Nanoparticle Formation in Pores Spaces

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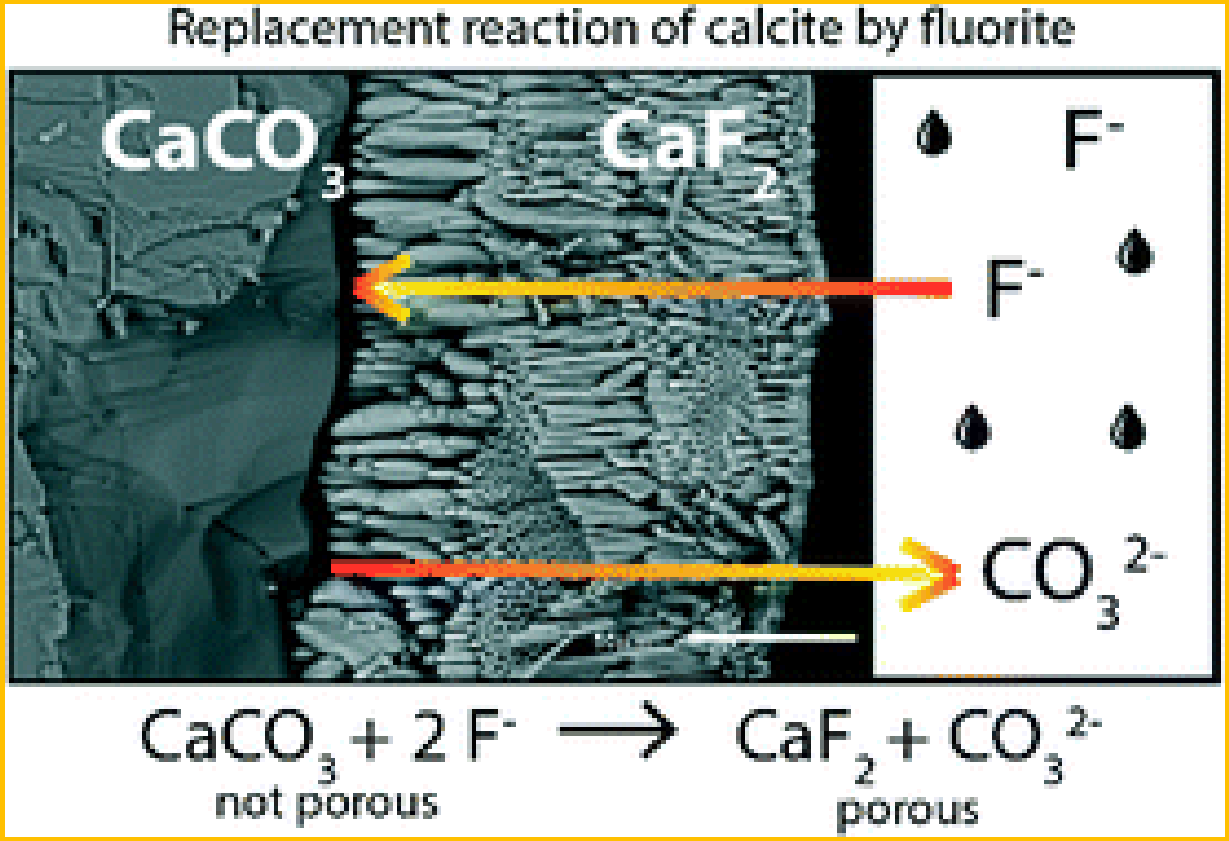
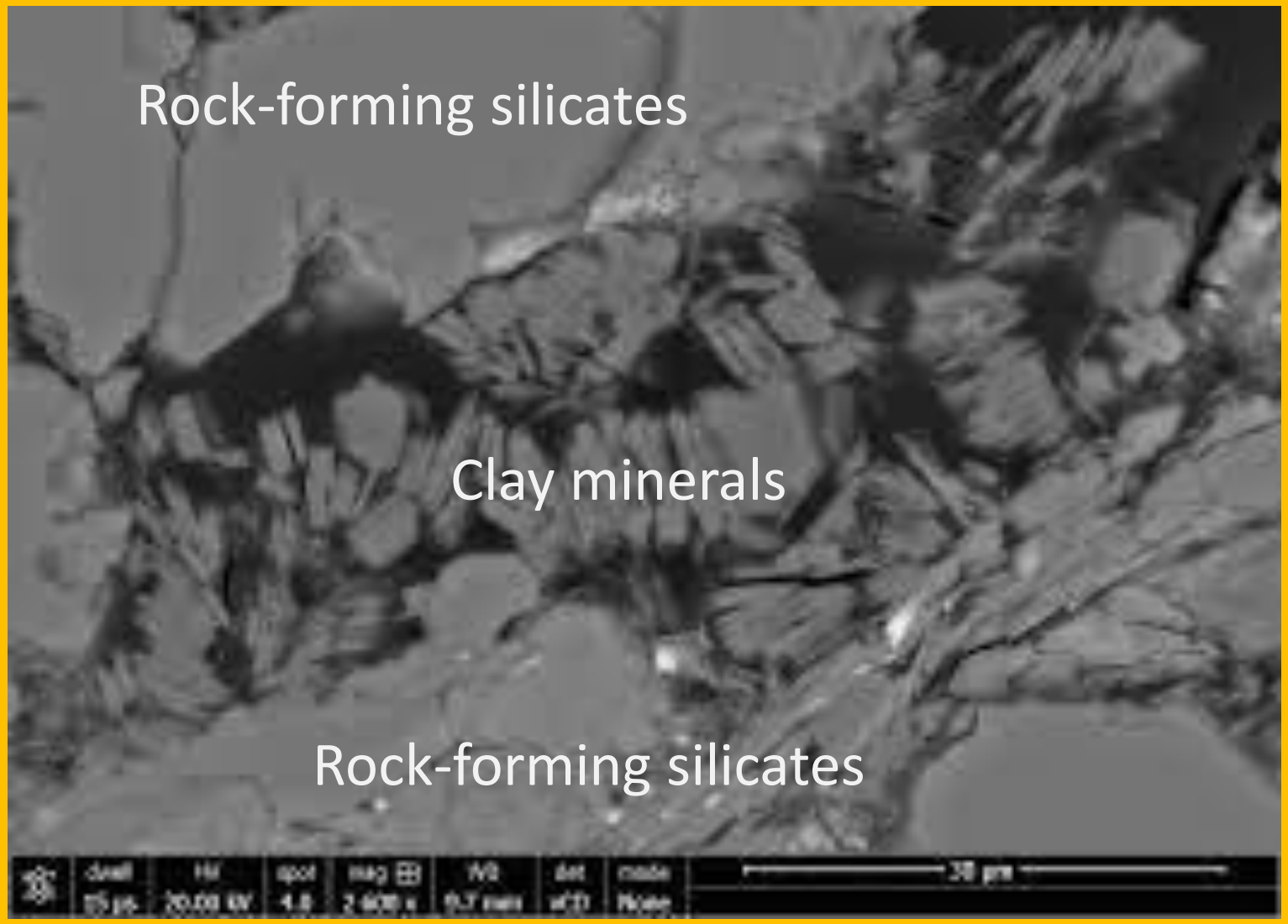
Weathering is a result of the re-equilibration of minerals due to changes in e.g. fluid composition, pH, Eh, T, P…

It involves often dissolution-re-precipitation processes with the replacement of a non-porous mother-phase by a porous daughter phase(s)



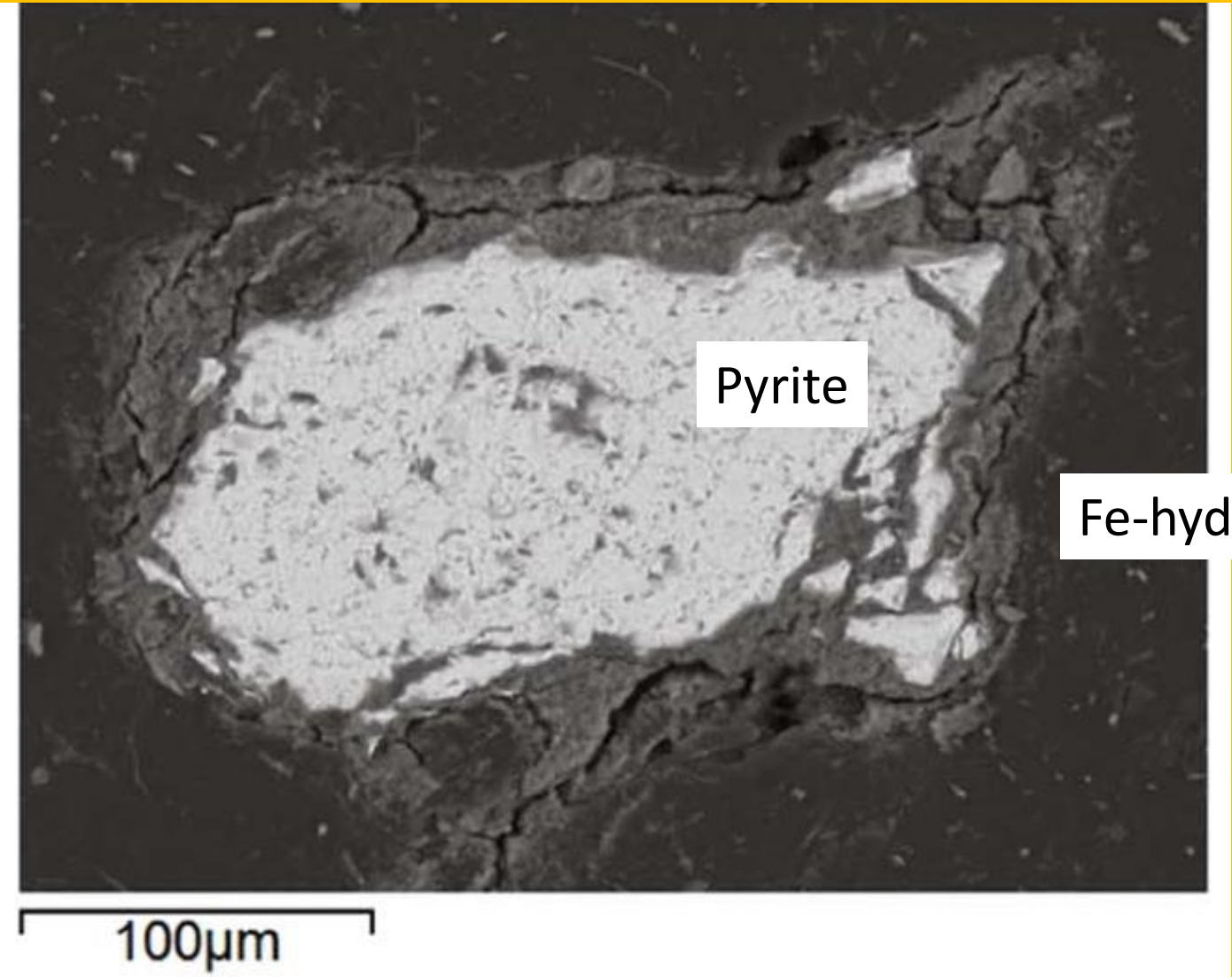
Pedrosa et al. (2016) Porosity generated during the fluid-mediated replacement of calcite by fluorite.
CrystEngComm, 2016,**18**, 6867-6874

