PHASE TRANSFORMATION OF FERRIC IRON BEARING MINERALS IN THE PRESENCE OF SUPERCRITICAL CO_2, SO_2 AND H_2S

Daniel R. Strongin
Department of Chemistry
Temple University

Martin Schoonen
Department of Geosciences
Stony Brook University

STONY BROOK UNIVERSITY

U.S. DEPARTMENT OF ENERGY

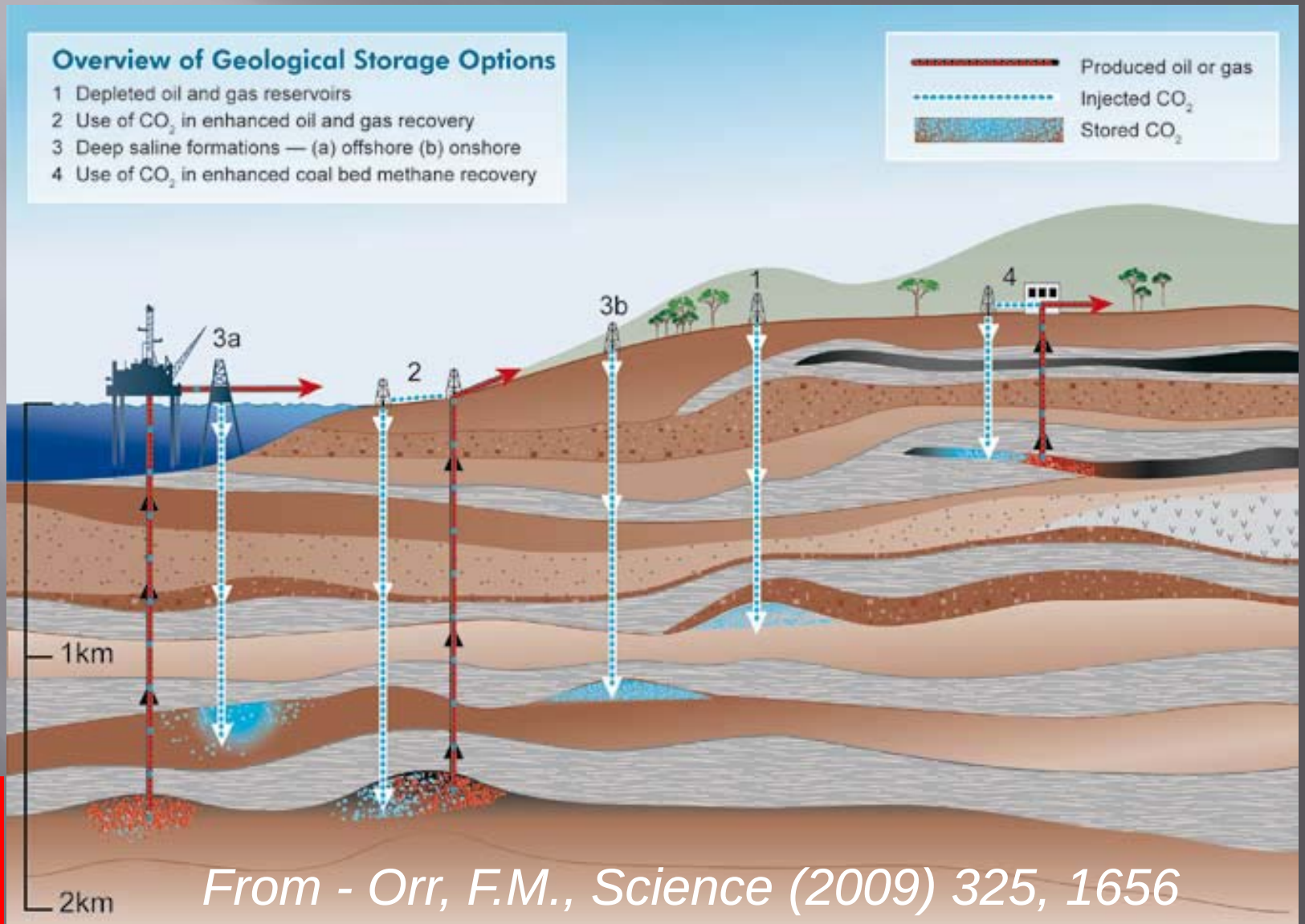
Acknowledgments

- Martin Schoonen – Stony Brook University
- Riley Murphy
- Kristin Lammers
- Amber Riendeau
- Alex Smirnov – Stony Brook University

Funding

U.S. DEPARTMENT OF ENERGY

Carbon Dioxide Sequestration



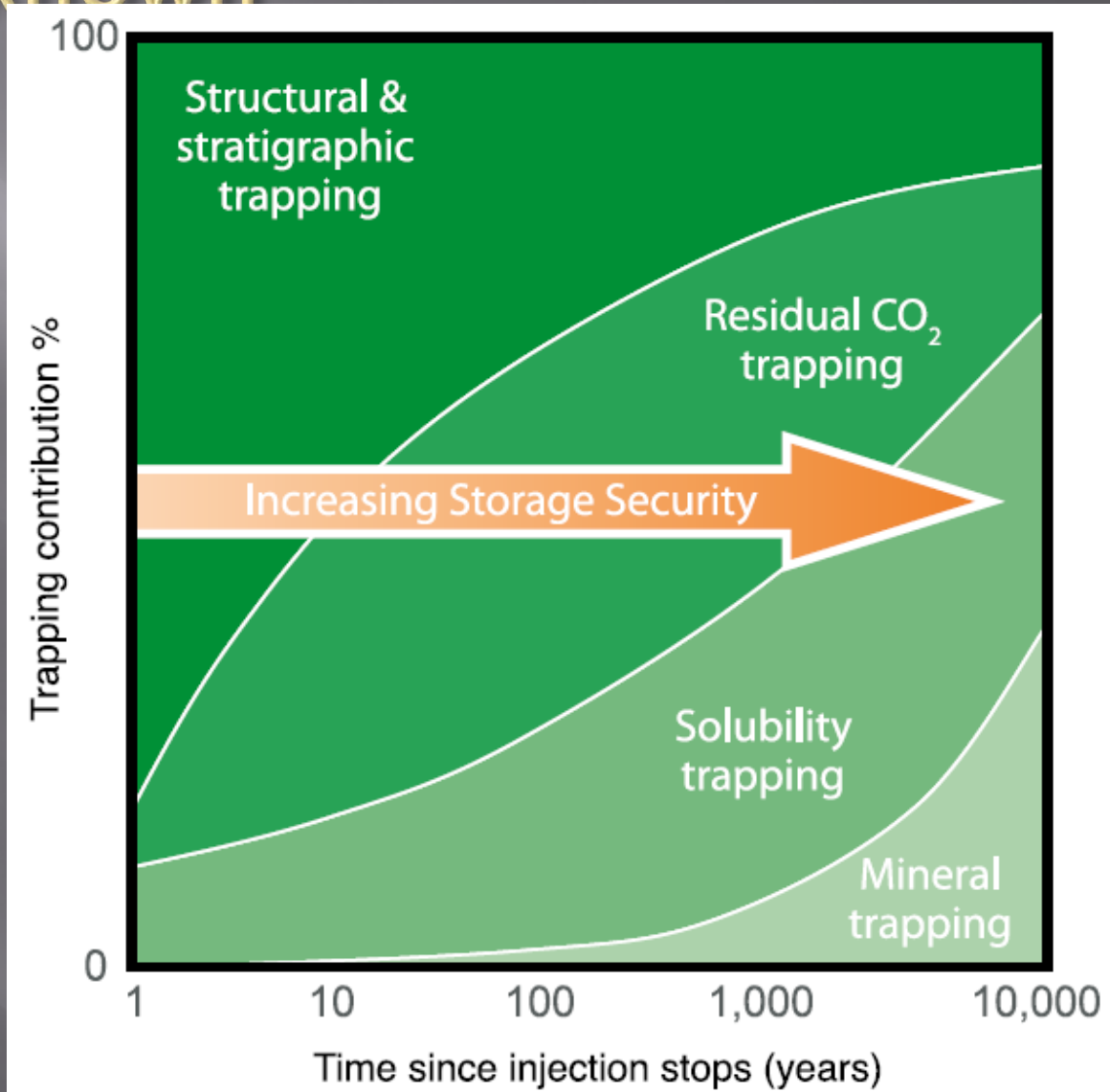
From - Orr, F.M., Science (2009) 325, 1656

Carbon Dioxide Sequestration

- The US emits about 6 Gtons ($6x10^9$ tons) of CO_2 per year.
- About 3.8 Gtons of the US emissions originate from large point sources, where large is defined as local emission in excess of 0.1 Mton ($0.1x10^6$) ton CO_2/year.
- The US and Canada combined have an estimated minimum CO_2 sequestration capacity of 3,800 Gtons in deep saline formations.

