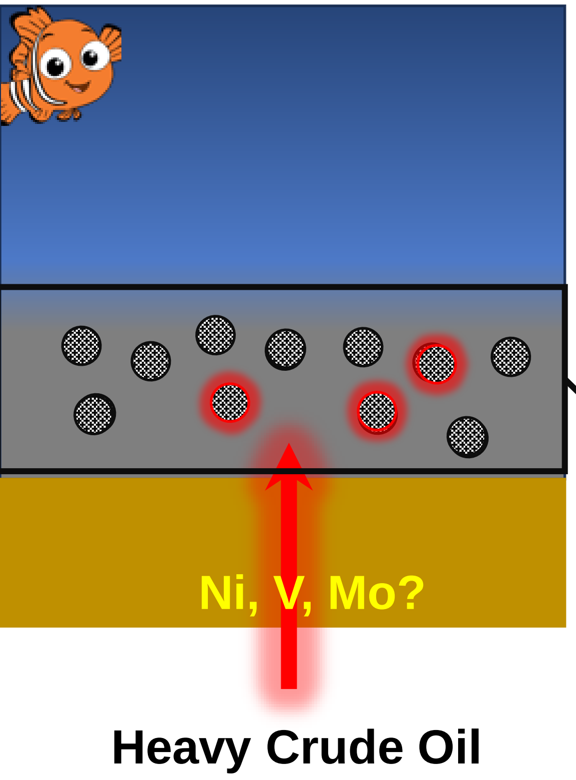


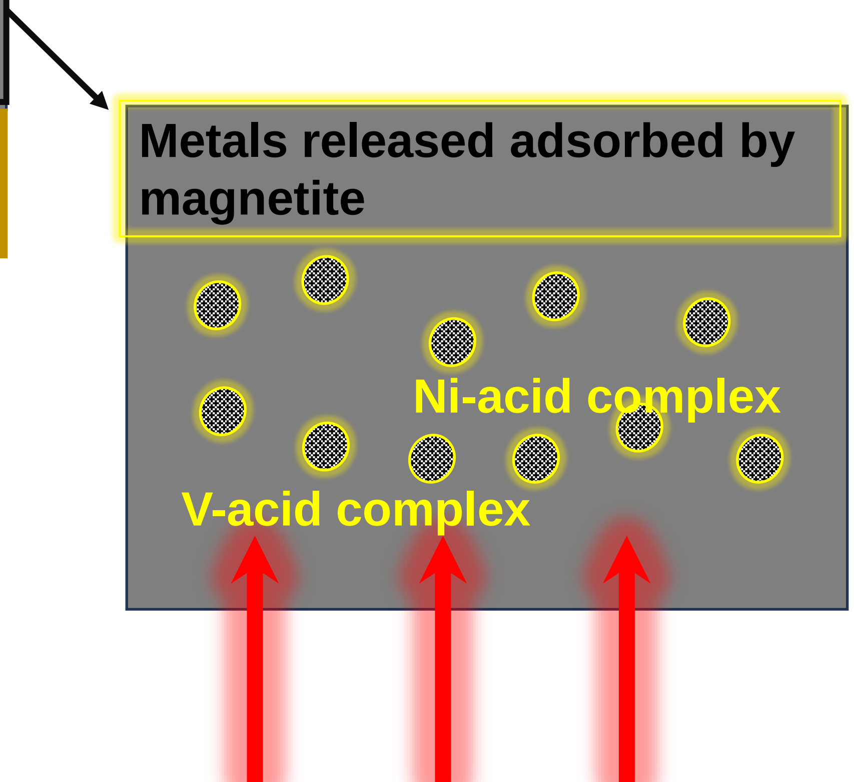
Heavy Crude Oil



Oil-seawater model (step 5)

The transformation or replacement of magnetite framboids by pyrite may have precluded the pyrites to incorporate the metals. Or because the precursors were magnetite?





Oil-seawater model (step 6)

We know that Co and Ni preferentially get incorporated in pyrite owing to their electronic configuration. But there are instances, as described by Large et al., 2018, that in the early stages of diagenesis, Co may be adsorbed on precursors but during transformation of these precursors to framboids – desorption of metals occur, and their saturation results within the framboid, finally causing metal sulphides to form around the framboids.

b) The transformation or replacement of magnetite framboids by pyrite may have precluded the pyrites to incorporate the metals. Or because the precursors were magnetite?

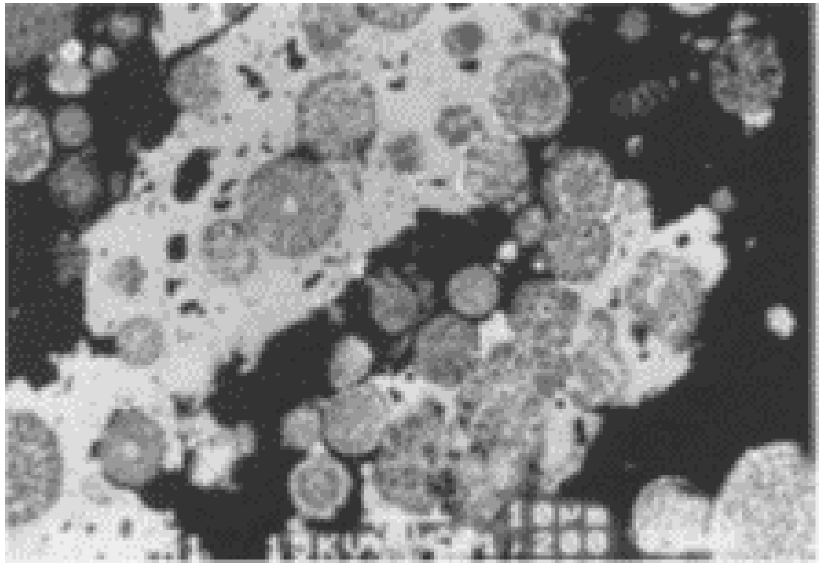
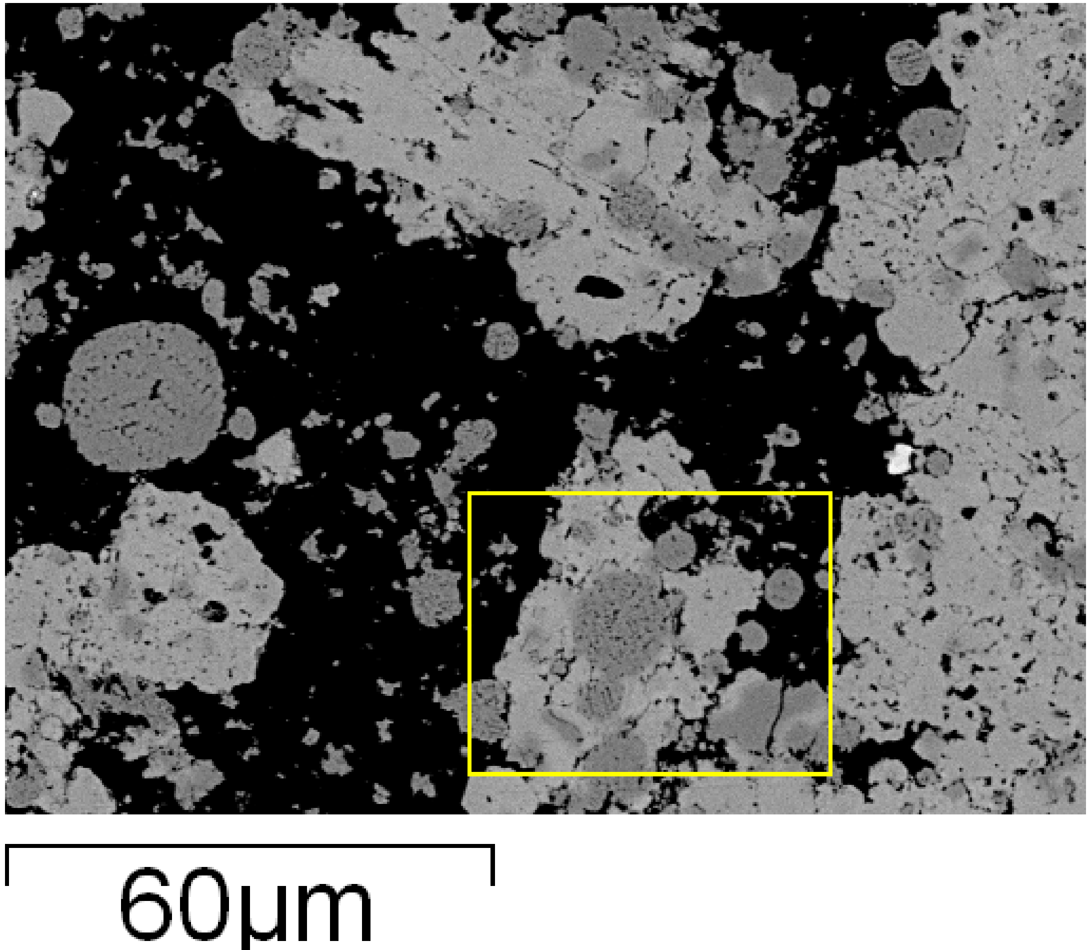
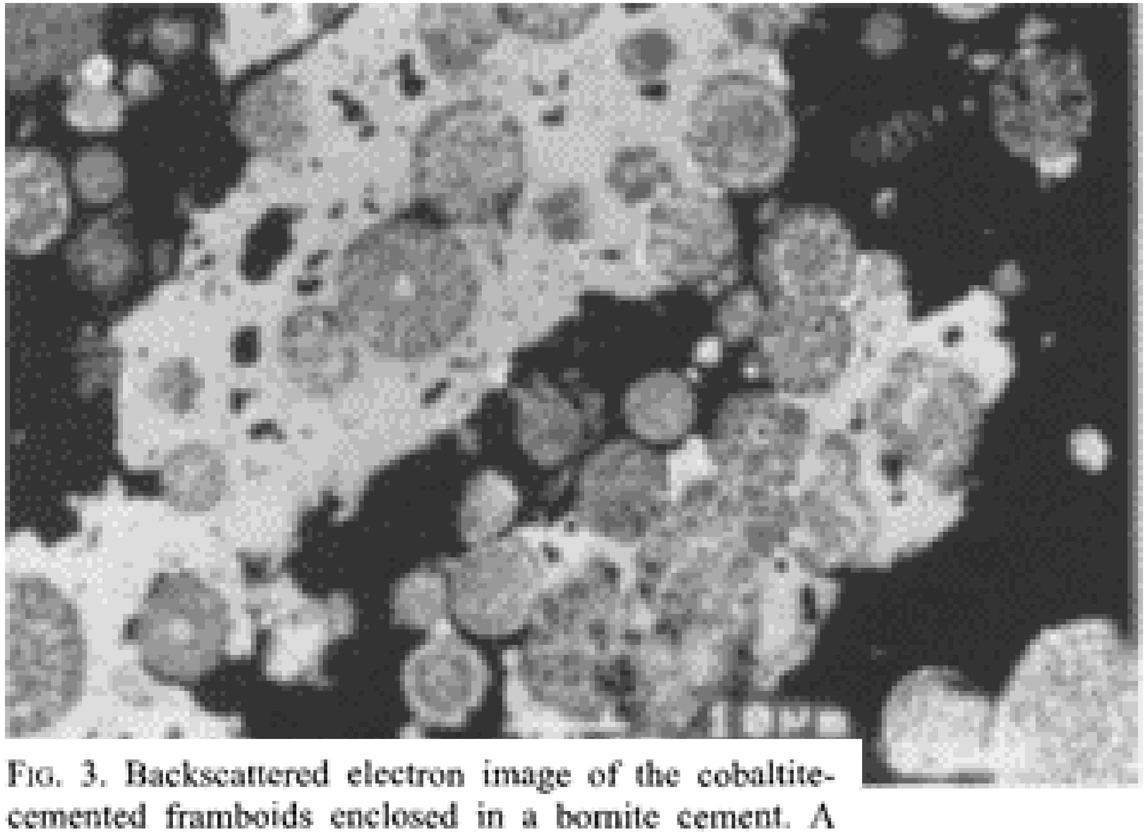