Porous Clay mineral surface coating on rock-forming silicates



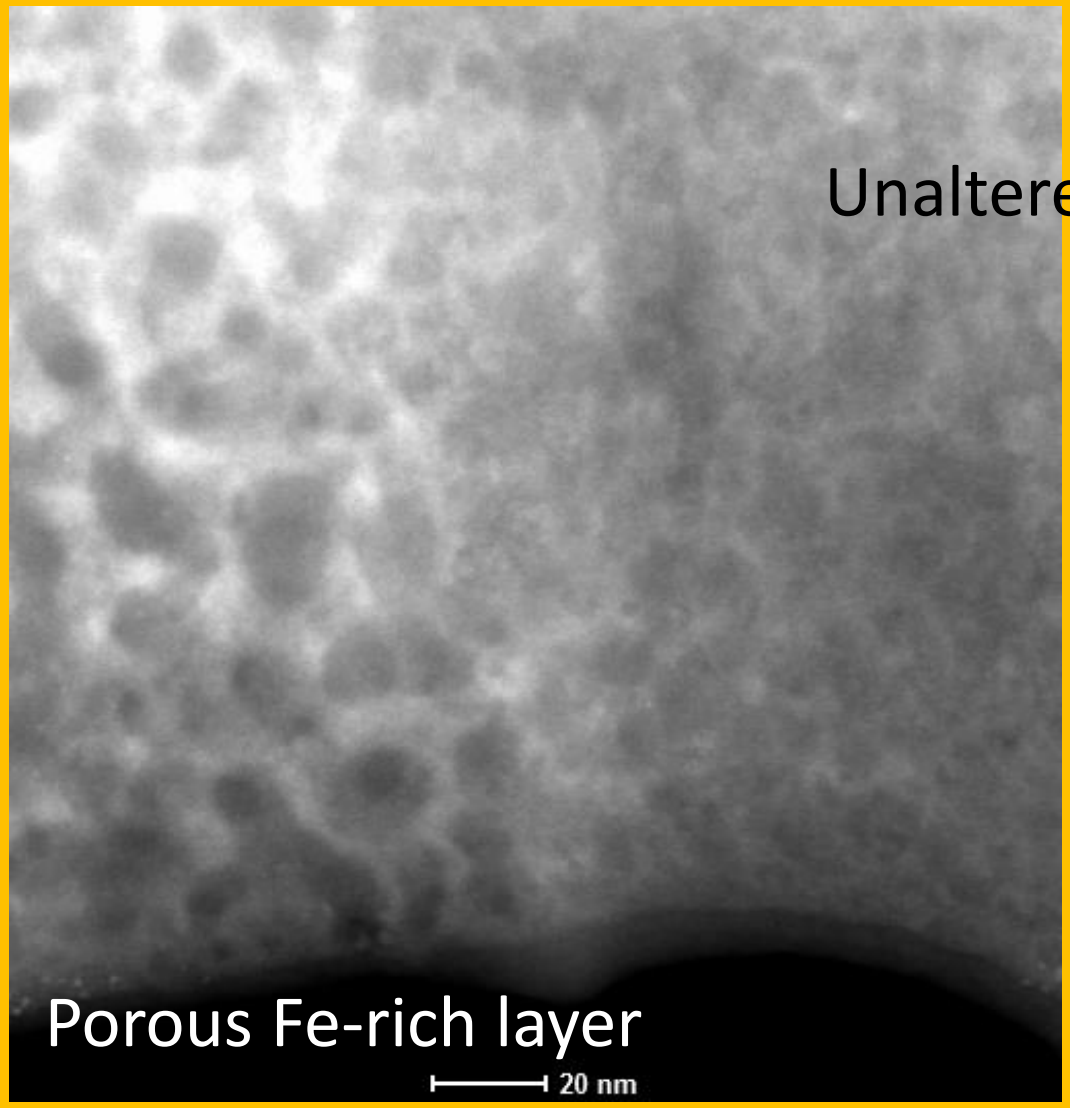
https://files.isgs.illinois.edu/sites/default/files/files/Giannetta_NCGSA_Presentation.pdf

Porous Fe-hydroxide coating on pyrite



Karagiorgakis et al. 2018, *Hydrometallurgy 177 9–20*

Alteration of volcanic glass



Schindler et al. (2019) Geochimica et Cosmochimica Acta 264, 43–66

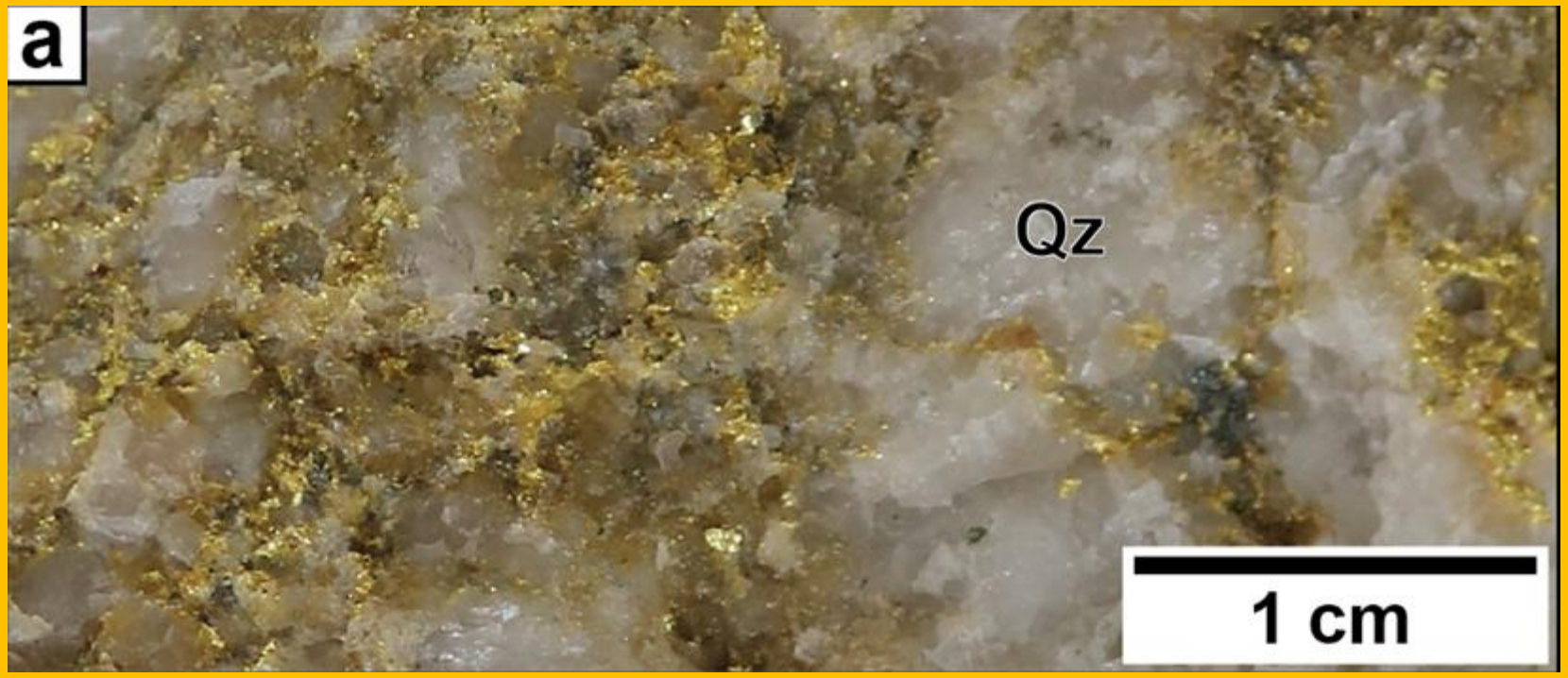
Nanoparticle formation during mineral replacement reactions under hydrothermal conditions

Two examples:

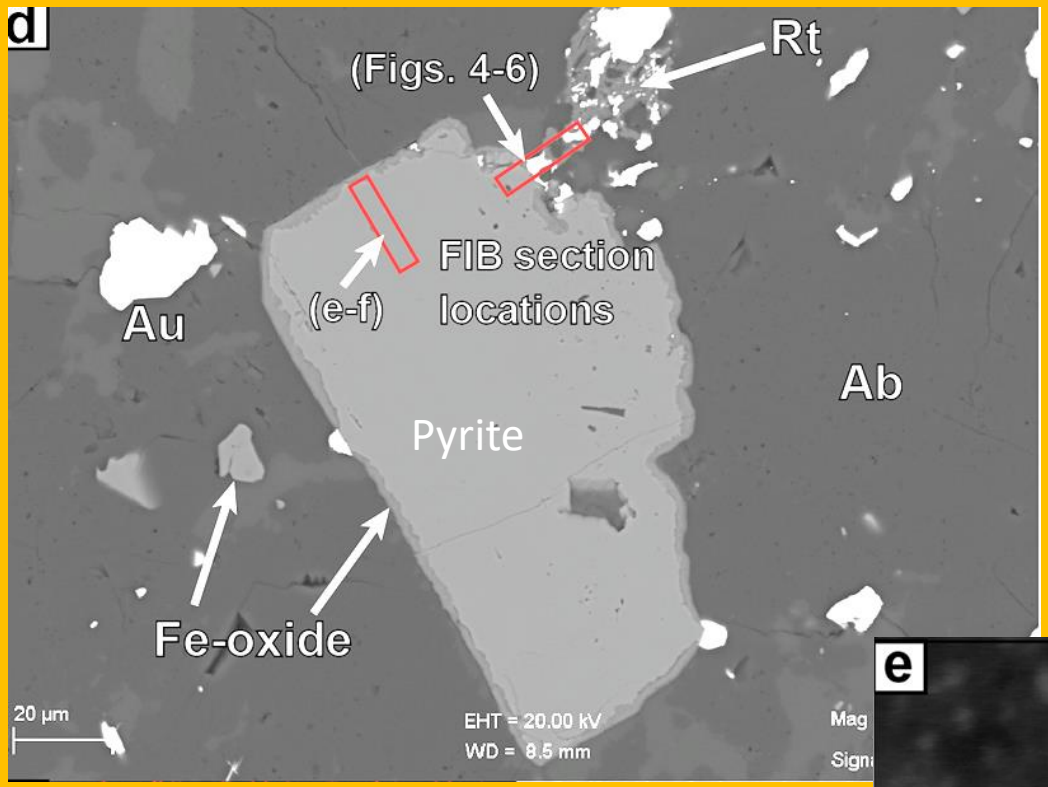
Gold nanoparticles and high-grade gold ore deposits