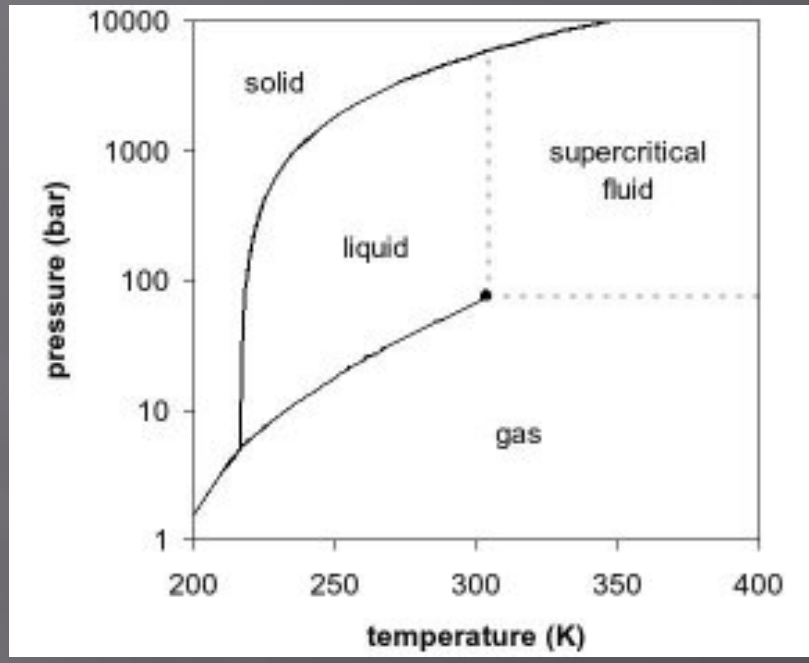
Effectiveness in the Long Term is Unknown

- Trapping Mechanisms:
  - Physical
  - Adsorptive
  - Dissolution
  - Mineral



IPCC Special Report on Carbon Dioxide Capture and Storage
CAMBRIDGE UNIVERSITY PRESS
Figure 5.9 pg208

Previous Studies



- Sequestration Conditions:
  - Supercritical CO_2
    - 31-100 C
    - ~75 bar
  - High Temperature (Geothermal Gradients)
  - Low initial pH (Mineral Dissolution)
- Divalent Cations form Carbonates
  - Ca^{2+}, Mg^{2+}, Fe^{2+}
- Mg Bearing Olivines and Serpentine Minerals form Magnesite
- Conversion to Carbonate Mineral is Kinetically Limited

Composition of $ScCO_2$ can be Complex mixture

- SO_2 Produced from Fuel Combustion
- H_2S results from Integrated Gas Combined Cycle (IGCC) plants.
- modeling studies suggest that H_2S and/or SO_2 constituents commonly found in $scCO_2$ injectate may alter the near field and far field conditions, which can affect both injectivity and long-term storage.

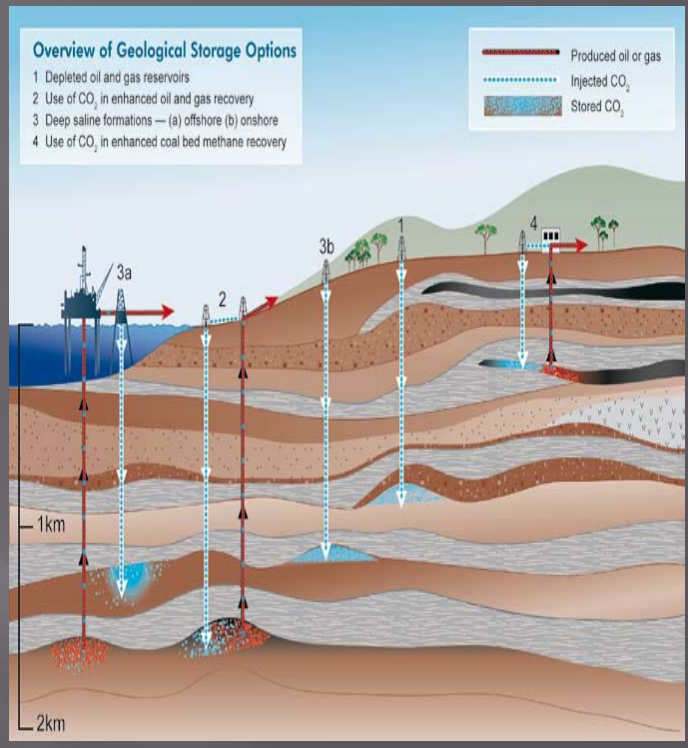
T.F. Xu, J.A. Apps, K. Pruess, H. Yamamoto, Numerical modeling of injection and mineral trapping Of CO2 with H2S and SO2 in a sandstone formation, Chemical Geology 242(2007) 319-346.

Key Research Issue

Can we drive the following redox reaction During CO_2 injection

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

to facilitate CO_2 Sequestration?



Hematite can Convert to Siderite and Pyrite after ~2 months at 150 °C ($SO_2 + CO_2 + H_2O$)

J.L. Palandri, R.J. Rosenbauer, Y.K. Kharaka, Ferric iron in sediments as a novel CO2 mineral trap: CO2-SO2 reaction with hematite, Applied Geochemistry 20(2005) 2038-2048.

Key Redox Reaction

Carbonate Formation

$$CO_2 + H_2O_{(l)}$$
$$\leftrightarrow$$
$$H_2CO_3$$
$$\leftrightarrow$$
$$HCO_3^- + H^+$$
$$\leftrightarrow$$
$$CO_3^{2-} + 2H^+$$