FIG. 3. Backscattered electron image of the cobaltite-cemented framboids enclosed in a bornite cement. A

An example from the Kupferschiefer (Large et al., 2018)

Oil-seawater model (step 6)

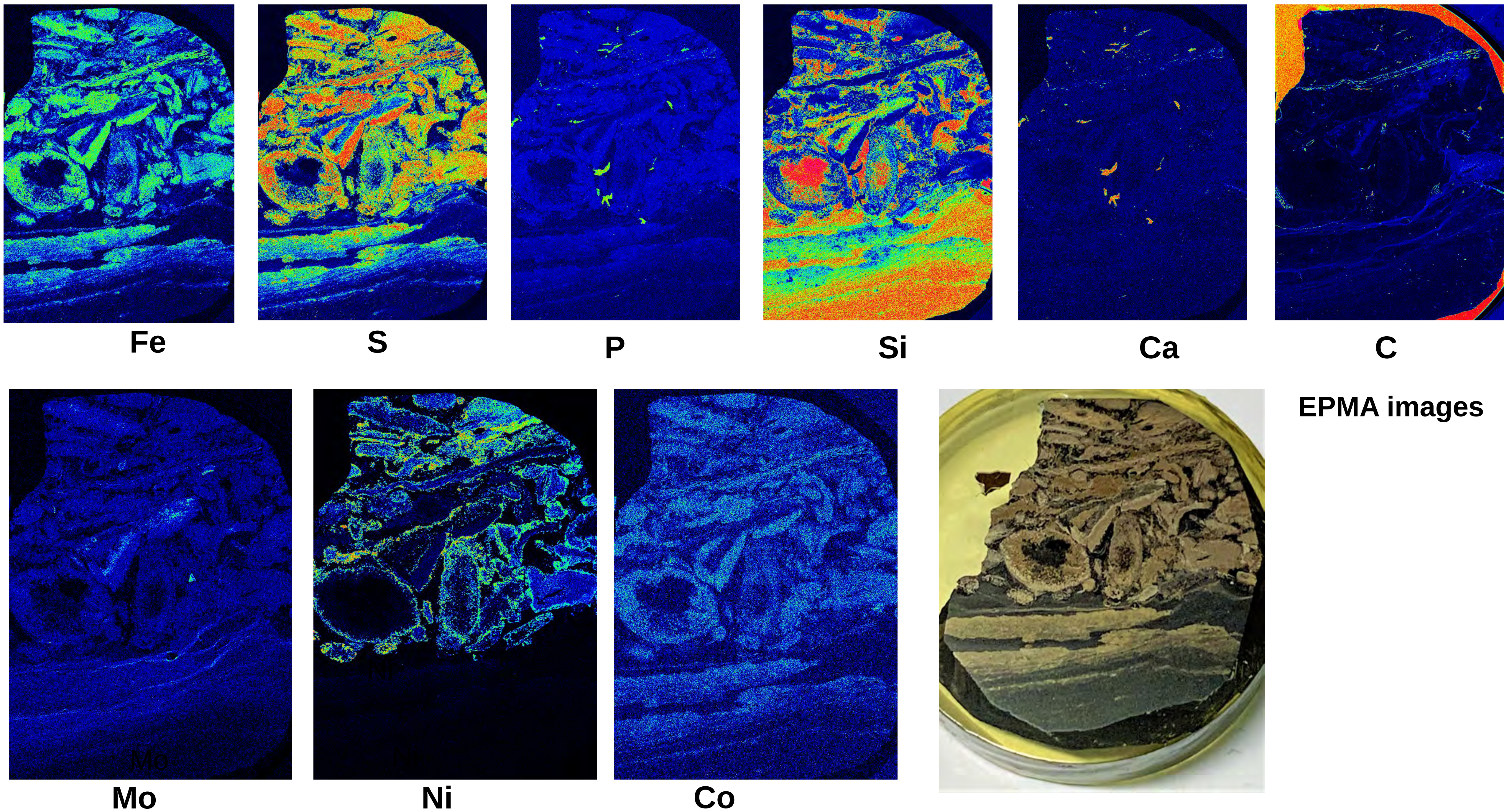


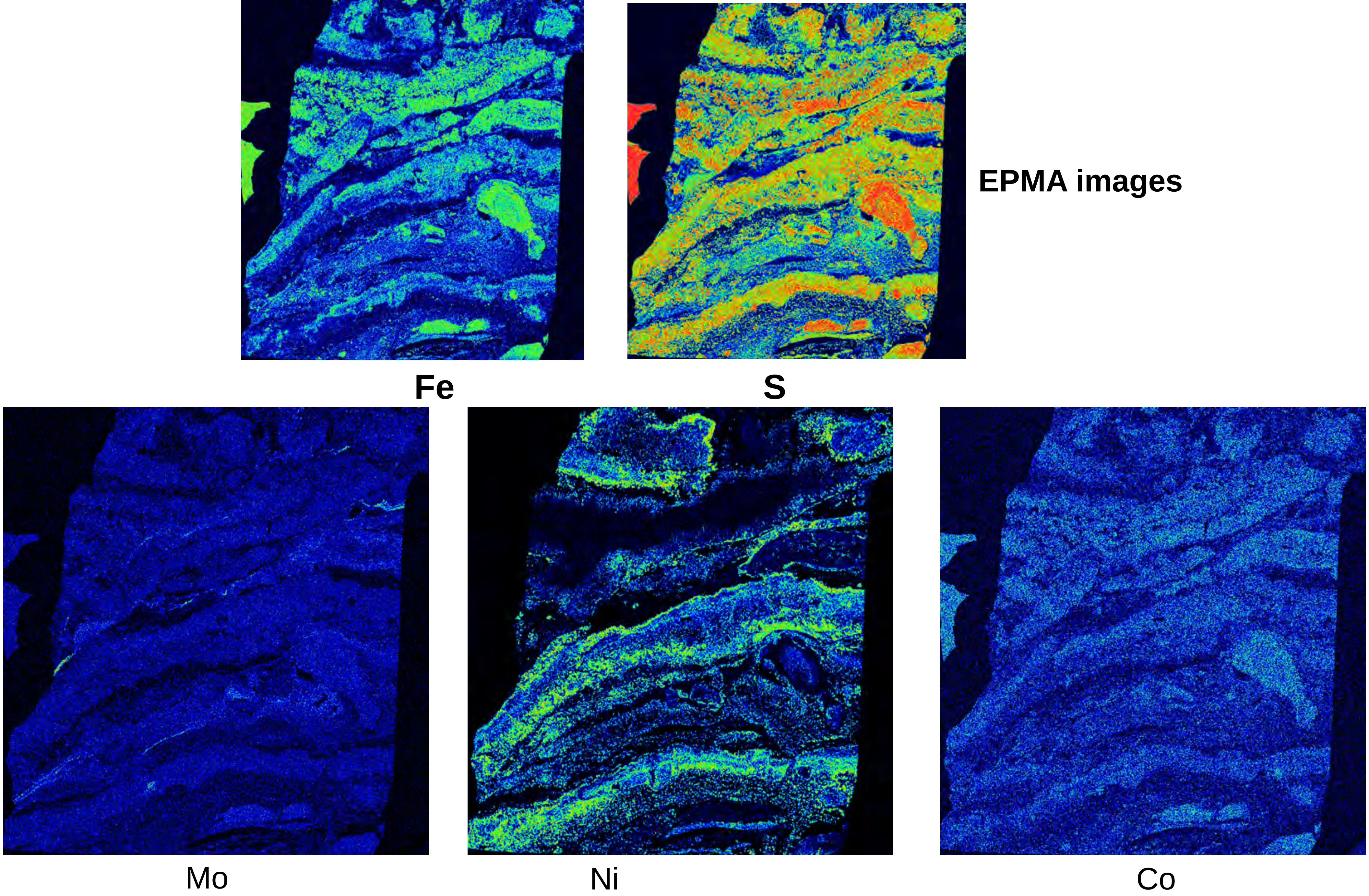


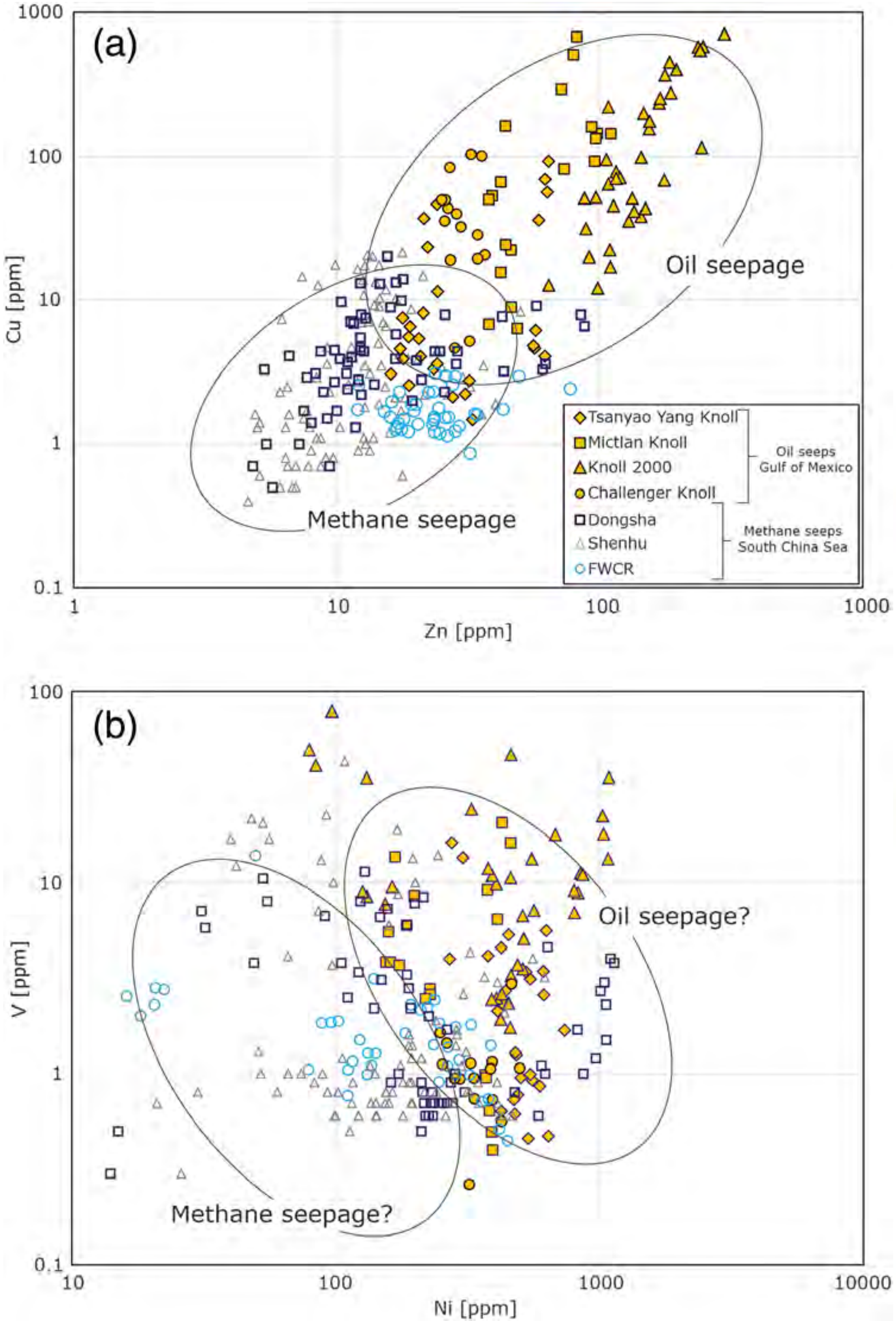
An example from the Kupferschiefer (Large et al., 2018)

As the environment became more and more reducing (along with diagenesis) – these framboids of magnetite transformed to pyrite. Canfield and Berner (1987) discussed pyritization of magnetite in anoxic marine sediments.

Dissolution of magnetite and their replacement of pyrite released the metals. By that stage, environments were reducing enough (high H_2S) for the metals to form their own sulphides around these pyritised framboids that served as nucleation sites.


Fe
S
P
Si
Ca
C
EPMA images
Mo
Ni
Co


EPMA images
Fe
S
Mo
Ni
Co



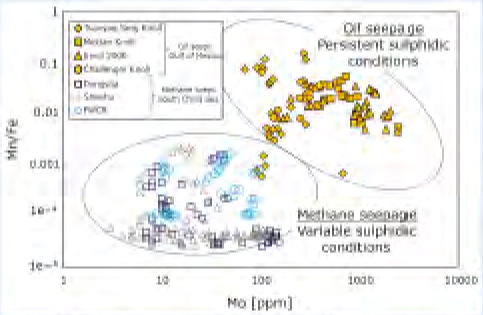
Geochemical Perspectives Letters

Pyrite-based trace element fingerprints for methane and oil seepage

D. Smrzka[1,2*], Z. Lin[3], P. Monien[2], T. Chen[4], W. Bach[1,2], J. Peckmann[3], G. Bohrmann[1,2]

Abstract

https://doi.org/10.7185/geochemlet.2409



Pyrite forms at marine hydrocarbon seeps as the result of the microbial oxidation of methane, organic matter, and crude oil coupled to sulphate reduction. Redox sensitive and nutrient trace elements in pyrite may hold valuable information on present and past seepage events, the evolution of fluid composition, as well as the presence of heavy hydrocarbon compounds from crude oil. This study uses the trace element compositions of pyrite that formed at methane seeps and crude oil-dominated seeps to constrain element mobilities during the sulphate reduction processes, and examine the degree to which specific trace elements are captured by pyrite. Pyrite forming at oil seeps shows high Mn/Fe ratios and high Mo content compared to pyrite from methane seeps. These patterns suggest either more intense or persistent sulphidic conditions, or an intensified manganese (oxy)hydroxide shuttle process at oil seeps. Copper and Zn are enriched in oil seepage-derived pyrite while Ni and V enrichment is less pronounced, suggesting either a selective uptake of specific elements by pyrite, or varying trace element compositions of organic compounds oxidised *via* microbial reduction.