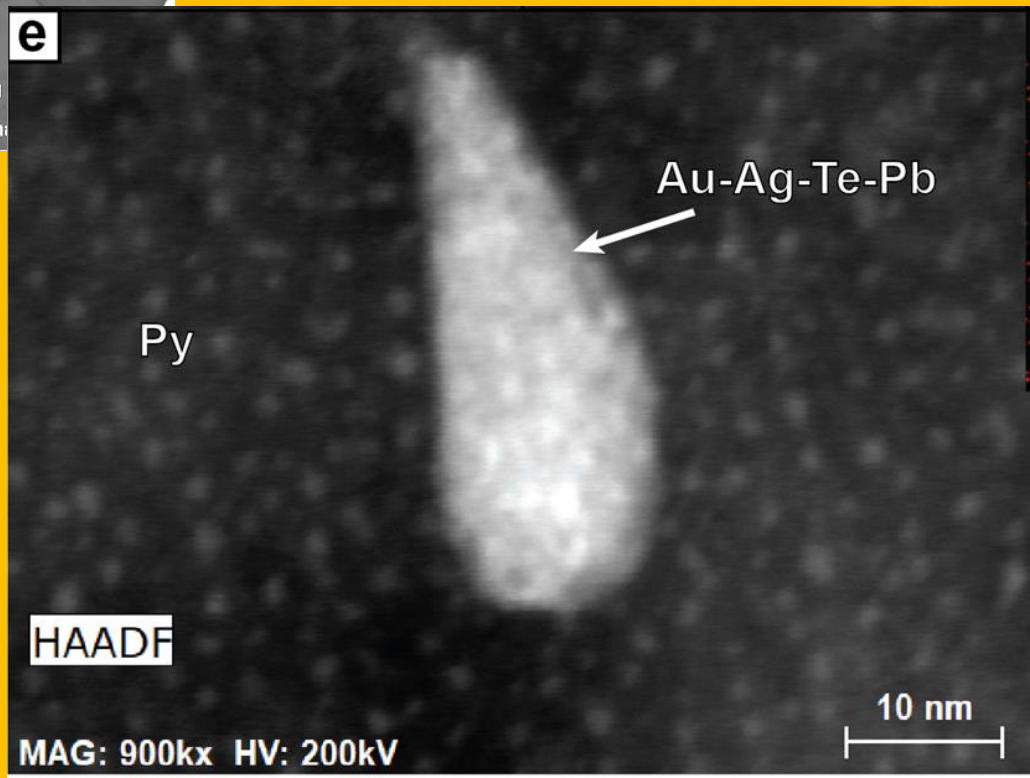
Chromite nanoparticles during greenschist metamorphism

High grade gold deposits in the Abitibi greenstone belt, Canada



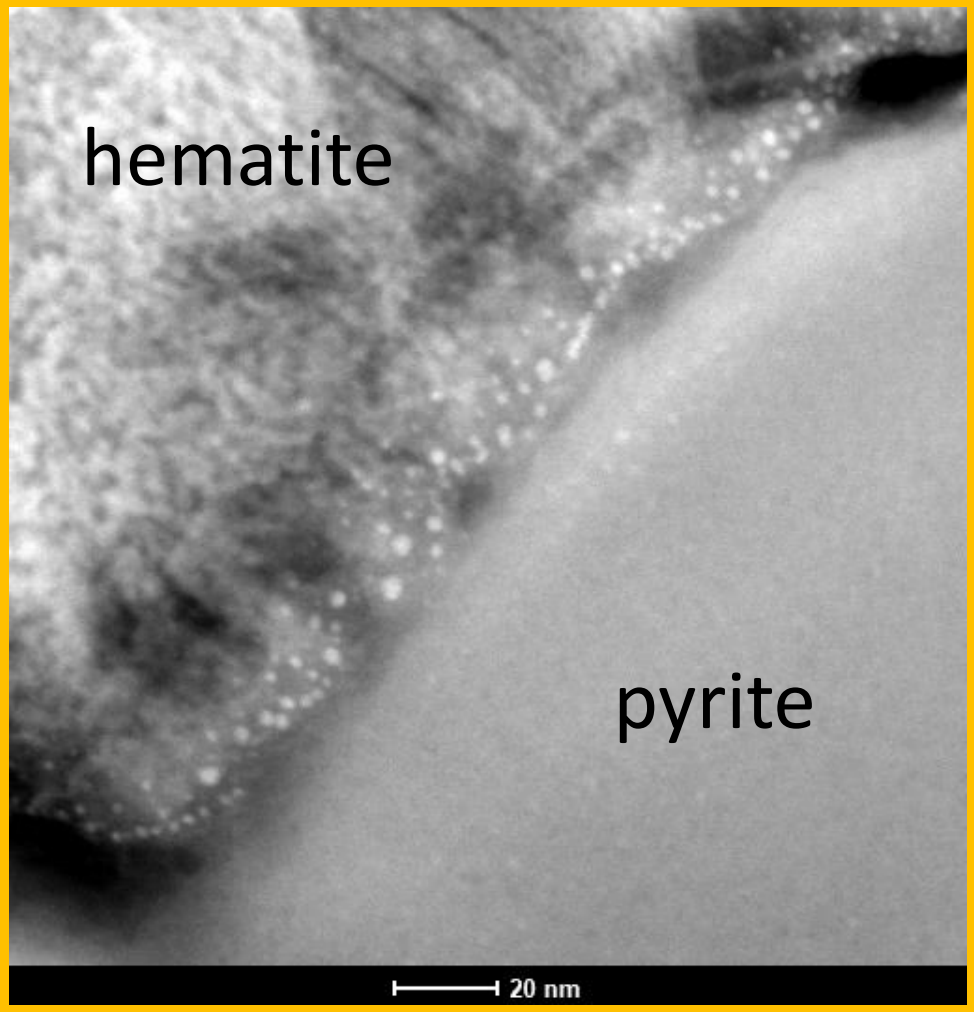
Gold-bearing Pyrite





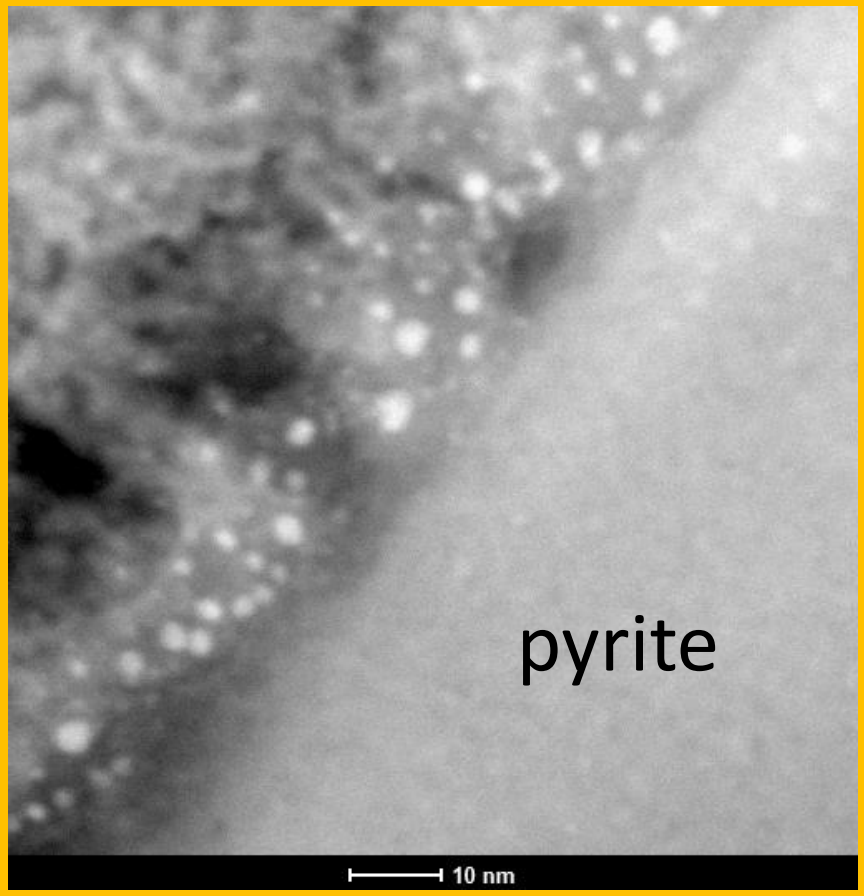
Hastie et al. 2021
Communications Earth & Environment