Iron Reduction and Siderite Formation

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S$$

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3$$

Net Reaction

$$Fe_2O_3 + H_2S + 2CO_2 \rightarrow 2FeCO_3 + S + H_2O$$

Experimental conditions based on Calculation

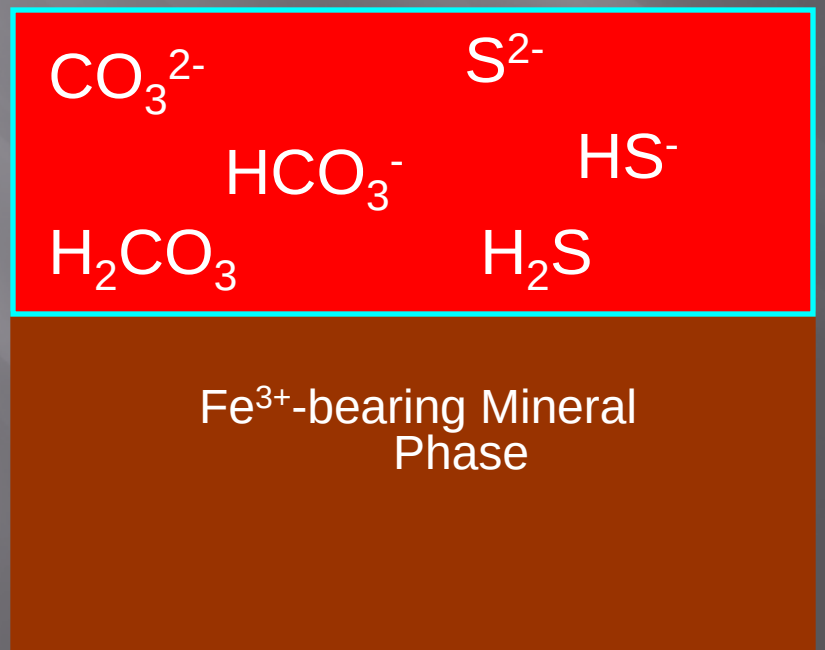
82 bar CO_2

0.82 bar H_2S

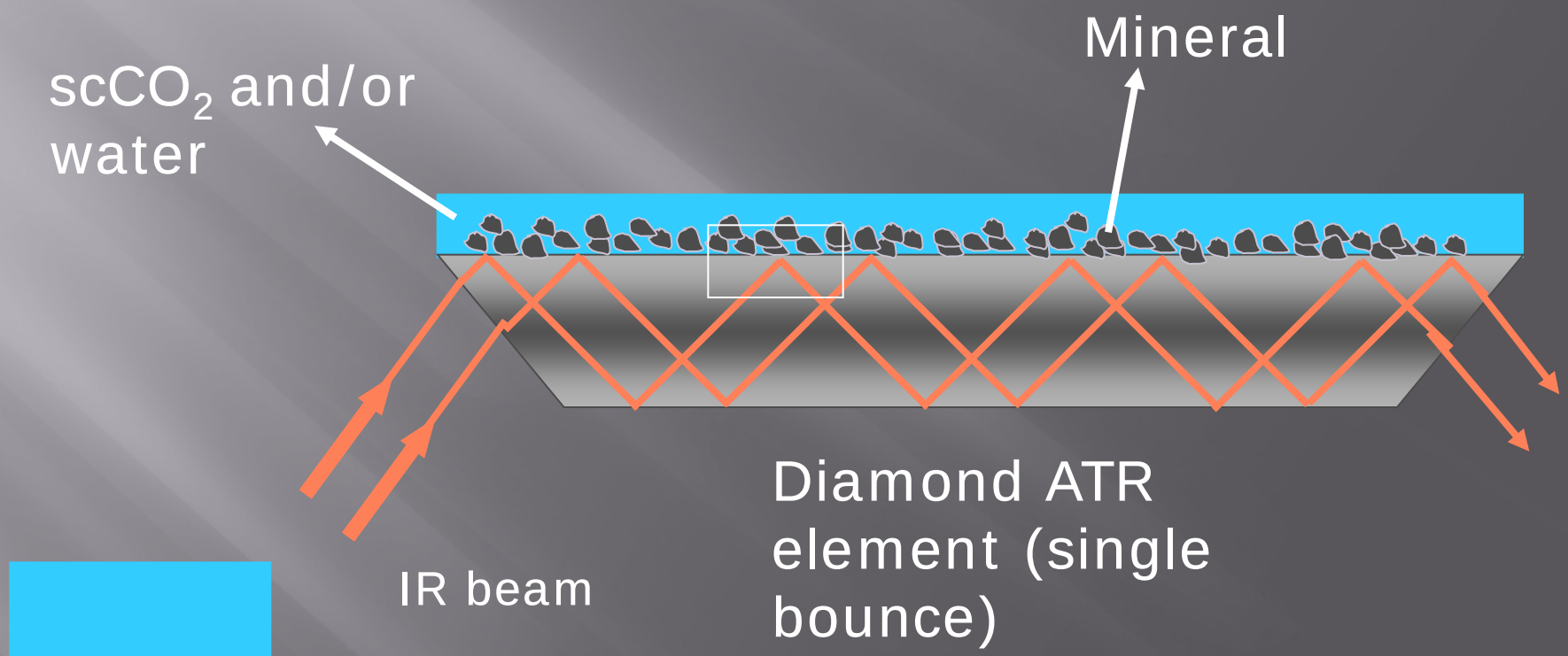
99% CO_2

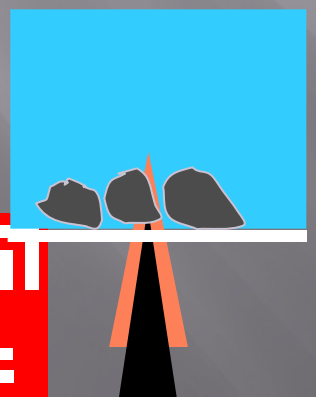
1% H_2S

25 mM HS^- and H_2S



Horizontal attenuated total reflectance FT-IR



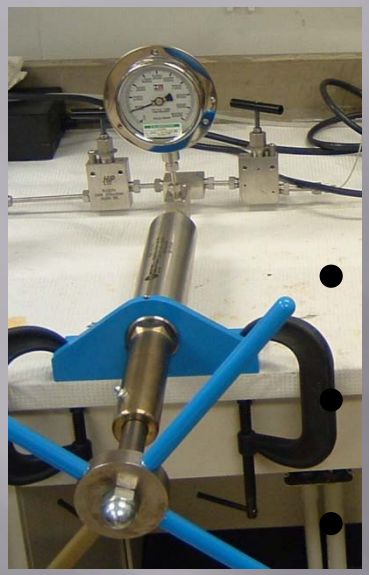


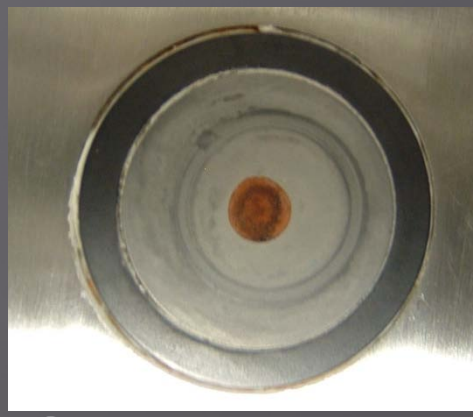
Evanescent wave probes aqueous/solid interface

$scCO_2$ generation

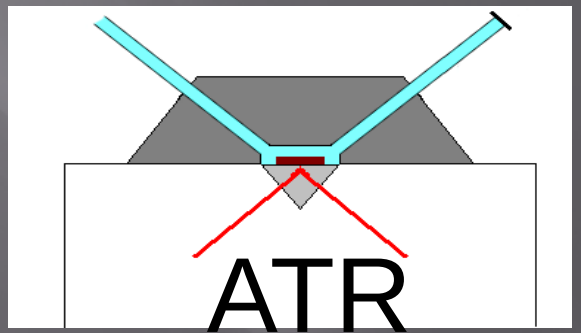
- scCO2 injected into reaction/infrared cell

Experimental Setup

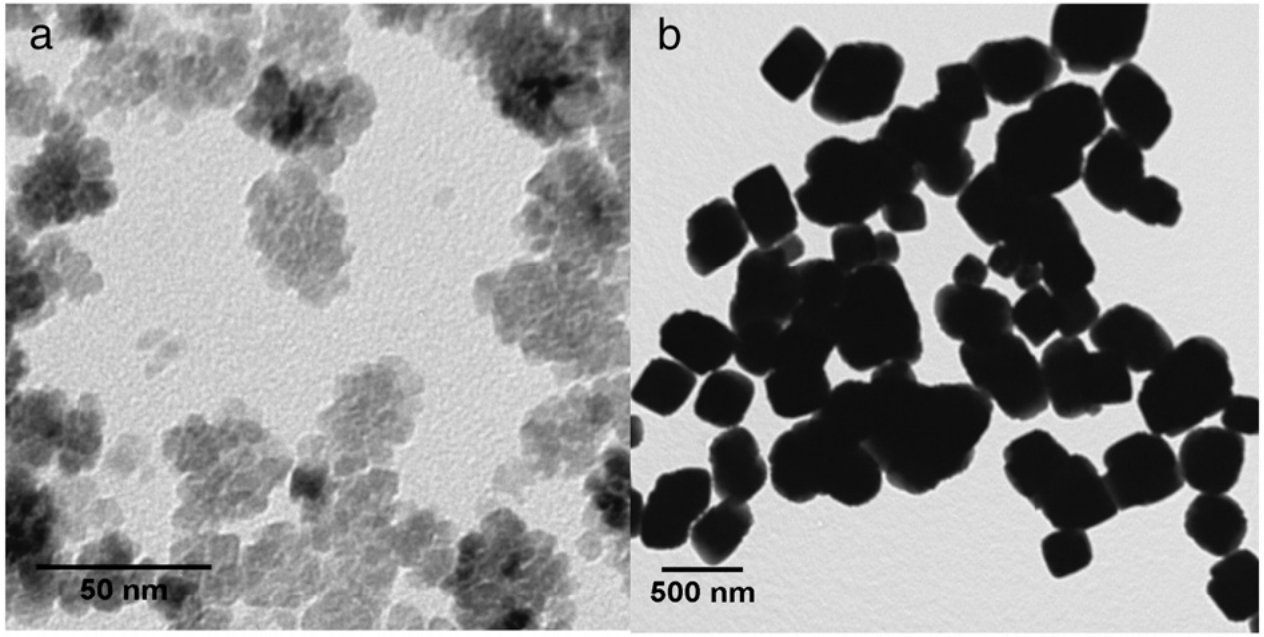




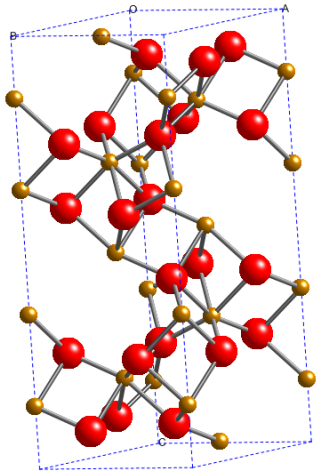
- Thin Film or Slurry
- Inject water
- Inject $Na_2S_{(aq)}$ and/or NaHS
- Pressurize (1200 psi)
- Heat (70 C)
- CO_2 Pressure