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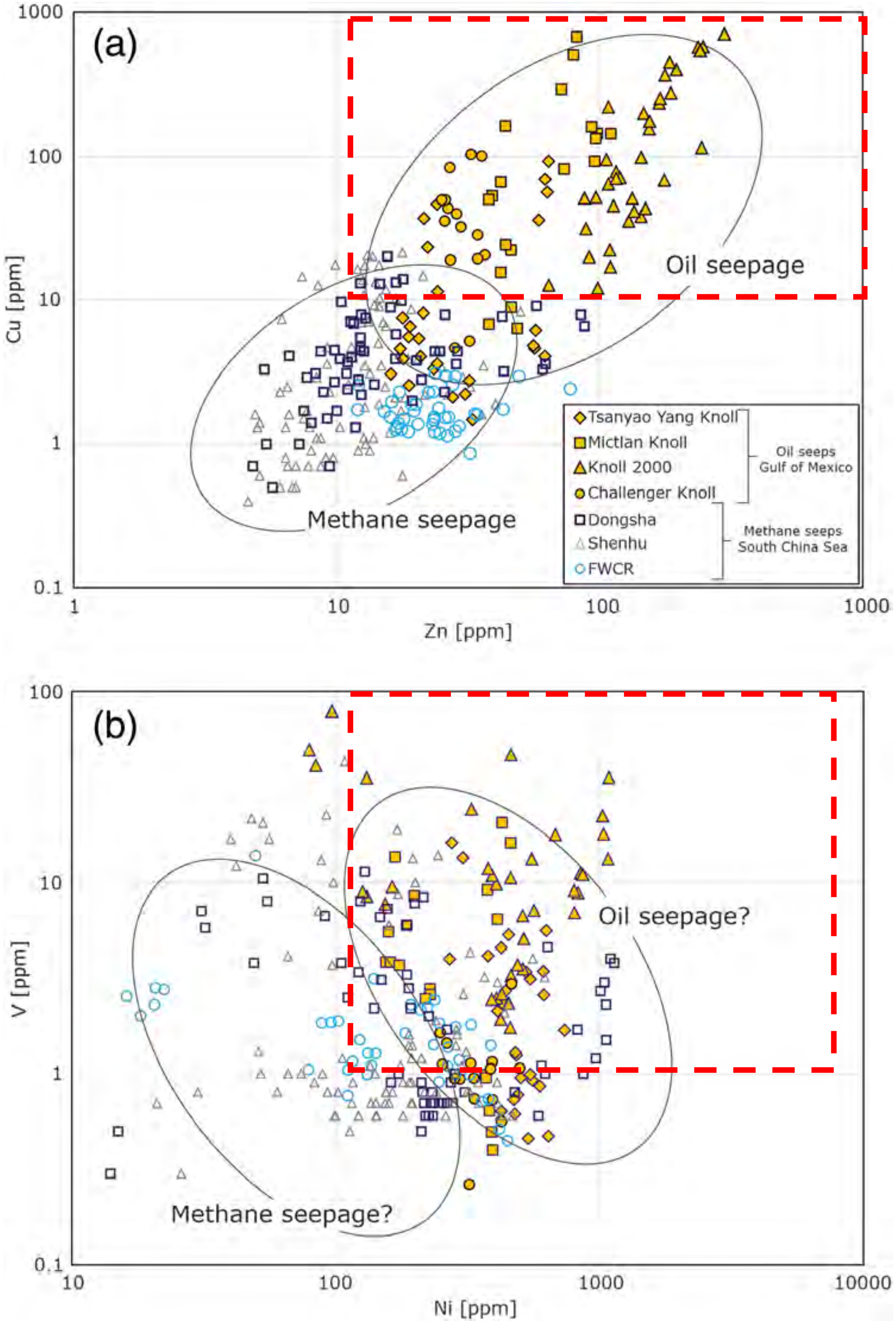
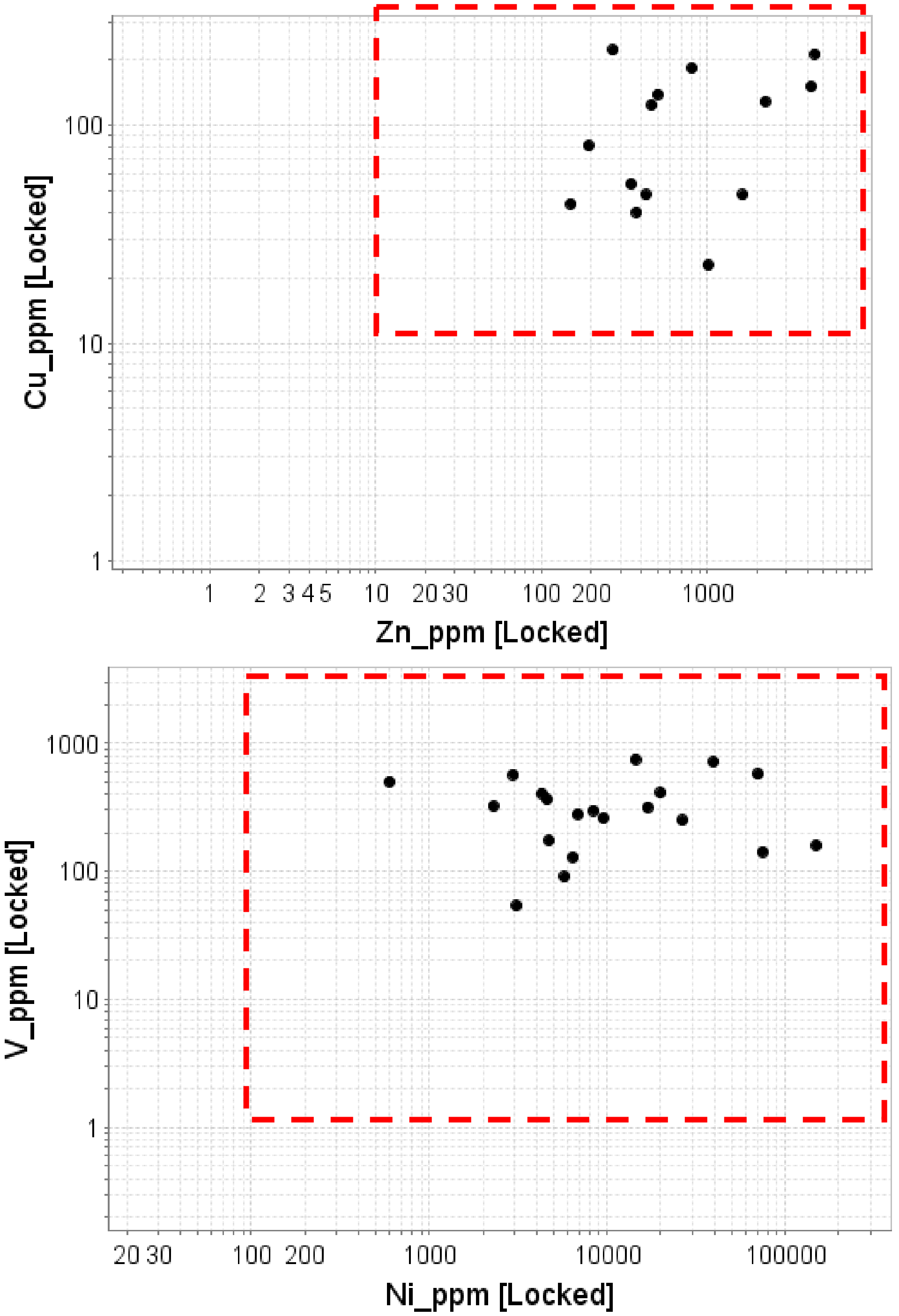

(a)
Oil seepage
Methane seepage
Cu [ppm]
Zn [ppm]
Tsanyao Yang Knoll
Mictlan Knoll
Knoll 2000
Challenger Knoll
Oil seeps Gulf of Mexico
Dongsha
Shenhu
FWCR
Methane seeps South China Sea
(b)
Oil seepage?
Methane seepage?
V [ppm]
Ni [ppm]


Cu_ppm [Locked]
Zn_ppm [Locked]
V_ppm [Locked]
Ni_ppm [Locked]