Formation of nanoparticles along the pyrite-hematite interface

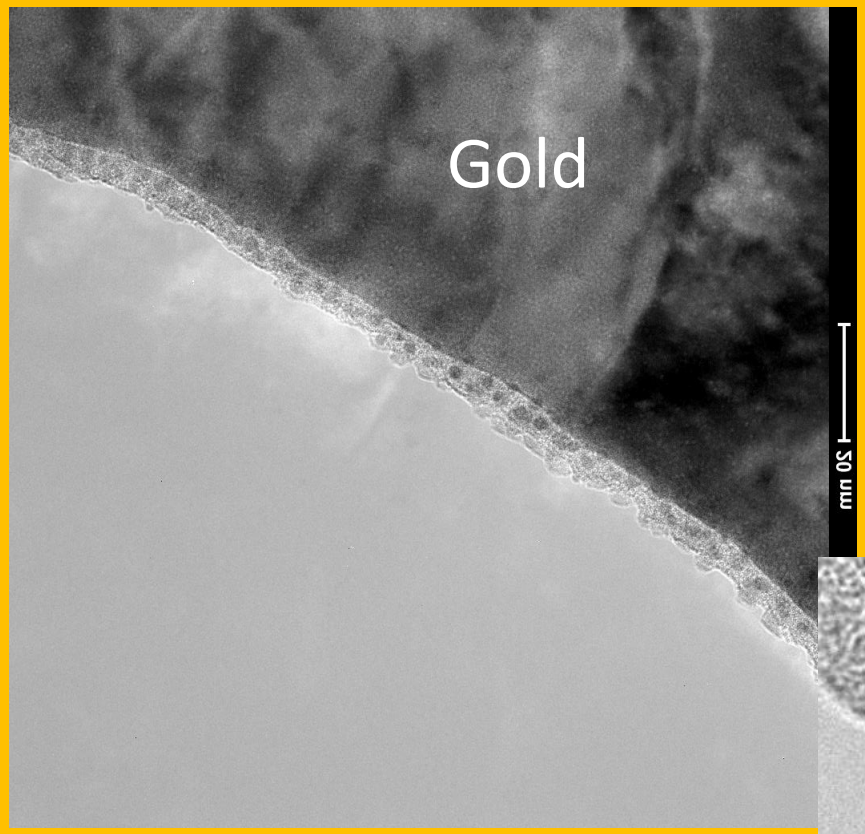


Nanoparticle size: 3-5 nm

Gold nanoparticles only visible in thinner part along interface

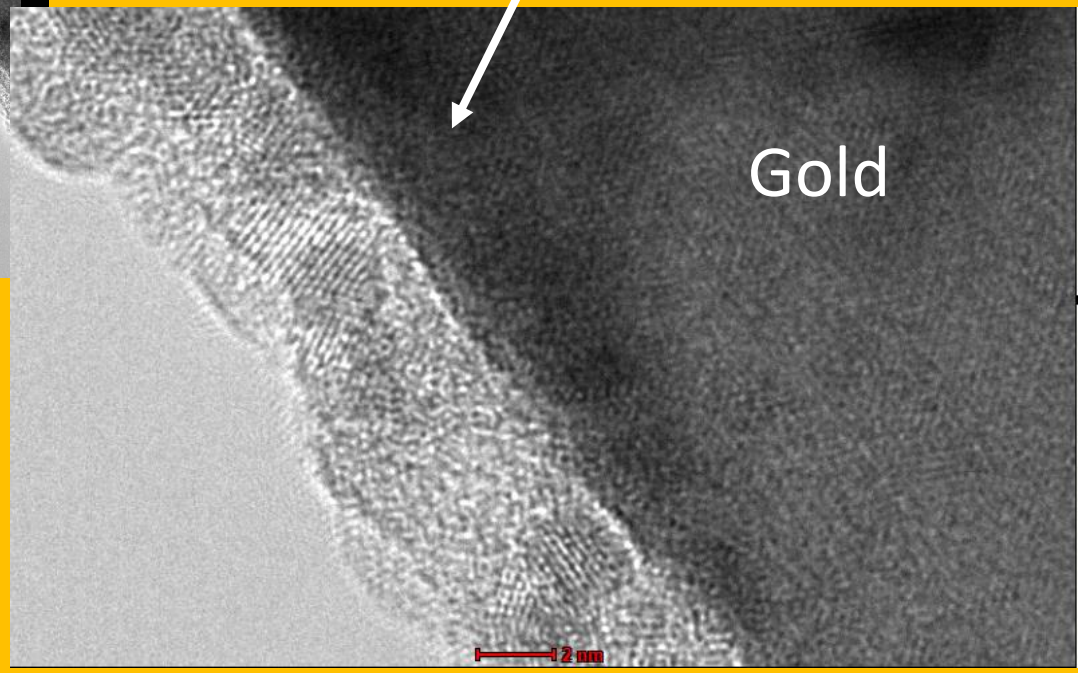


Consequence of gold nanoparticle formation: gold coarsening through gold nanoparticle attachment



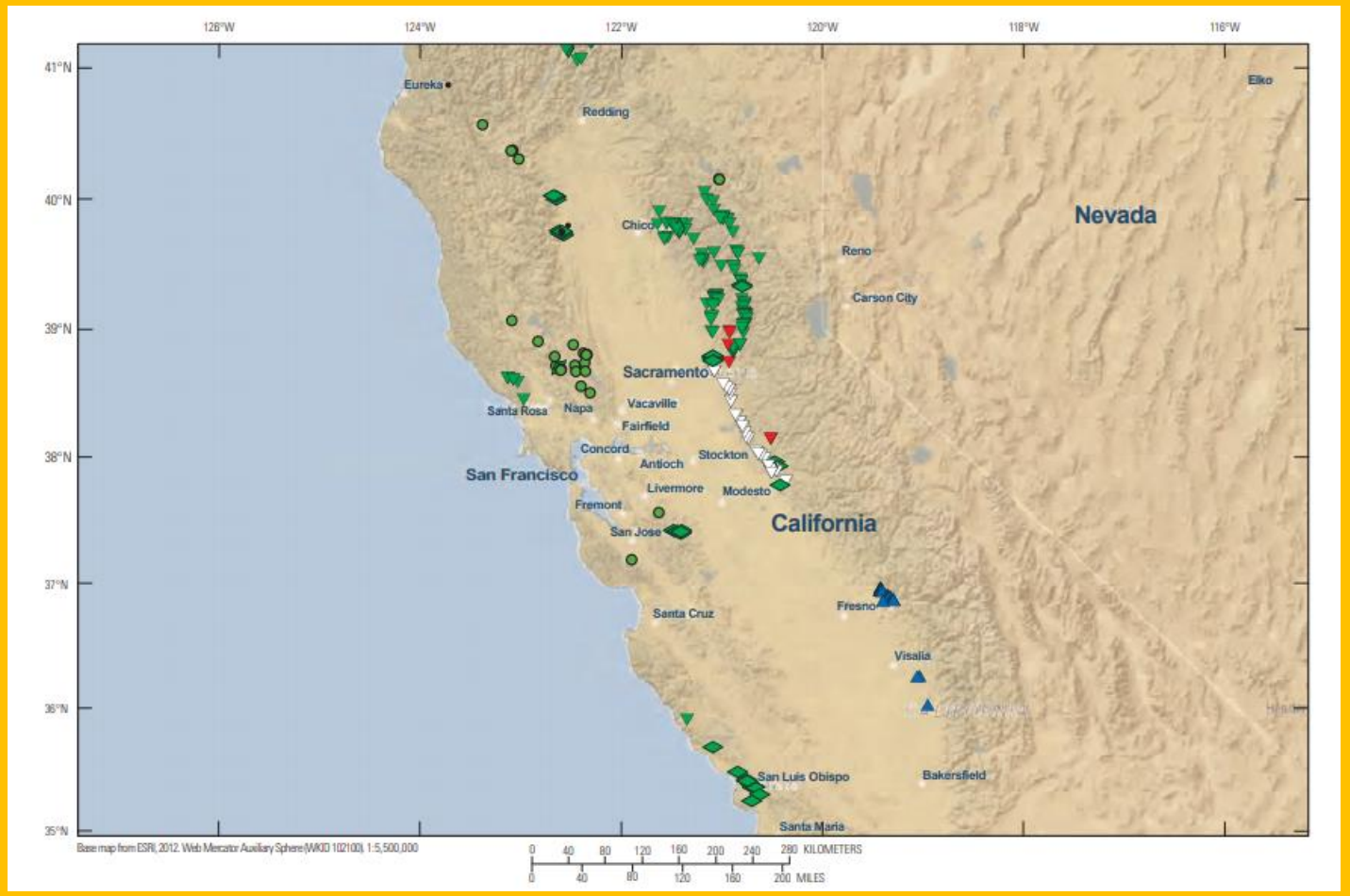
Gold nanoparticles in FeOx layer

Ostwald ripening

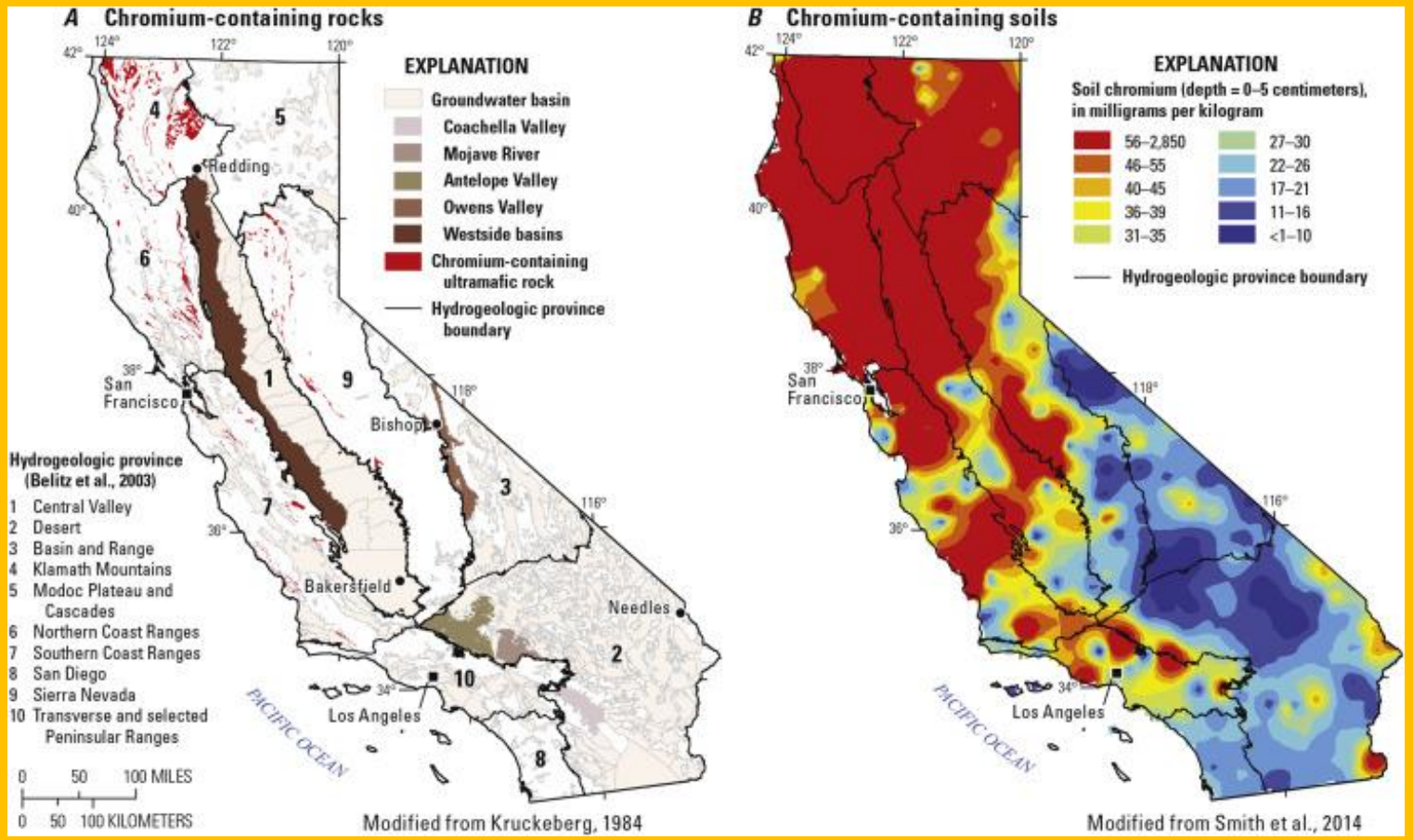


The formation of Chromite nanoparticles

Chromite ore deposits related to ultra mafic rocks (ophiolites from the oceanic crust)