Nano Hematite



2 different hematite diameters to look at size dependence



Experimental conditions based on Calculation

82 bar CO_2

0.82 bar H_2S

99% CO_2

1% H_2S

50 mM HS^- and H_2S

CO_3^{2-} S^{2-}

HCO_3^- HS^-

H_2CO_3 H_2S

Hematite slurry

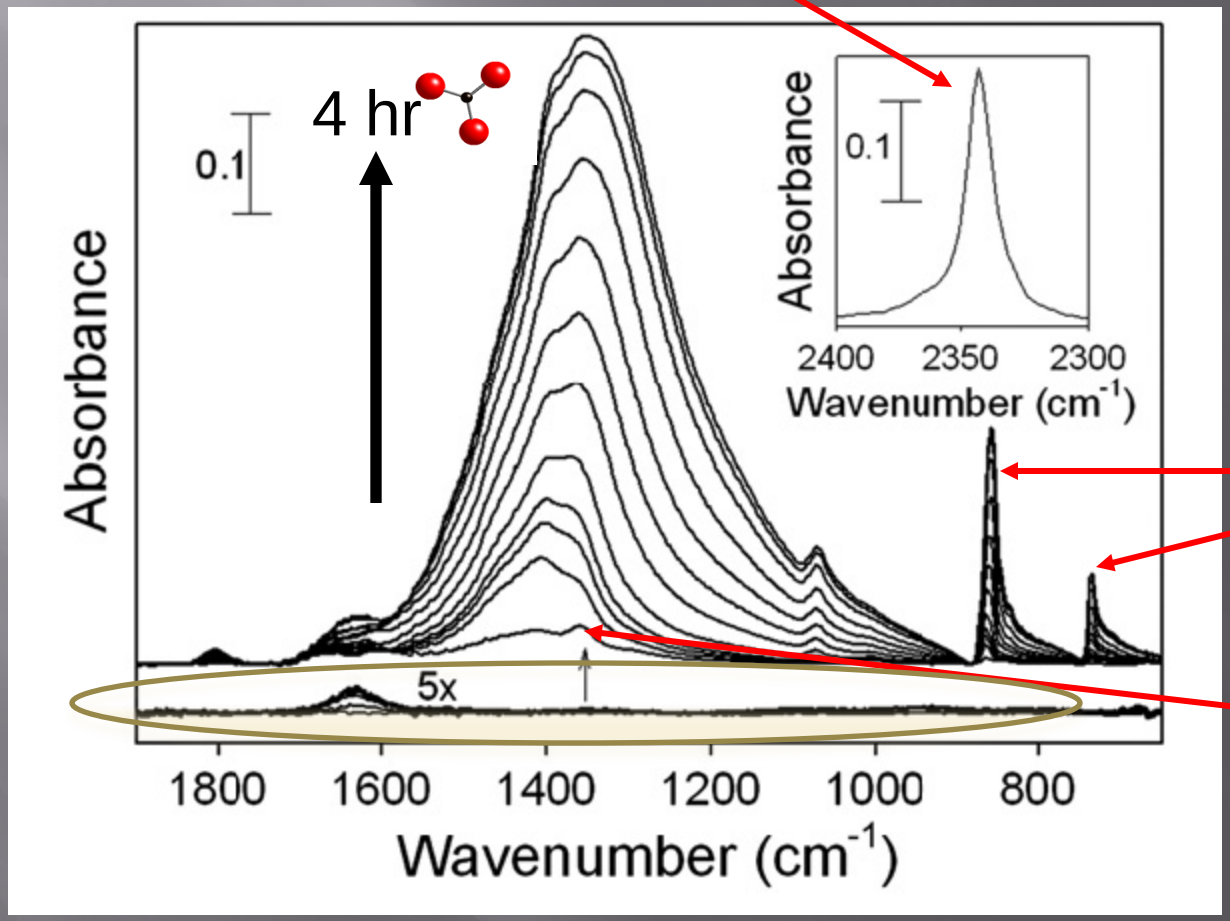
Hematite conversion to Siderite

82 bar CO_2

0.82 bar H_2S

T=70°C

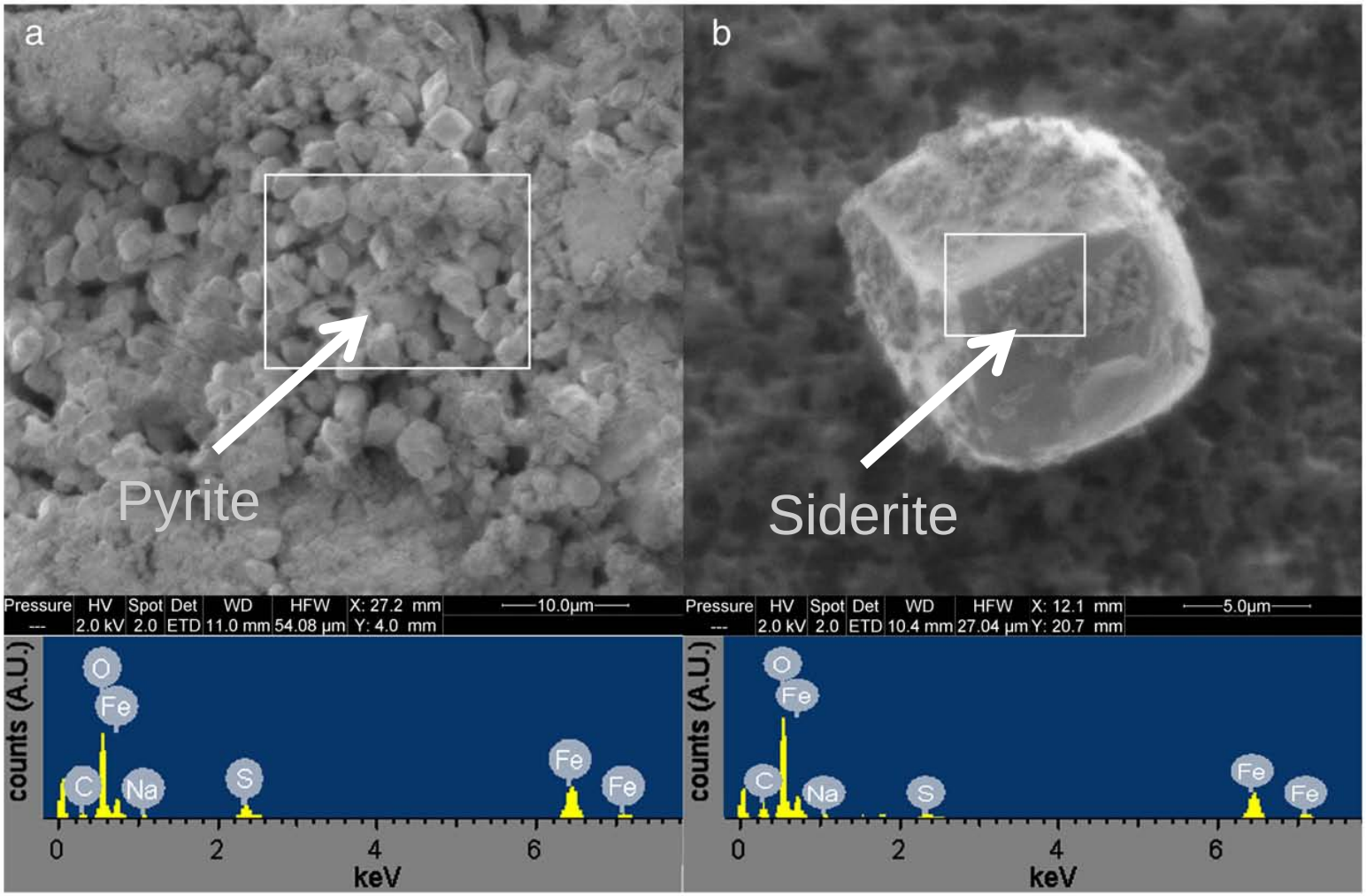
Dissolved CO_2



$FeCO_3$

HCO_3^-

SEM of Post Reaction Product



Some Key Considerations

$4Fe_2O_3$(hematite) + $15H^+ + HS^- = 8Fe^{2+} + SO_4^{2-} + 8H_2O$
(reduction of Fe^{3+})

$H_2CO_3 + Fe^{2+} = FeCO_3 + 2H^+$
(generation of siderite)

$4Fe_2O_3$(hematite) + $15H_2S + H_2SO_4 = 8FeS_2 + 16H_2O$ (formation of pyrite)