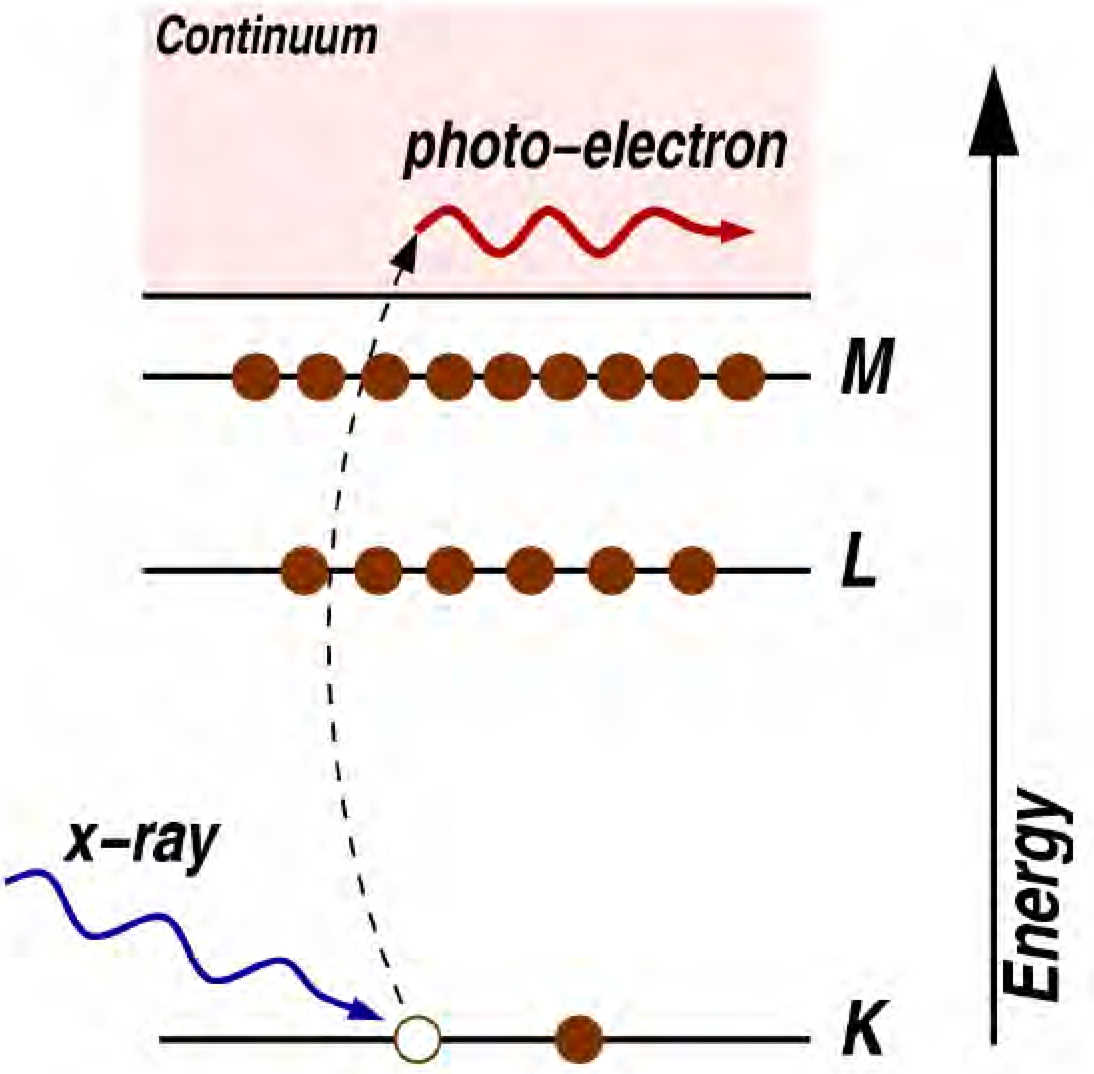
LA-ICP-MS analyses

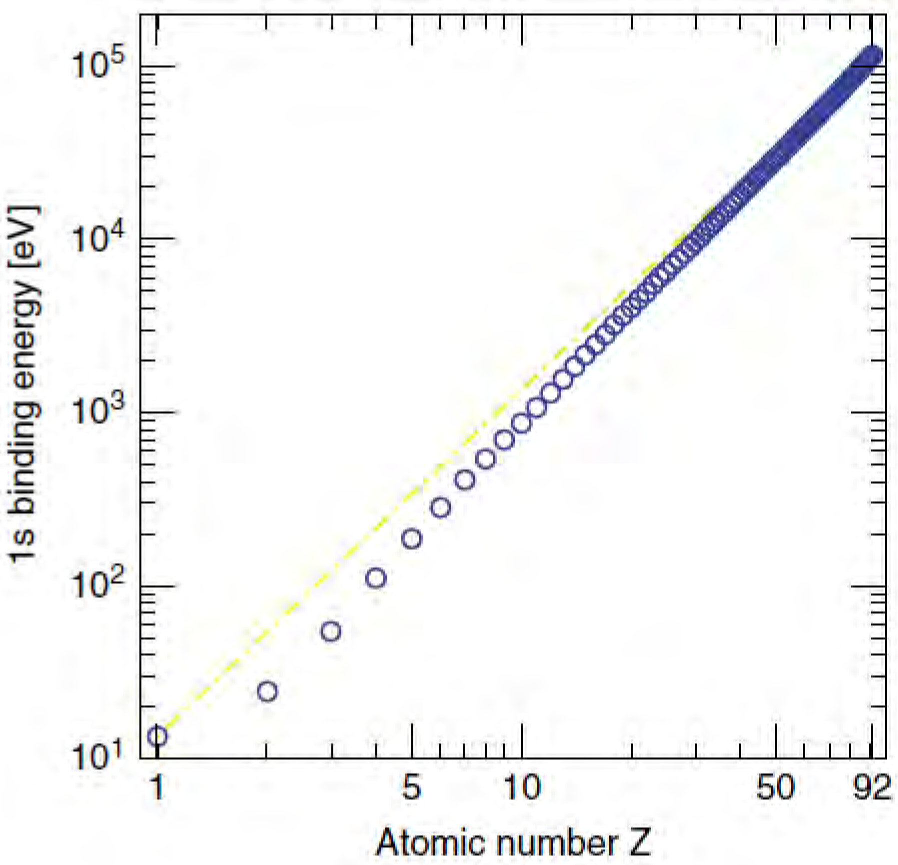
Parameters	Nick samples	Pyrite ore database
No. of analyses	20	~3000
Ti	84 ppm	89 ppm
V	338 ppm	4.5 ppm