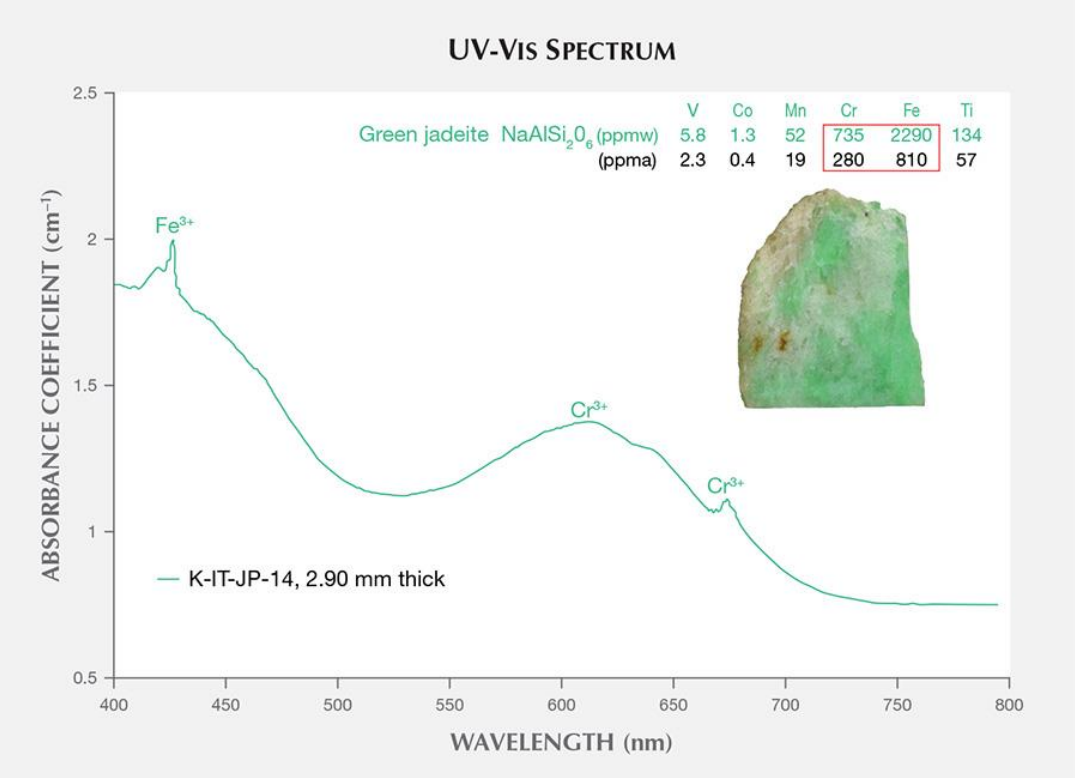
Cr concentrations in surficial soils in California



2850 mg/kg maximum Cr

Izbicki et al. 2015, Applied Geochemistry 63, 203-217

Cr^{3+} structurally incorporated into pyroxenes, $A+B^{3+}Si_2O_6$



(https://www.gia.edu)

Cr^{3+} is structurally incorporated into pyroxenes

Jadeite $NaAlSi_2O_6$

Greenschist metamorphism

300–450 °C

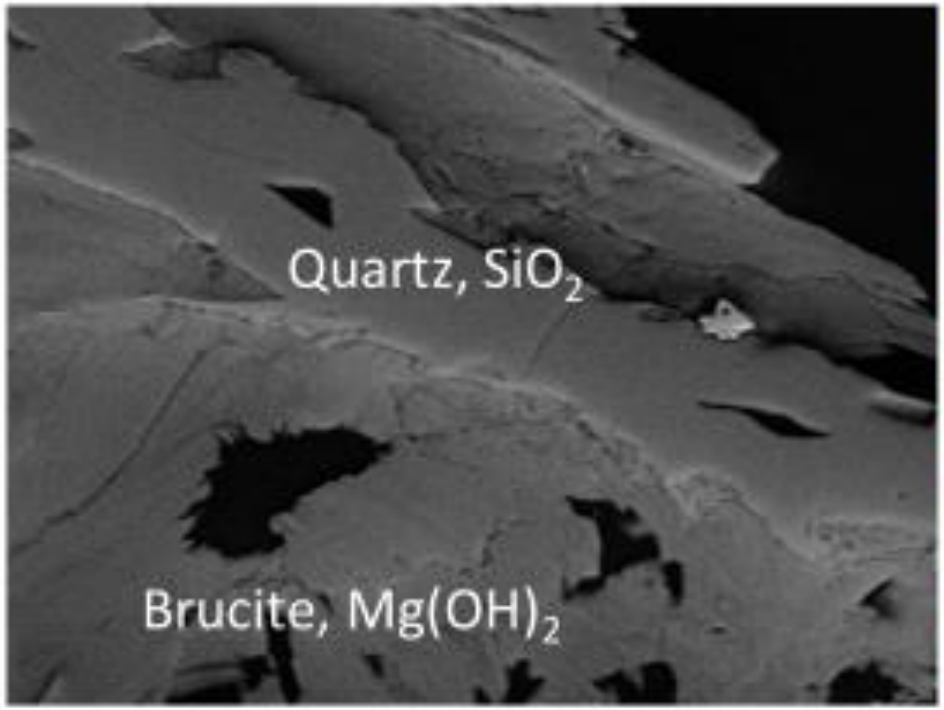
2–10 kilobars

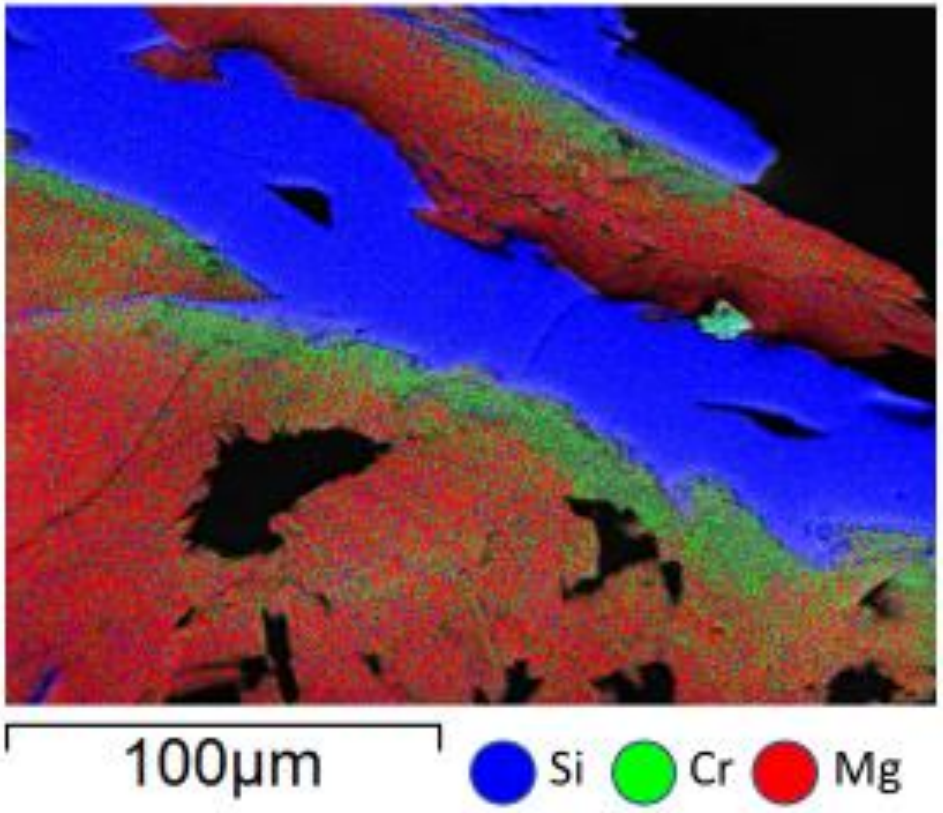
Mg-pyroxenes and -amphiboles

Mg-rich minerals of the chlorite- and serpentinite-group or brucite $Mg(OH)_2$ + quartz

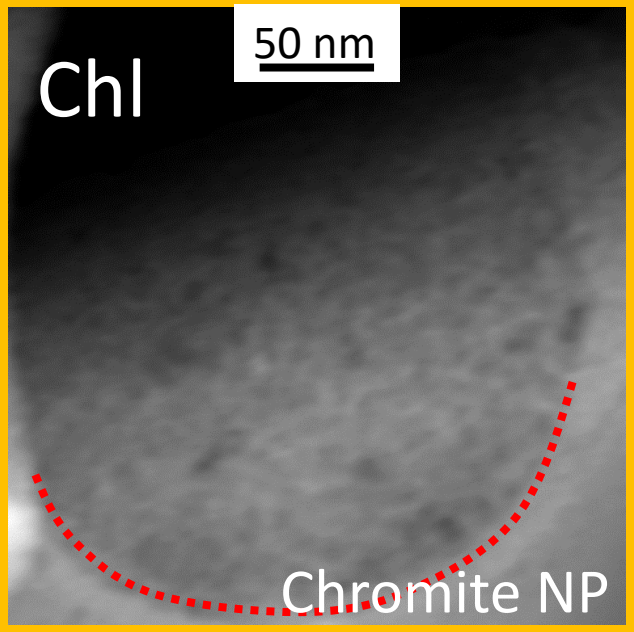
Transformation involves again dissolution-reprecipitation and thus porosity