Effect of aqueous sulfide concentration

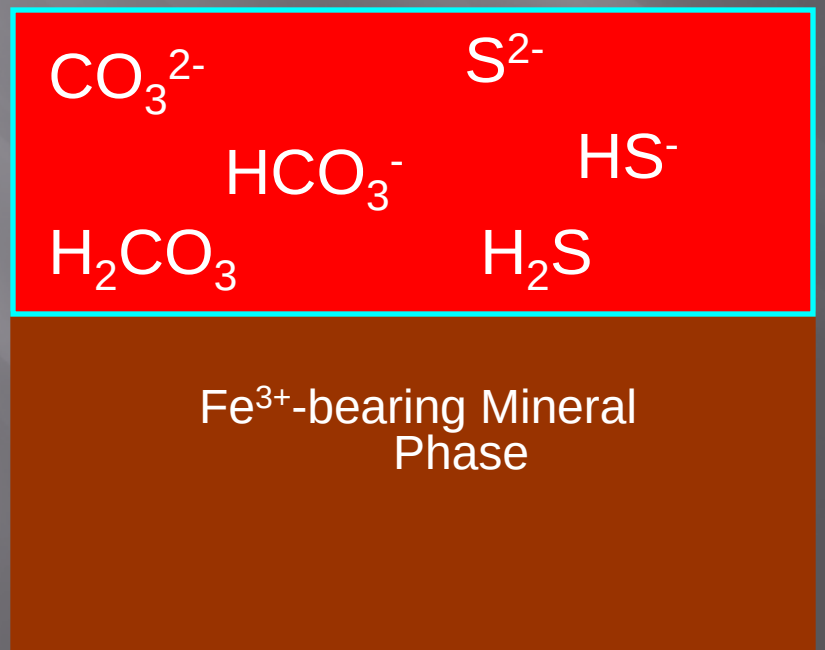
82 bar CO_2

8.2 bar H_2S

99% CO_2

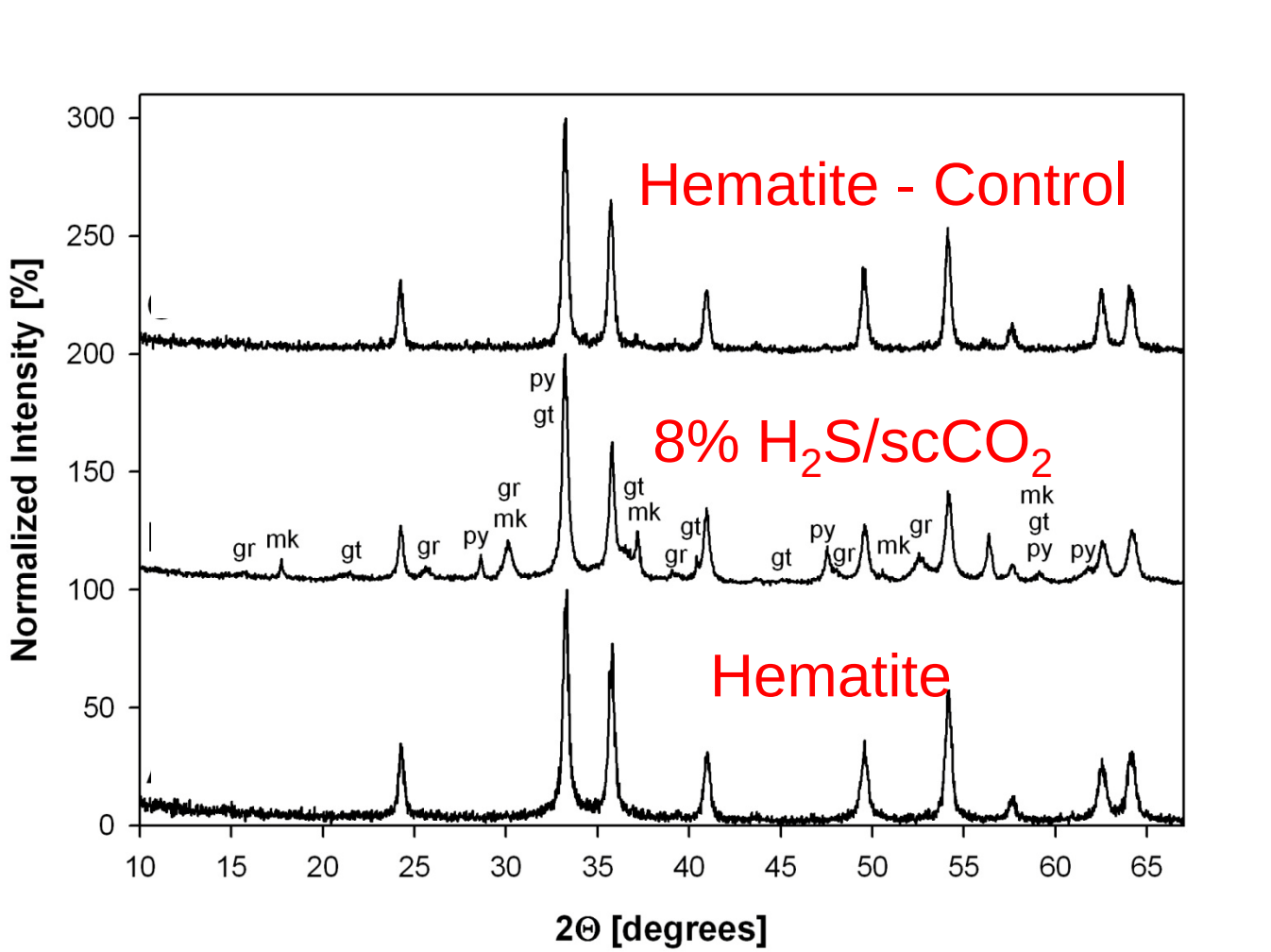
1% H_2S

180 mM HS^- and H_2S



Hematite conversion to Pyrite with higher sulfide concentration

py – pyrite
mk – mackinawite
gr - greigite



Pyrite Formation

$4Fe_2O_3$(hematite) + $15H^+ + HS^- = 8Fe^{2+} + SO_4^{2-} + 8H_2O$

(reduction of Fe^{3+})

$H_2CO_3 + Fe^{2+} = FeCO_3 + 2H^+$

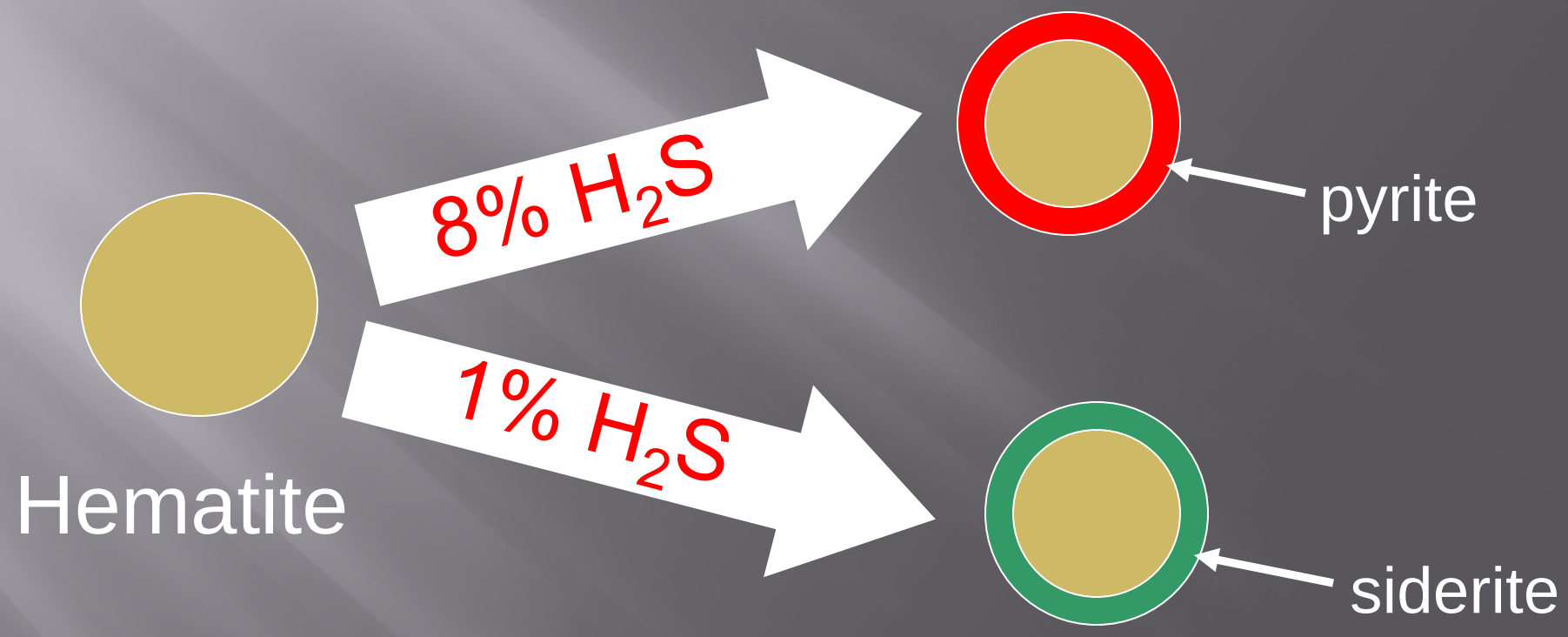
(generation of siderite)

$4Fe_2O_3$(hematite) + $15H_2S + H_2SO_4 = 8FeS_2 + 16H_2O$ (formation of pyrite)

$4Fe^{2+} + SO_4^{2-} + 7HS^- + H+ = 4FeS_2 + 4H_2O$

(formation of pyrite)

Secondary Phase Coating?