Fe_3O_4

Ti, V can be incorporated in the structure of magnetite not pyrite

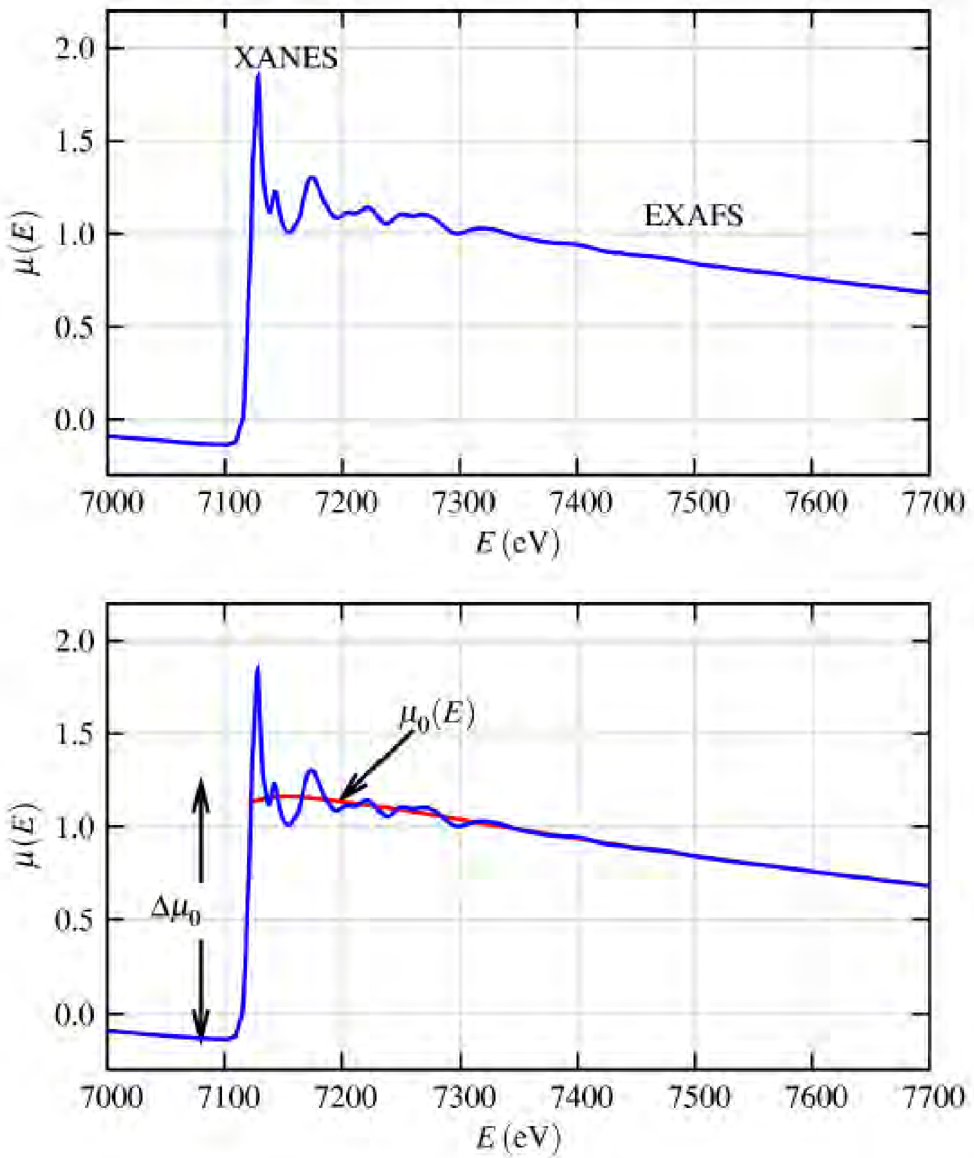
Synchrotron analyses





Willmott, 2019

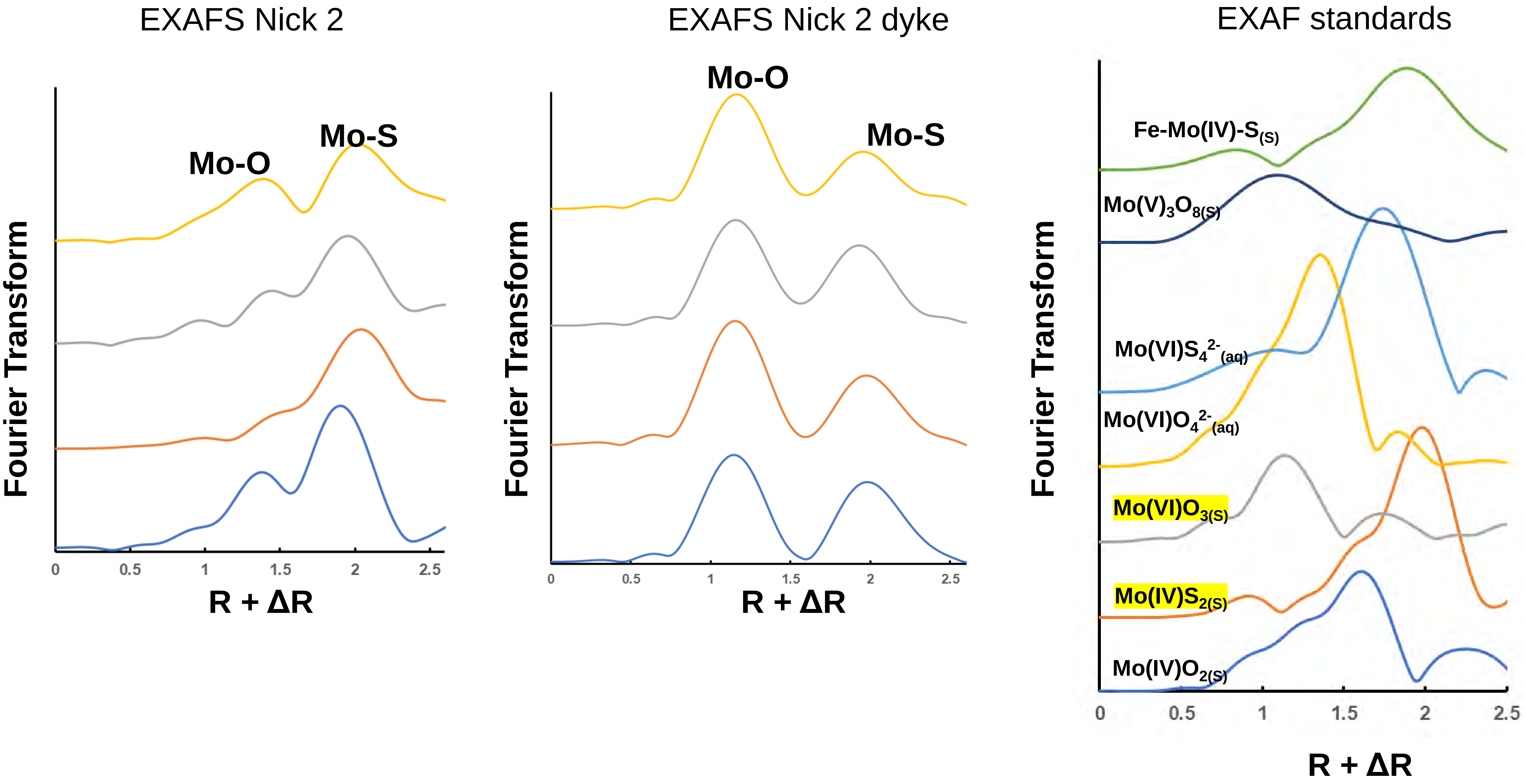
Synchrotron analyses



X-ray absorption near edge structure (XANES)

Extended X-ray Absorption Fine Structure (EXAFS)

Willmott, 2019


EXAFS Nick 2
Mo-O
Mo-S
Fourier Transform
0
0.5
1
1.5
2
2.5
R + ΔR
EXAFS Nick 2 dyke
Mo-O
Mo-S
Fourier Transform
0
0.5
1
1.5
2
2.5
R + ΔR
EXAF standards
Fe-Mo(IV)-$S_{(S)}$
$Mo(V)_3O_{8(S)}$
$Mo(VI)S_4^{2-}{}_{(aq)}$
$Mo(VI)O_4^{2-}{}_{(aq)}$
$Mo(VI)O_{3(S)}$
$Mo(IV)S_{2(S)}$
$Mo(IV)O_{2(S)}$
Fourier Transform
0
0.5
1
1.5
2
2.5
R + ΔR

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Molybdenum speciation tracking hydrocarbon migration in fine-grained sedimentary rocks

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[b] Depertment of Geoscience, University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada
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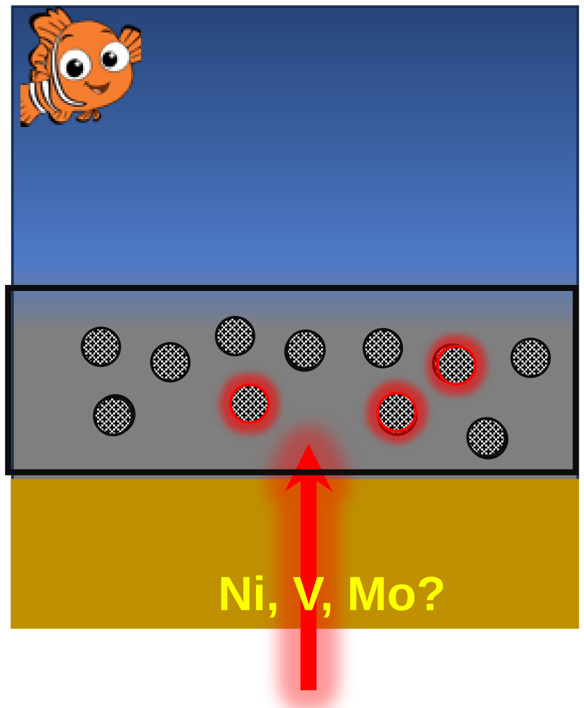
The reduced Mo species are distributed in the vicinity of fault-related hydrothermal diagenesis/dolomitization zones. In contrast, the oxidized Mo species are found associated with samples enriched with solid bitumen/pyrobitumen. The results of our study show Mo speciation can significantly help to elucidate complex paleo-redox histories.

How did we go finding Ni-Mo

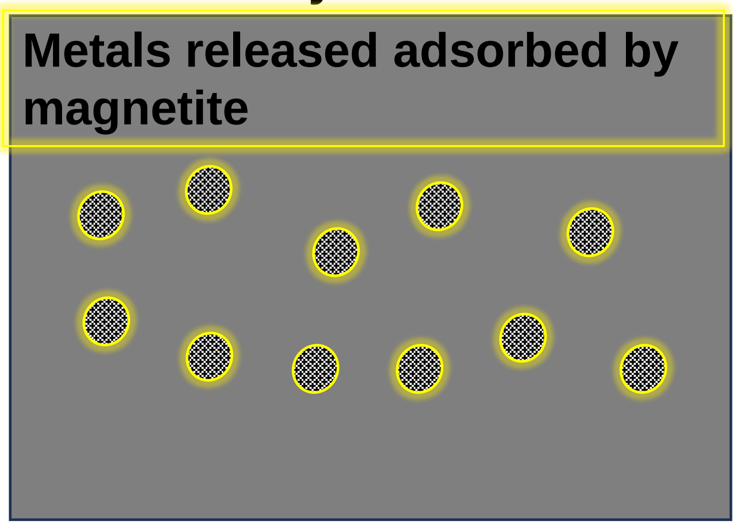
- Oil exhalation – bitumen dyke in the Nick Prospect, overabundance of framboidal pyrite textures (initially magnetite?); High V in pyrite – associated with magnetite?