On the micrometer scale: enrichment of Chromium along phase boundaries

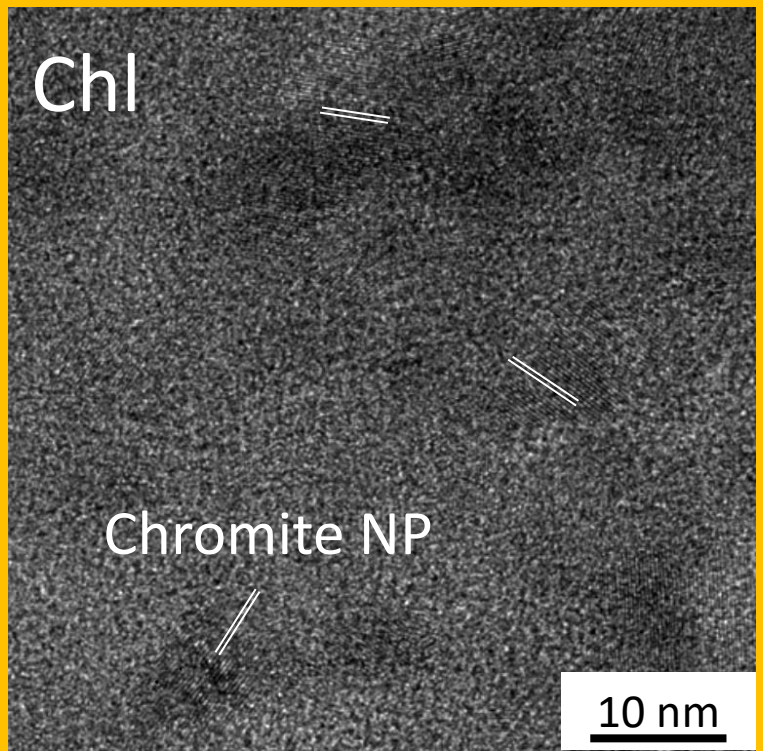


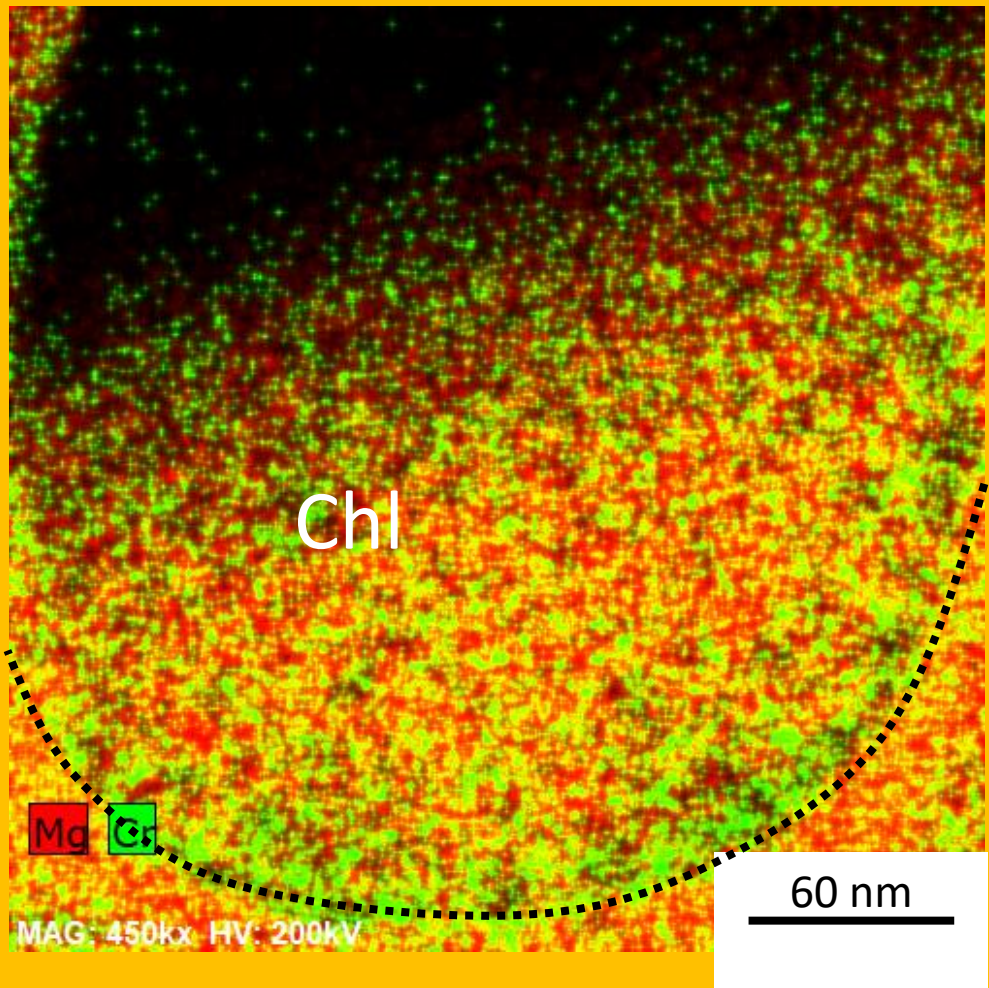


McClenaghan & Schindler 2021
American MIneralogist



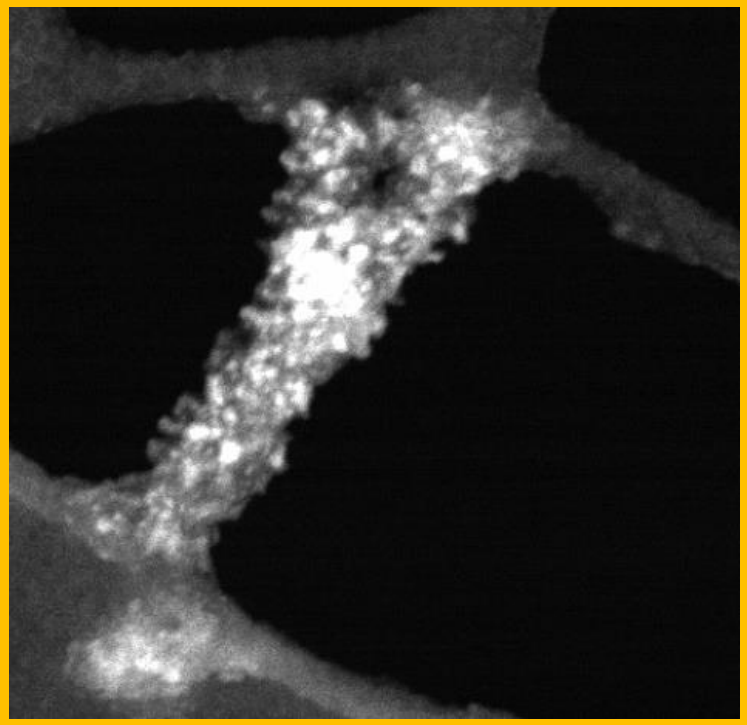
On the nanometer-scale: chromite nanoparticles along clinochlore grain boundaries





Environmental Relevance

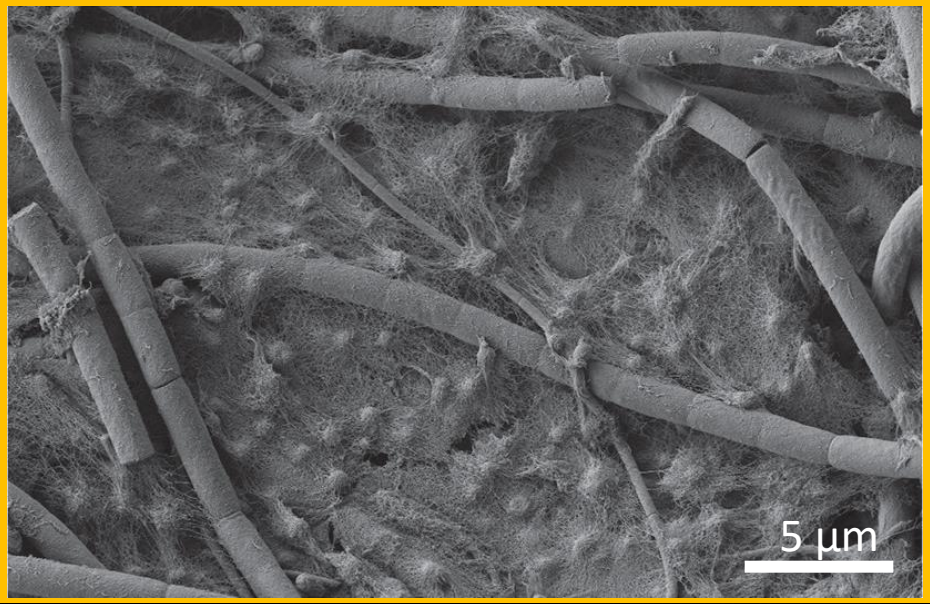
Release of chromite nanoparticles
during weathering of Cr-bearing clinochlore



Chromite nanoparticles attached
on amorphous Al-hydroxide colloid
after 3 months leaching of clinochlore
at pH =5

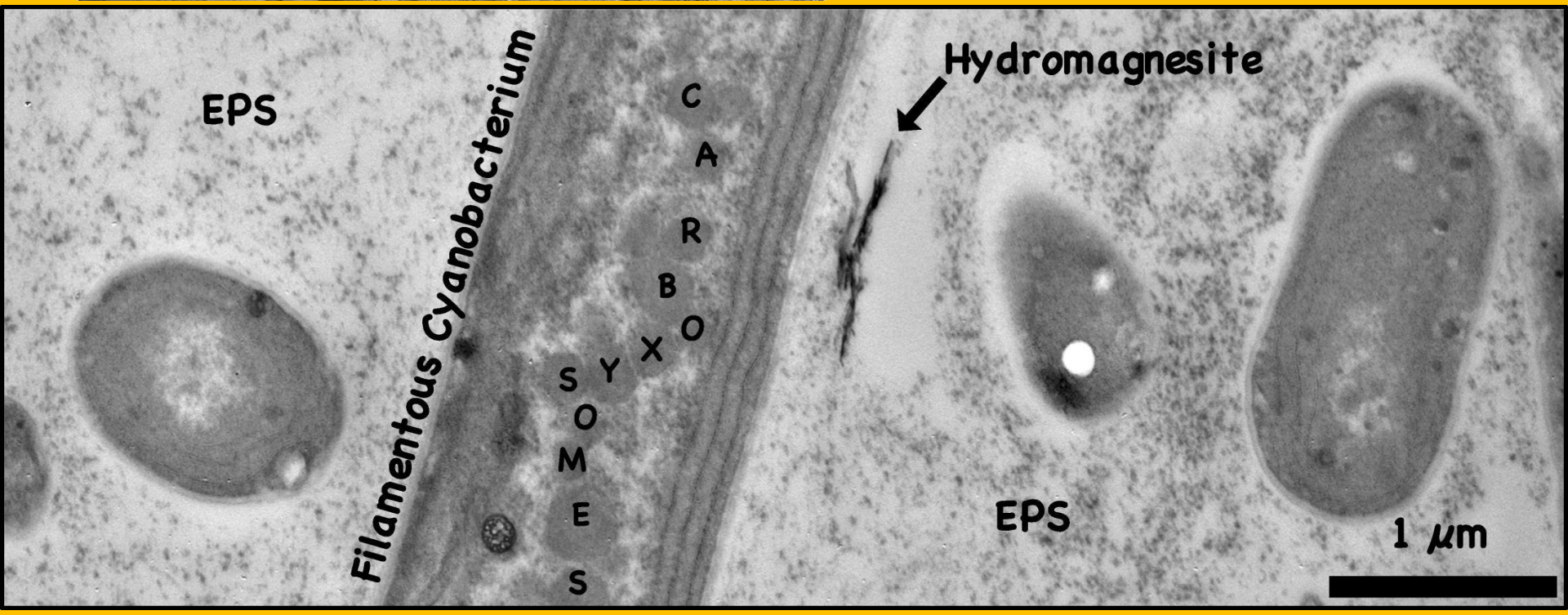
McClenaghan & Schindler 2021
American Mineralogist, in press