Summary of Model System

- Conversion of iron oxyhydroxides and oxides can be converted to siderite under $ScCO_2$ conditions
- Degree of conversion is a function of particle morphology. High surface to volume ratio convert well. Nano-hematite (20 nm) shows more conversion than larger goethite particles (micron size).
- Concentration of reductant important (i.e., HS^-). Oxides may convert to stable sulfide phases instead of carbonate at high concentrations of sulfide.

What about Real Systems?

Model Hematite system

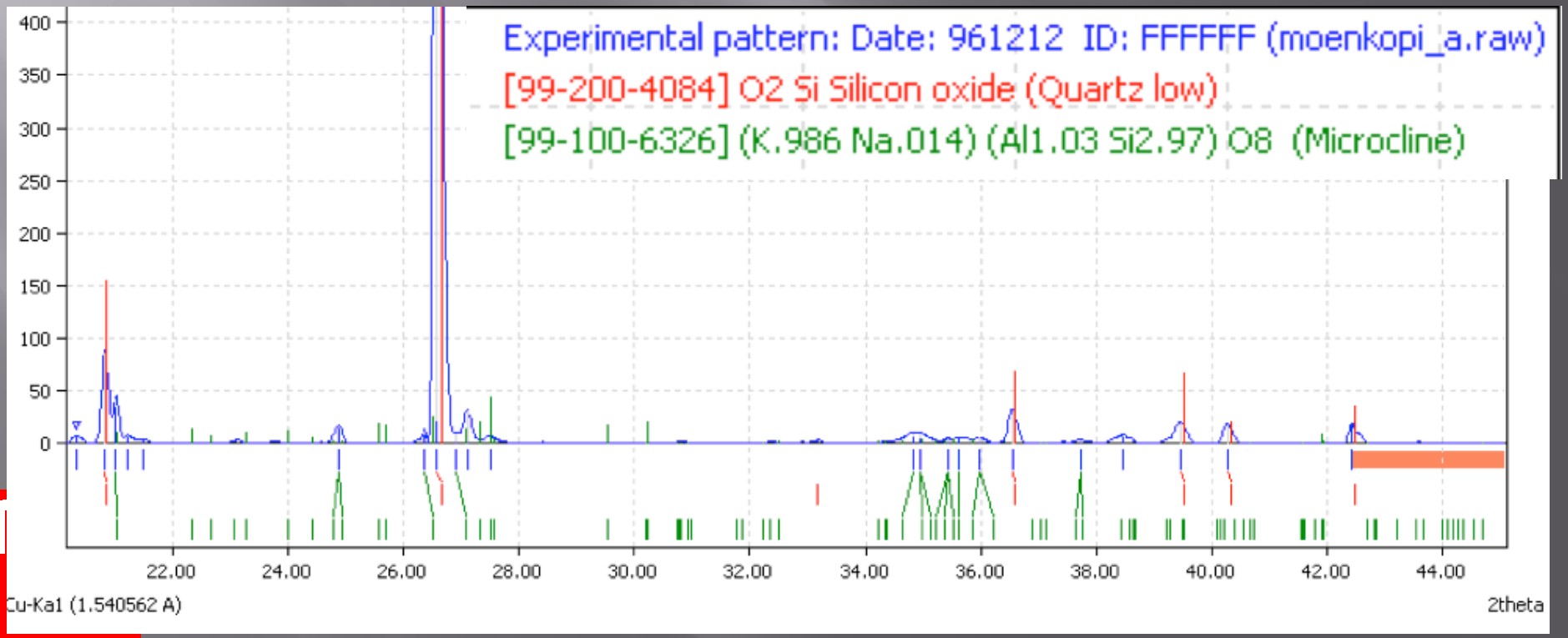
↓

Sandstone

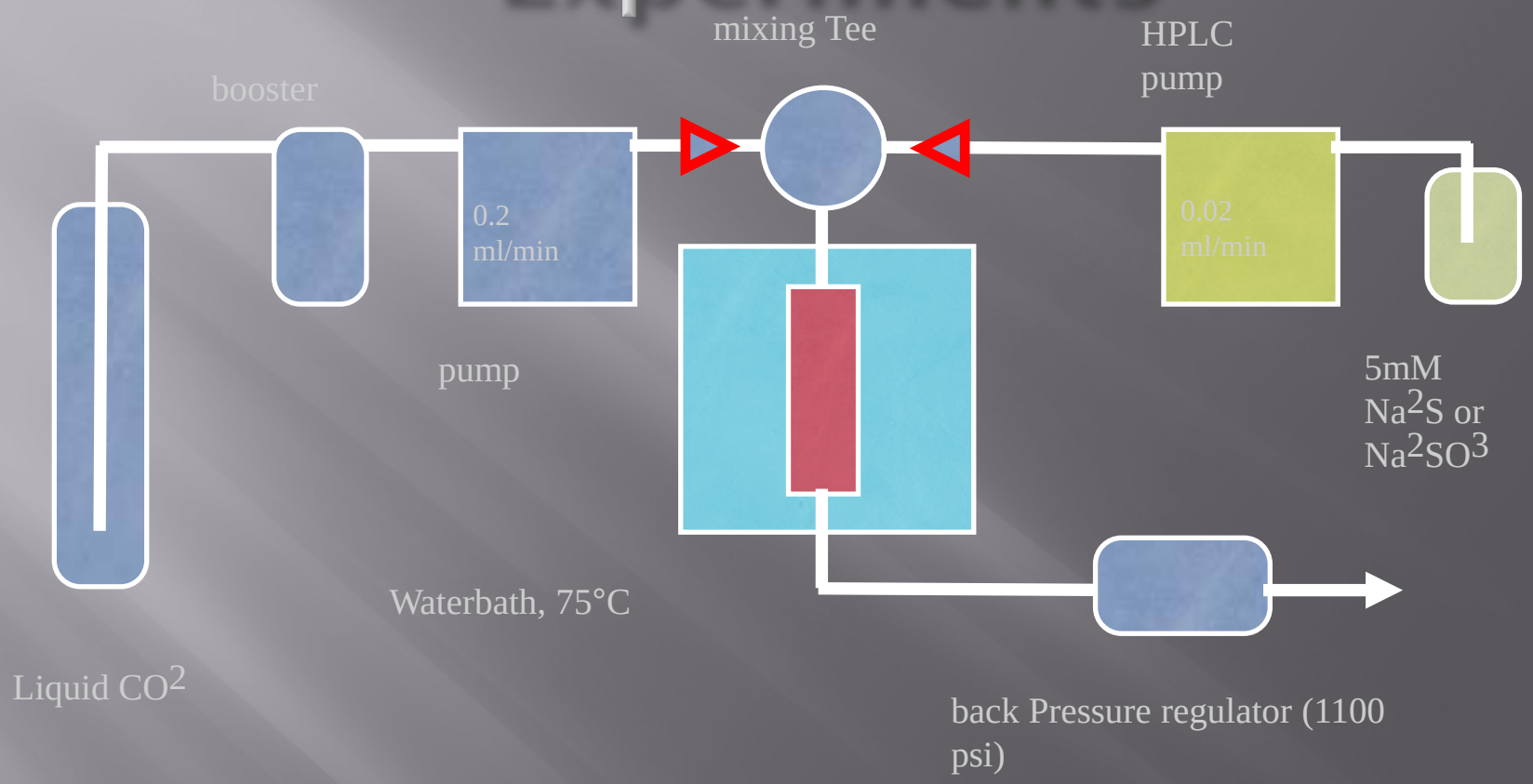
Moenkopi Sand Stone, Lower to Middle Triassic, sample collected in Arizona by Alden Carpenter

used <180µm fraction, 9.98 m^2/g

XRF: 67.2% SiO^2, 20.6% Al^2O^3, 5.1% Fe^2O^3, 3.7% K^2O



Flow-Through Experiments



Analyzed crushed (red) sandstone using XRD, FTIR, Raman and Mössbauer after 80 hrs exposure