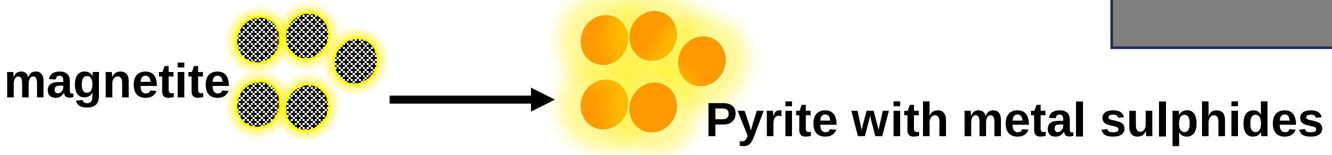
- Availability of the organics and anoxic conditions - organic matter rich samples; Mo speciation in the bitumen dyke confirms the organic matter association

- Metals released from oil adsorbed onto magnetite and subsequently pyrite and formed their own sulphides as the environment became more reducing. Mo speciation in the pyrite confirms Mo oxidation state is +4. This is consistent with Mo being buried under sulfide conditions, probably from an euxinic water column, in association with Fe(II) – reduced S species (Mo-Fe-S cubane, pyrite(ish)). However, EXAF results show its more complex with the presence of Mo-O bonds

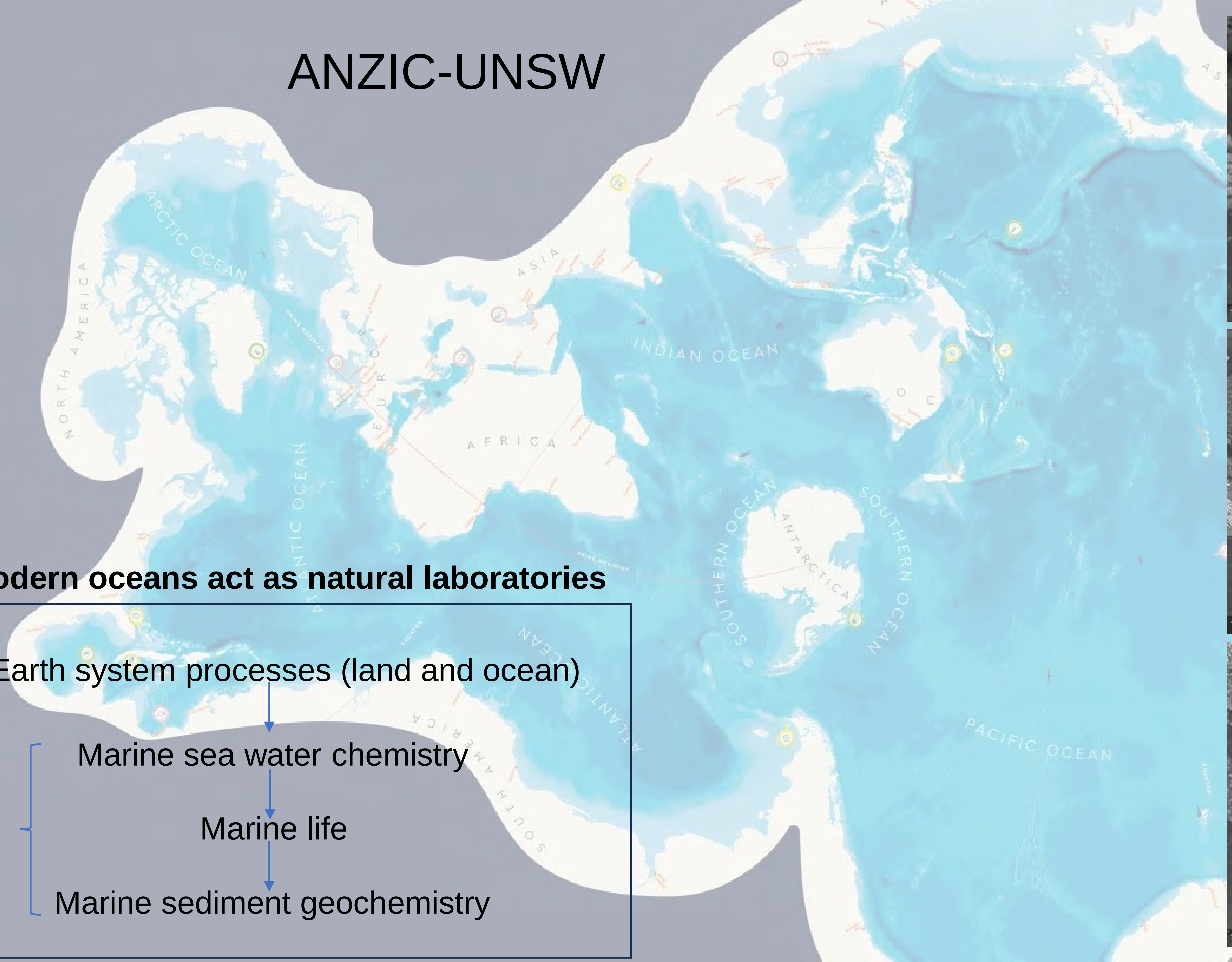


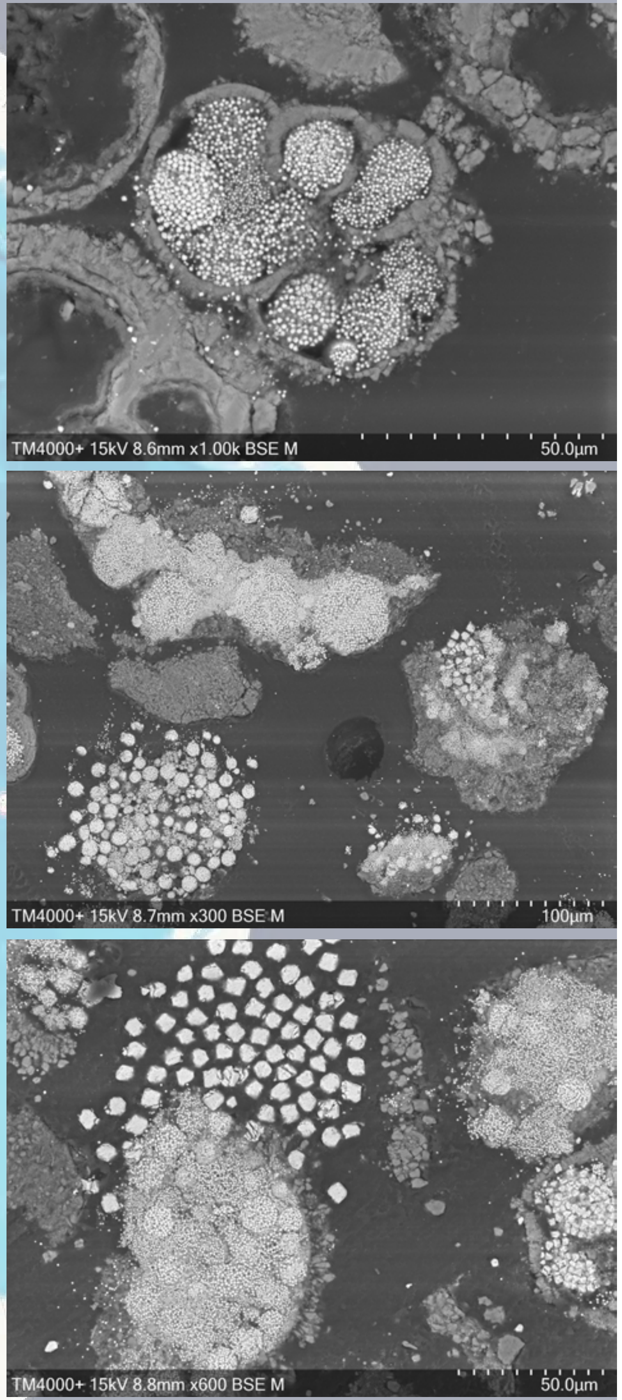
Heavy Crude Oil





ANZIC-UNSW





Modern oceans act as natural laboratories

Earth system processes (land and ocean)