Nanoparticle formation during low-T weathering processes



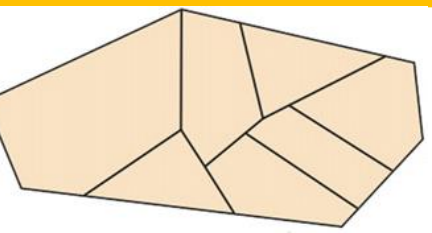
Interior and surroundings of a bacterium (EPS)
may also contain
nano-size pore spaces

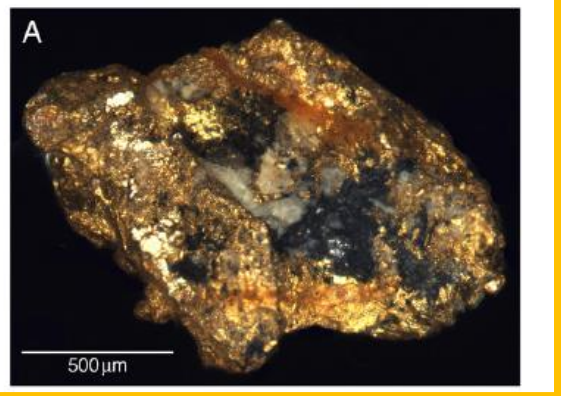
EPS = extracellular polymeric substances

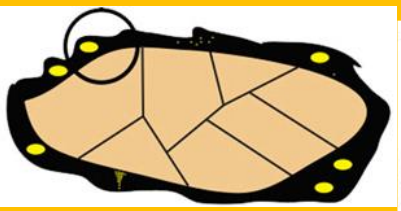


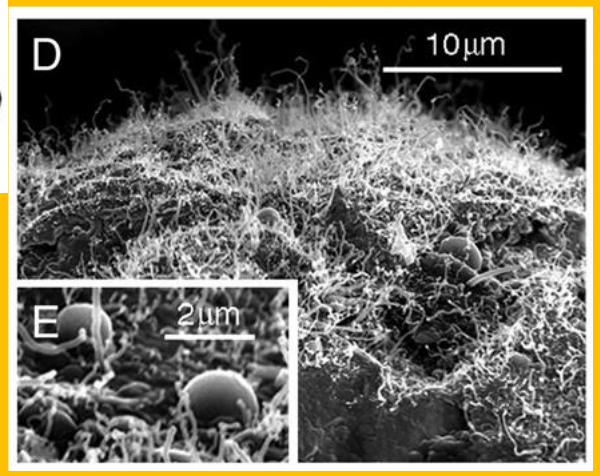
McCutcheona & Southam

Low Temperature processes:
A. biotic-controlled weathering of gold in Australia









Primary gold with Ag and Cu

~80-90% Au

↓

"Porosity" in Biofilms

↓ Abiotic and biotic processes in biofilms

↓

"Purified" gold nanoparticles

Au > 95 wt% Au

Fairbrother et al. 2012
Chemical Geology 320–321 (2012) 17–31

Reith et al (2010) termed Biofilms:
"Nanoparticles factories"
Geology 38, 843–846.

Consequences

Cycles of Bioflim formation and destruction results in the

release of gold as gold nanoparticles and thus in a

high mobility of Au in many near surface environments

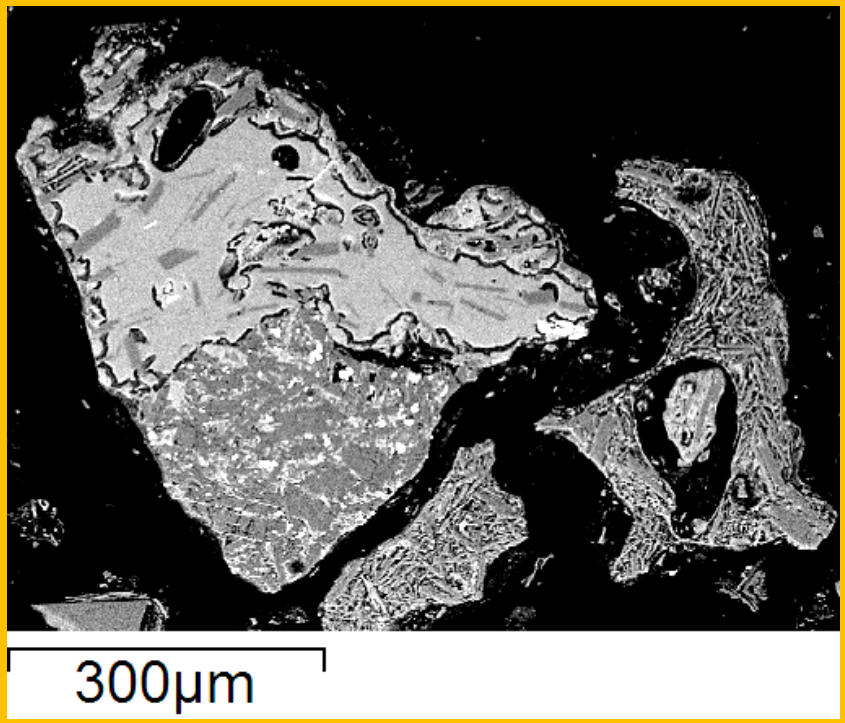
the formation of secondary Au deposits

the development of geochemical halos around buried mineralization

Reith et al (2010)
Geology 38, 843–846.

Low Temperature processes:
B. Abiotic-controlled weathering

Alteration of volcanic glass in a Martian analogue, JSC-1



Schindler et al. (2019) Geochimica et Cosmochimica Acta 264, 43–66

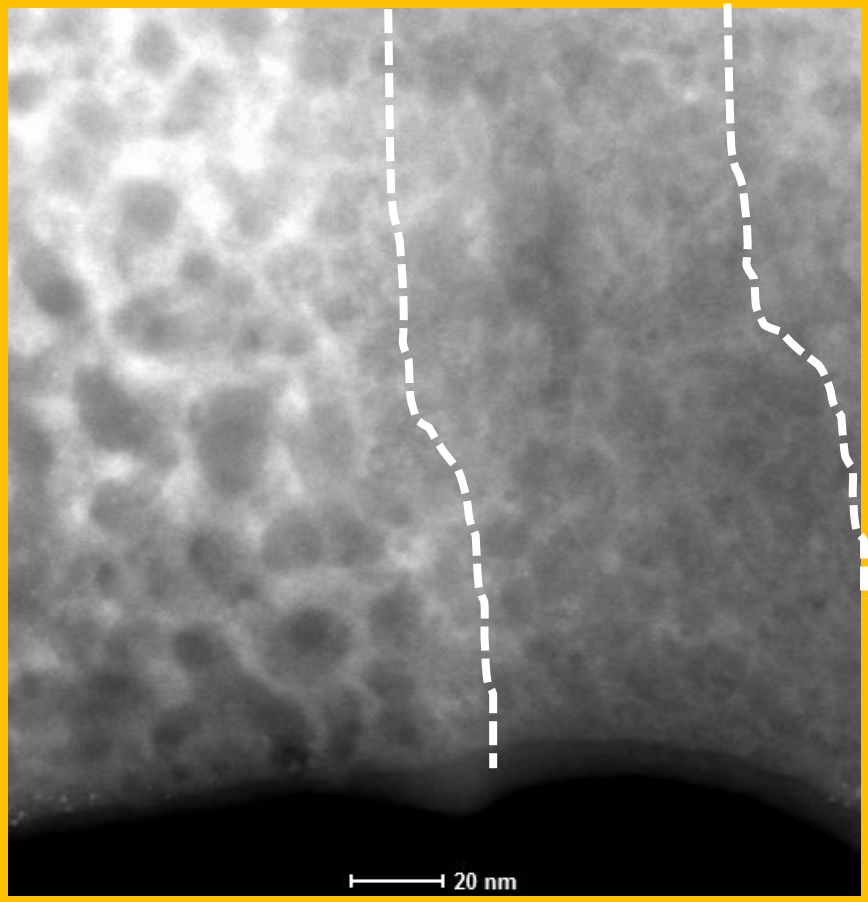
Dissolution of glass and re-precipitation of Ferrihydrite and hydrous amorphous silica

Porous Alteration layer

Reaction front

porosity

"glass"