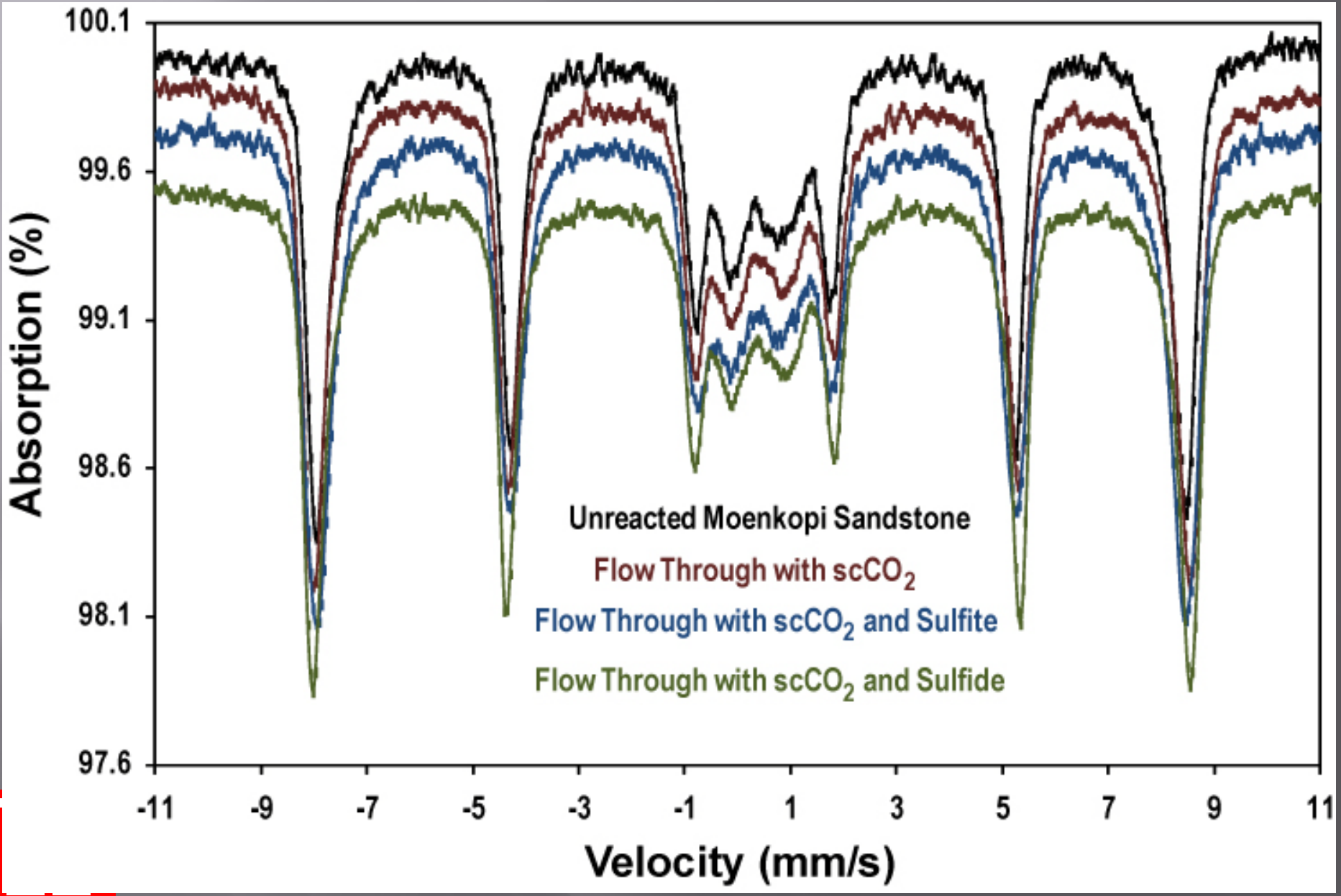
Moenkopi
unreacted

Flow Through
$scCO_2$

Flow Through
$scCO_2 + H_2O +$
Na_2SO_3

Flow Through
$scCO_2 + H_2O +$
Na_2S

Results for FLOW-THROUGH experiments



Batch Experiment

- Parr bomb (23 mL) loaded with dry ice, 700 mg crushed red sandstone, 1mL aqueous solution
- allowed to react for 8 days at 75°C
- measured pH of aqueous fluid after experiment (6.5-7.5)