↓

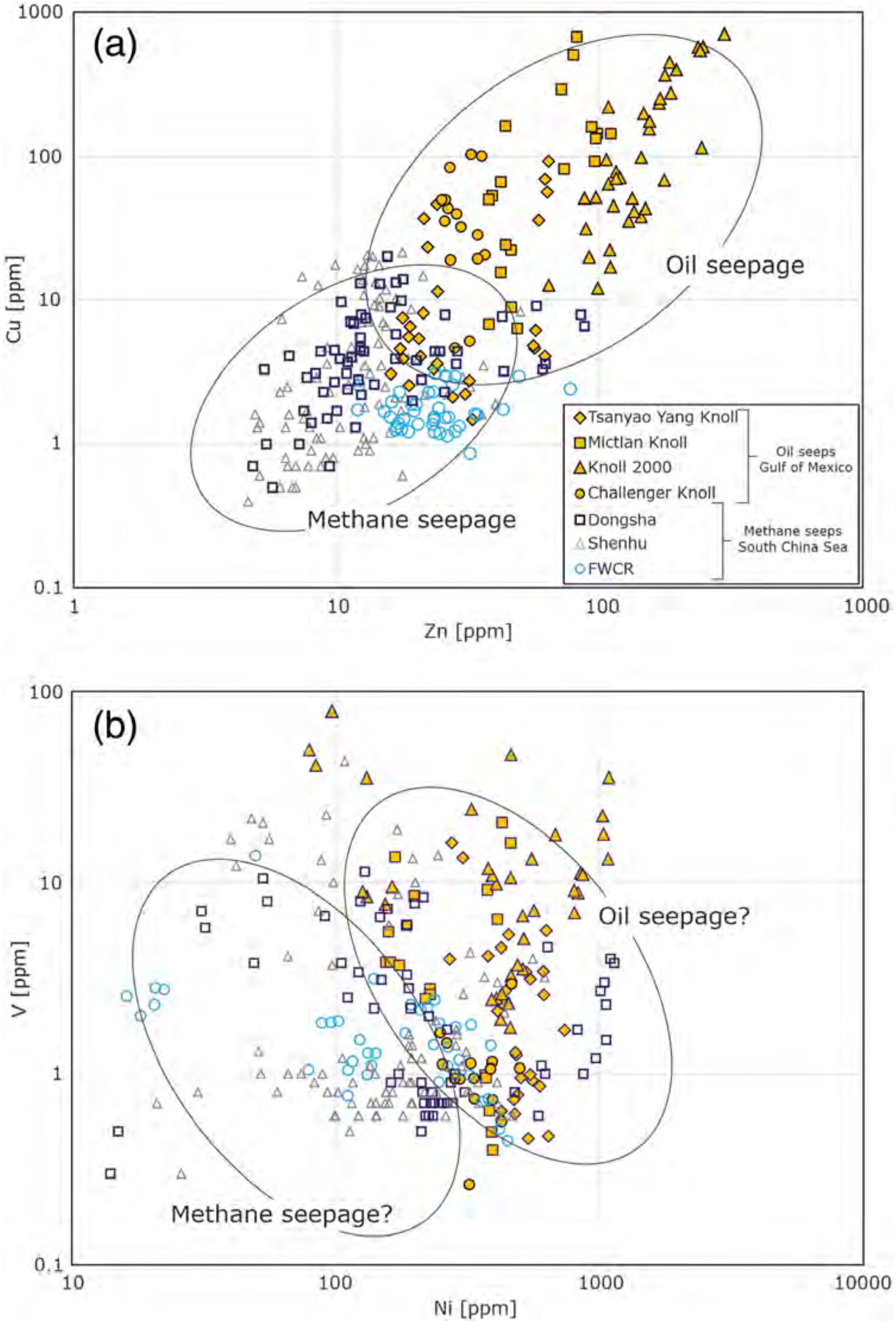
Marine sea water chemistry

↓

Marine life

↓

Marine sediment geochemistry



Geochemical Perspectives Letters

Pyrite-based trace element fingerprints for methane and oil seepage

D. Smrzka[1,2*], Z. Lin[3], P. Monien[2], T. Chen[4], W. Bach[1,2], J. Peckmann[3], G. Bohrmann[1,2]

Abstract

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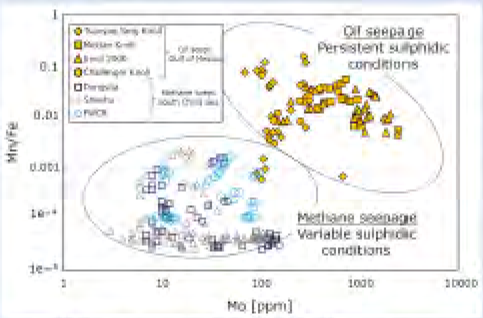

Pyrite forms at marine hydrocarbon seeps as the result of the microbial oxidation of methane, organic matter, and crude oil coupled to sulphate reduction. Redox sensitive and nutrient trace elements in pyrite may hold valuable information on present and past seepage events, the evolution of fluid composition, as well as the presence of heavy hydrocarbon compounds from crude oil. This study uses the trace element compositions of pyrite that formed at methane seeps and crude oil-dominated seeps to constrain element mobilities during the sulphate reduction processes, and examine the degree to which specific trace elements are captured by pyrite. Pyrite forming at oil seeps shows high Mn/Fe ratios and high Mo content compared to pyrite from methane seeps. These patterns suggest either more intense or persistent sulphidic conditions, or an intensified manganese (oxy)hydroxide shuttle process at oil seeps. Copper and Zn are enriched in oil seepage-derived pyrite while Ni and V enrichment is less pronounced, suggesting either a selective uptake of specific elements by pyrite, or varying trace element compositions of organic compounds oxidised *via* microbial reduction.

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Maresa Moustakis

Hydrothermal Mineralisation In The Mediterranean Sea: Key to the Past?

Aiming to characterise hydrothermally influenced marine sediments using bulk (ICP-MS) and in-situ (LA-ICP-MS) techniques in the Mediterranean Sea at varied distances (0km–350km) from two vent systems.

We will determine which trace element enrichment patterns are associated with hydrothermal fluids vs primary seawater. If the effect is significant at any of our 5 sites, to what distance does it extend to?

SAMPLE LOCATIONS

Key:

IODP/ODP/DSDP Drilled core

Drilled core used in study

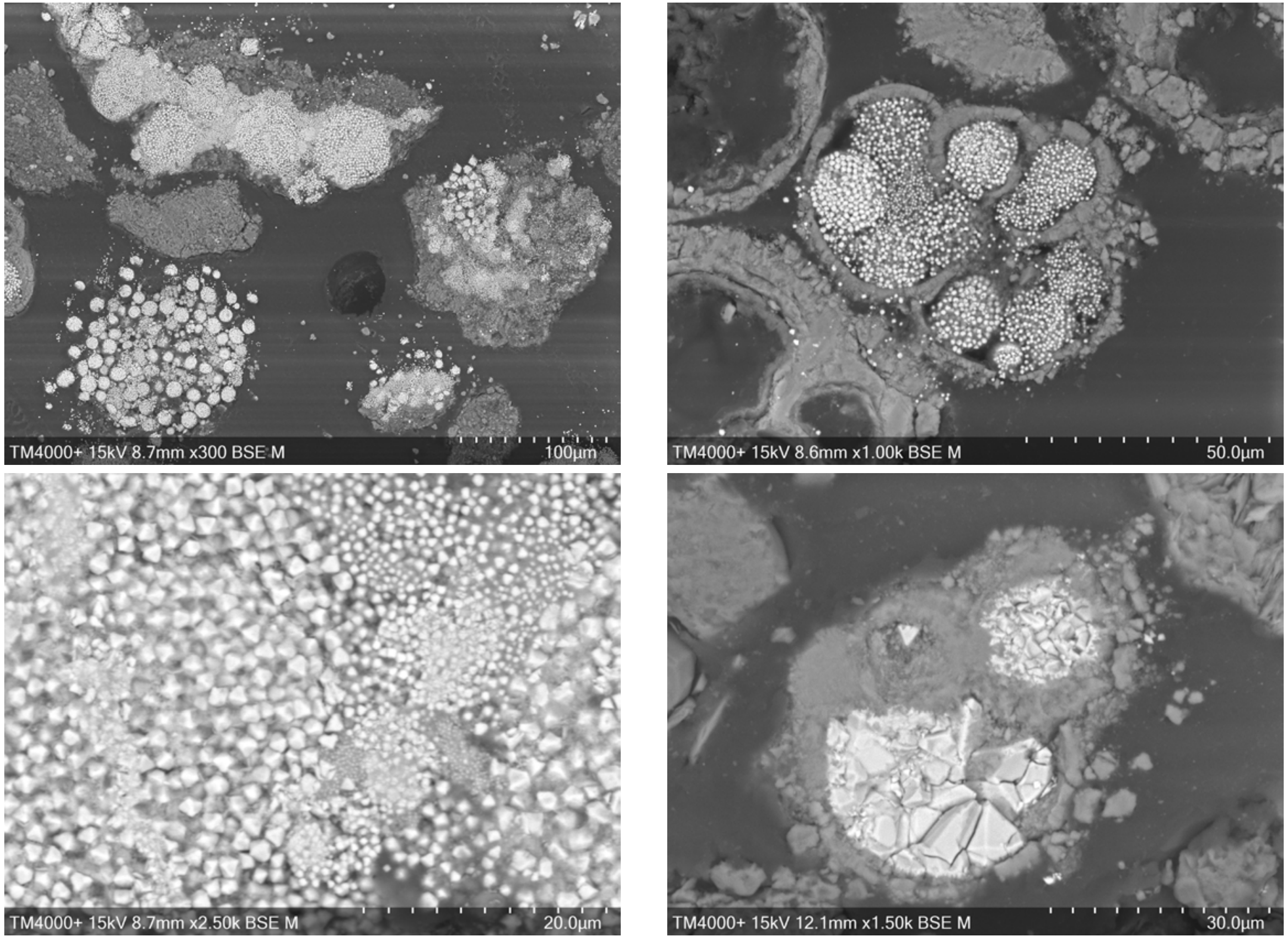
Hydrothermal vent field centre

Area with active hydrothermal venting

UNSW
Earth and Sustainability
Science Research Centre

UNSW
CMSI
Centre for Marine
Science & Innovation

Photo credit: Maresa Moustakis



Sulphide textures and chemistry: Clues to past life and economic mineralisation