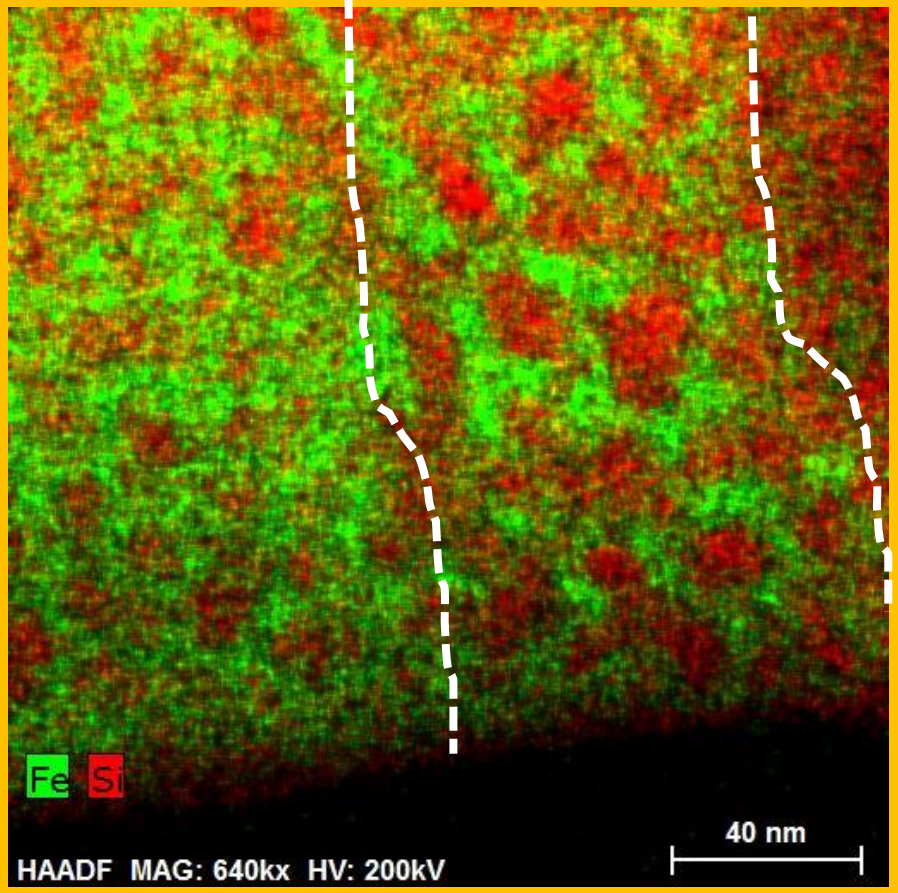


Fe-hydroxide aggregation

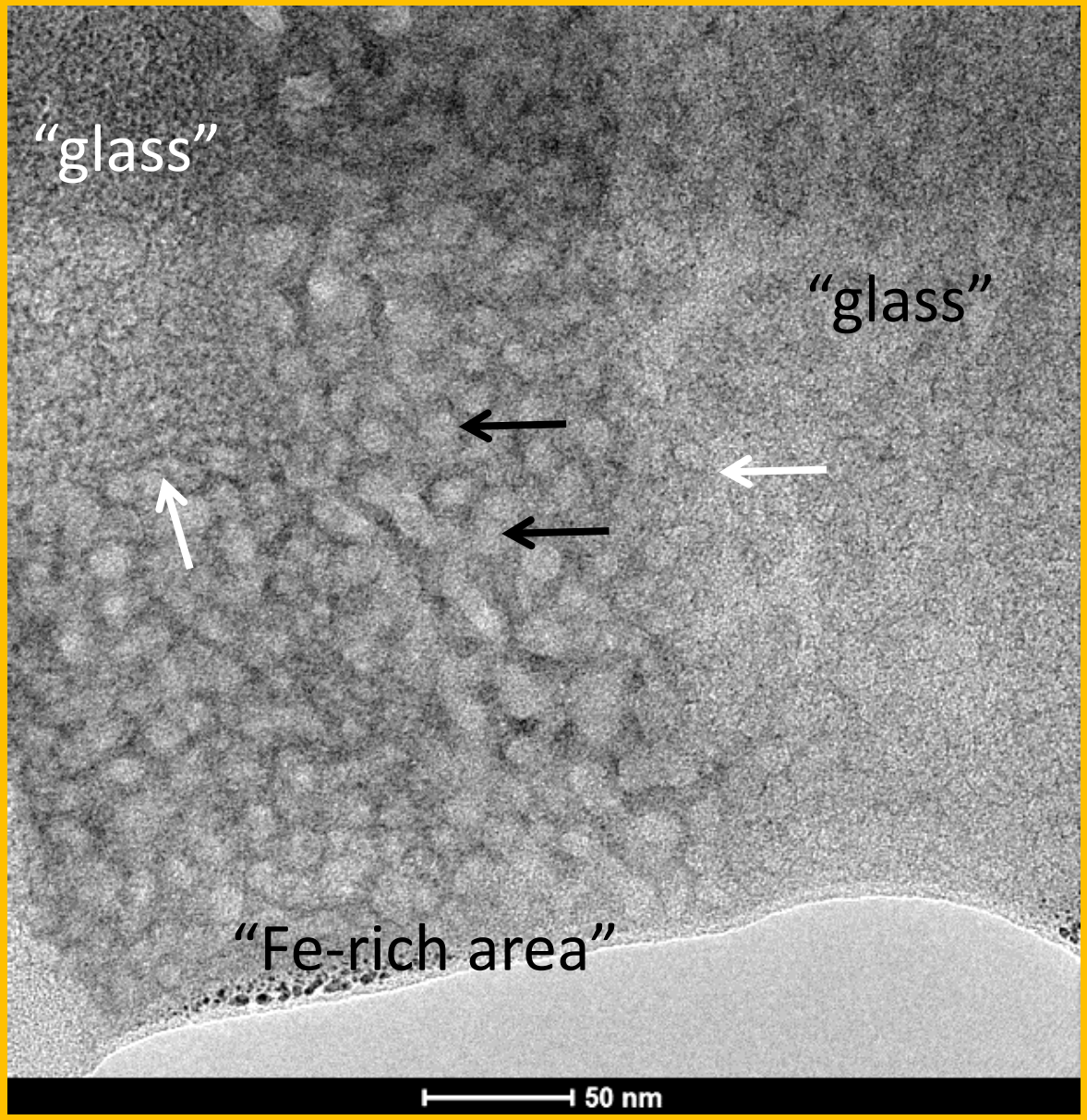
Reaction front

Fe-hydroxide formation

"glass"



Ferrihydrite “nano-domains” in pore spaces between hydrous amorphous silica



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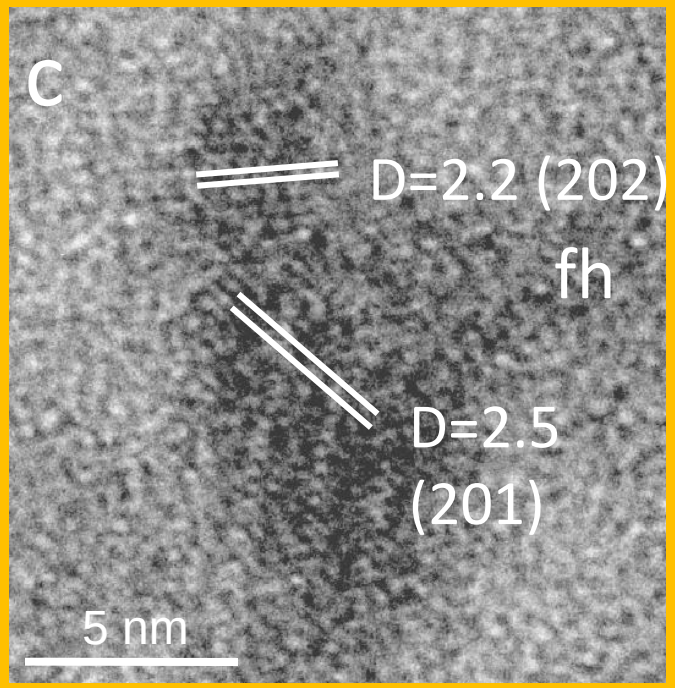
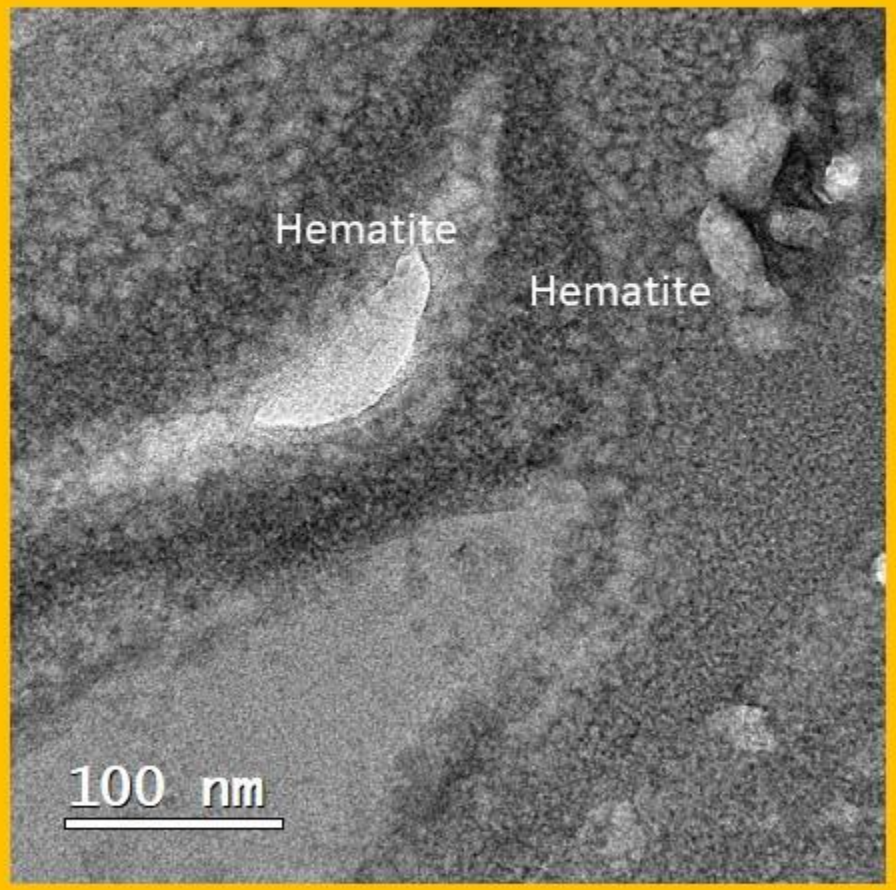


Consequence:
Porosity created during the alteration of volcanic glass is one of the "birthplaces" of Fe-oxide nanoparticles in volcanic soils on Earth and perhaps on Mars



Schindler et al. *Geochimica et Cosmochimica Acta* 264, 43–66

Conclusions

One common feature:
Enrichment (sometimes termed supergene process) of an element in the form of nanoparticles as a consequent of re-equilibration

Au-bearing pyrite → Gold nanoparticles

Cr-bearing pyroxene → Chromite nanoparticles

Primary Au-Ag-Cu ore → High fineness gold nanoparticles

Fe-bearing Volcanic glass → Fe-oxide nanoparticles

…and many more examples can be found in the literature

Thank you to

….and all my students and collaborators