- analyzed solids with FTIR, Raman, XRD, Mössbauer

Batch Experiment

$scCO_2 + H_2O$

Batch Experiment

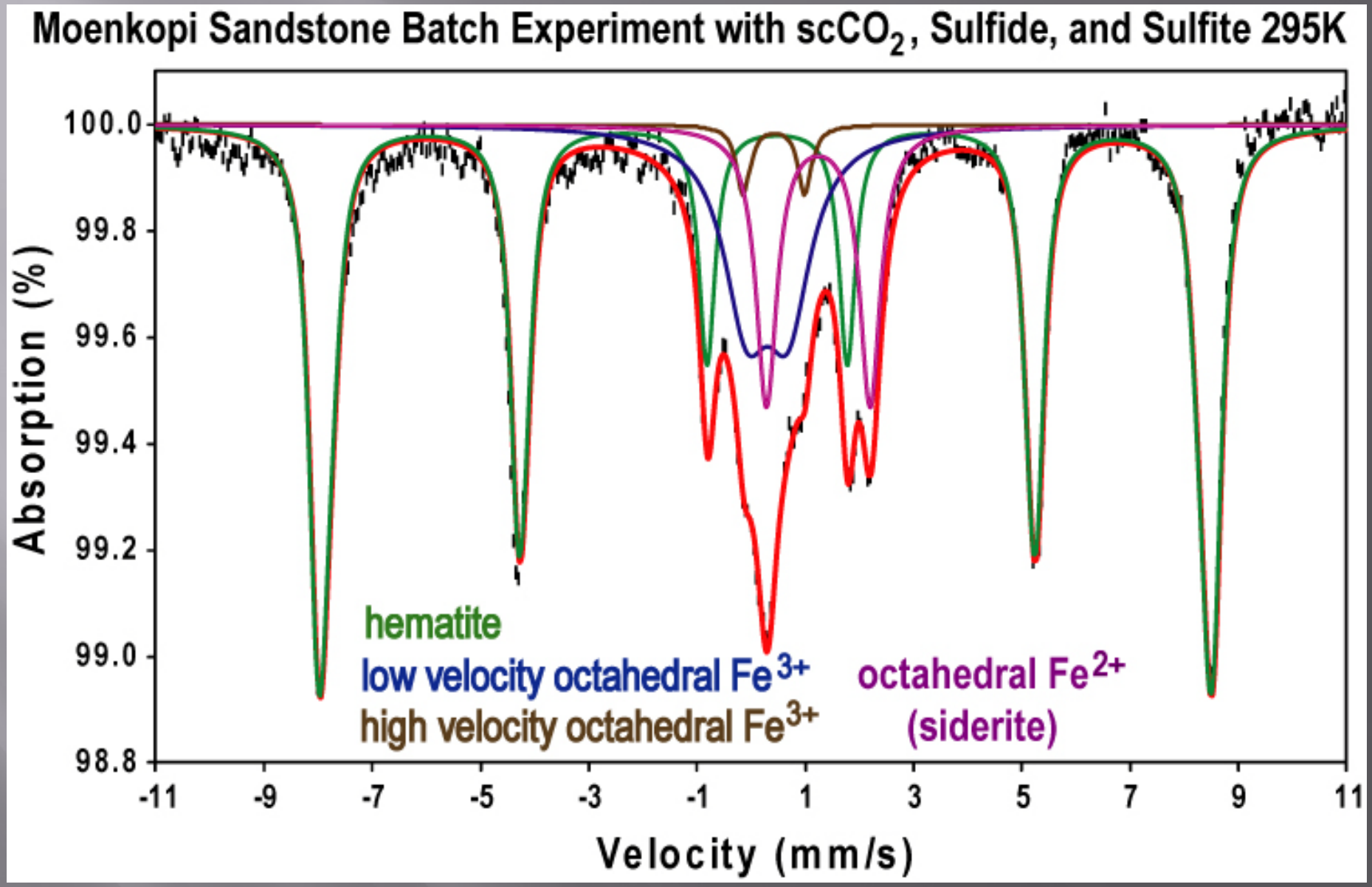
$scCO_2 + Na_2SO_3 + H_2O$

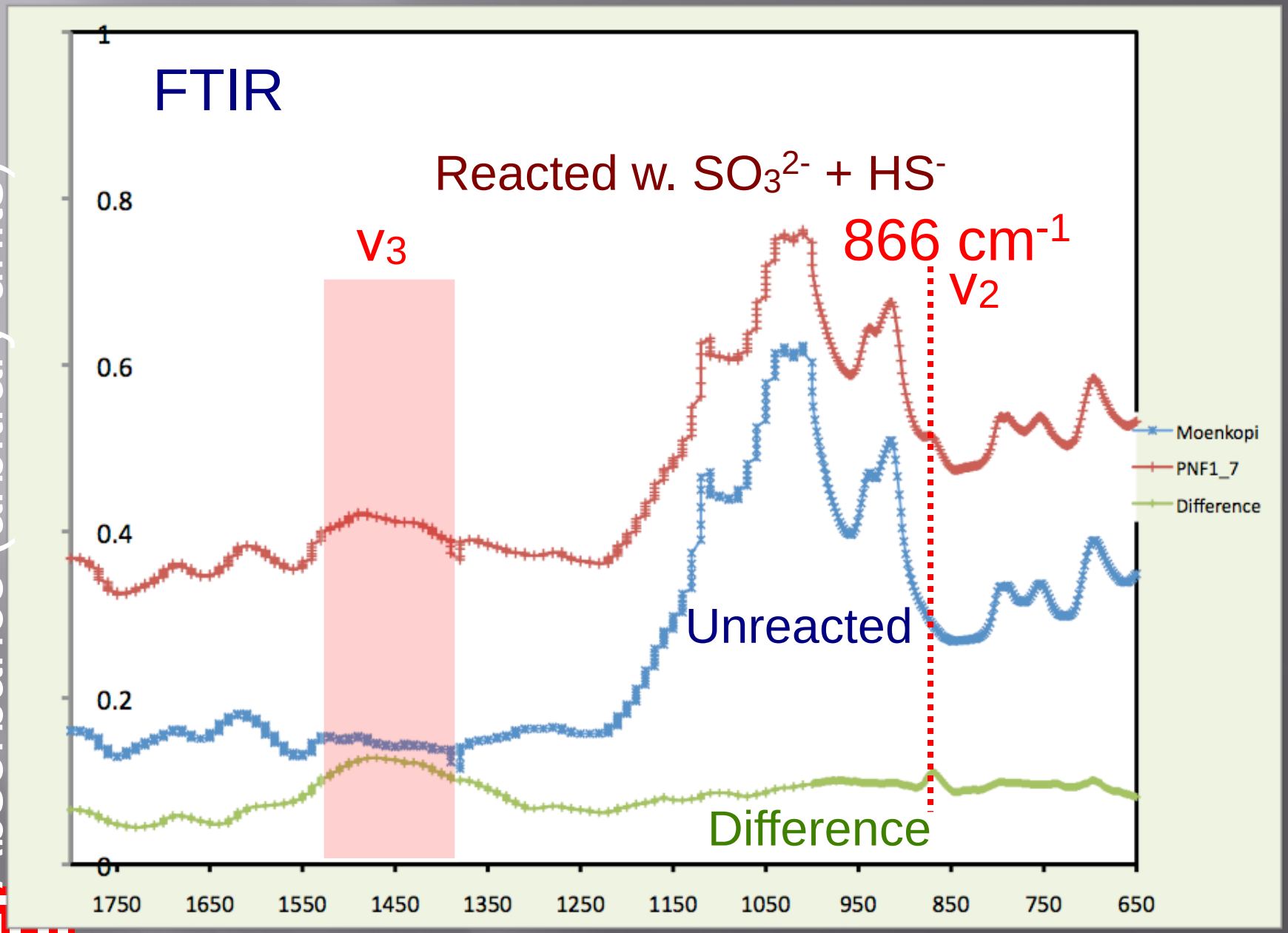
Batch Experiment

$scCO_2 + H_2O + Na_2SO_3 + Na_2S$

Batch Experiment

$scCO_2 + Na_2S + H_2O$


Moenkopi Sandstone Batch Experiment with scCO2, Sulfide, and Sulfite 295K
Absorption (%)
100.0
99.8
99.6
99.4
99.2
99.0
98.8
-11
-9
-7
-5
-3
-1
1
3
5
7
9
11
Velocity (mm/s)
hematite
low velocity octahedral Fe3+
high velocity octahedral Fe3+
octahedral Fe2+
(siderite)



Absorbance (arbitrary units)

Frequency (cm^{-1})

Conclusions

- Under near-field conditions addition of either H_2S + H_2O or SO_2 + H_2O has no effect on the reactivity of the iron bearing minerals. No conversion of hematite in Moenkopi sandstone.
- In CO_2-saturated aqueous fluid, the addition of sulfide + sulfite leads to the formation of siderite.
- In CO_2-saturated aqueous fluid, the addition of sulfide alone leads to the formation of pyrite but not siderite.

Implications

- Near field: little reactivity expected of $scCO_2$ with S-bearing gas and water as co-injectate around point of injection and in CO_2 plume. Preserve porosity and permeability.
- Edge of $scCO_2$ plume: iron-bearing minerals may react if S-bearing gas is co-injected. Porosity and permeability may change as a result.

Acknowledgments

- Martin Schoonen – Stony Brook University
- Riley Murphy
- Kristin Lammers
- Amber Riendeau
- Alex Smirnov – Stony Brook University

Funding

U.S. DEPARTMENT OF ENERGY

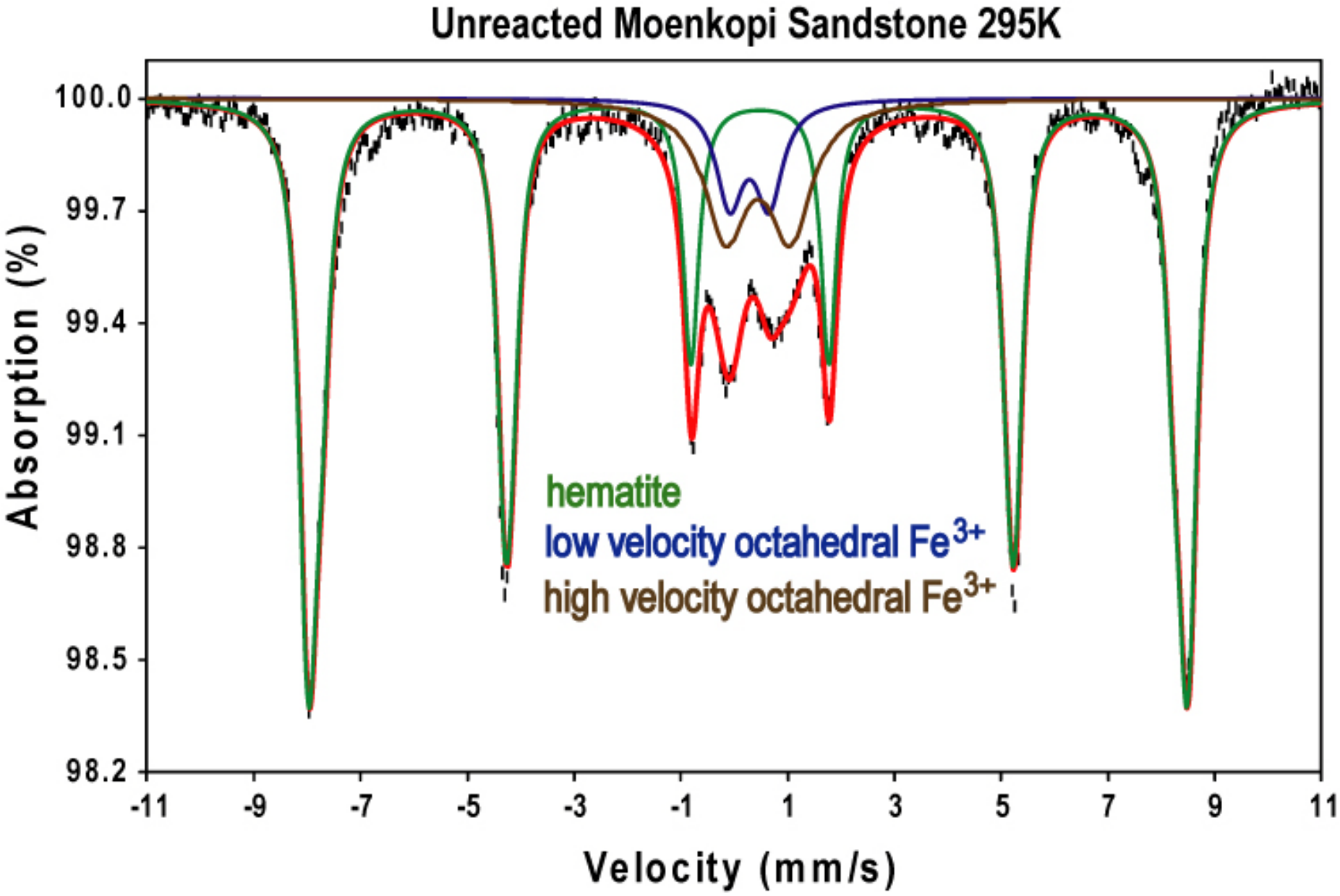
Future Direction

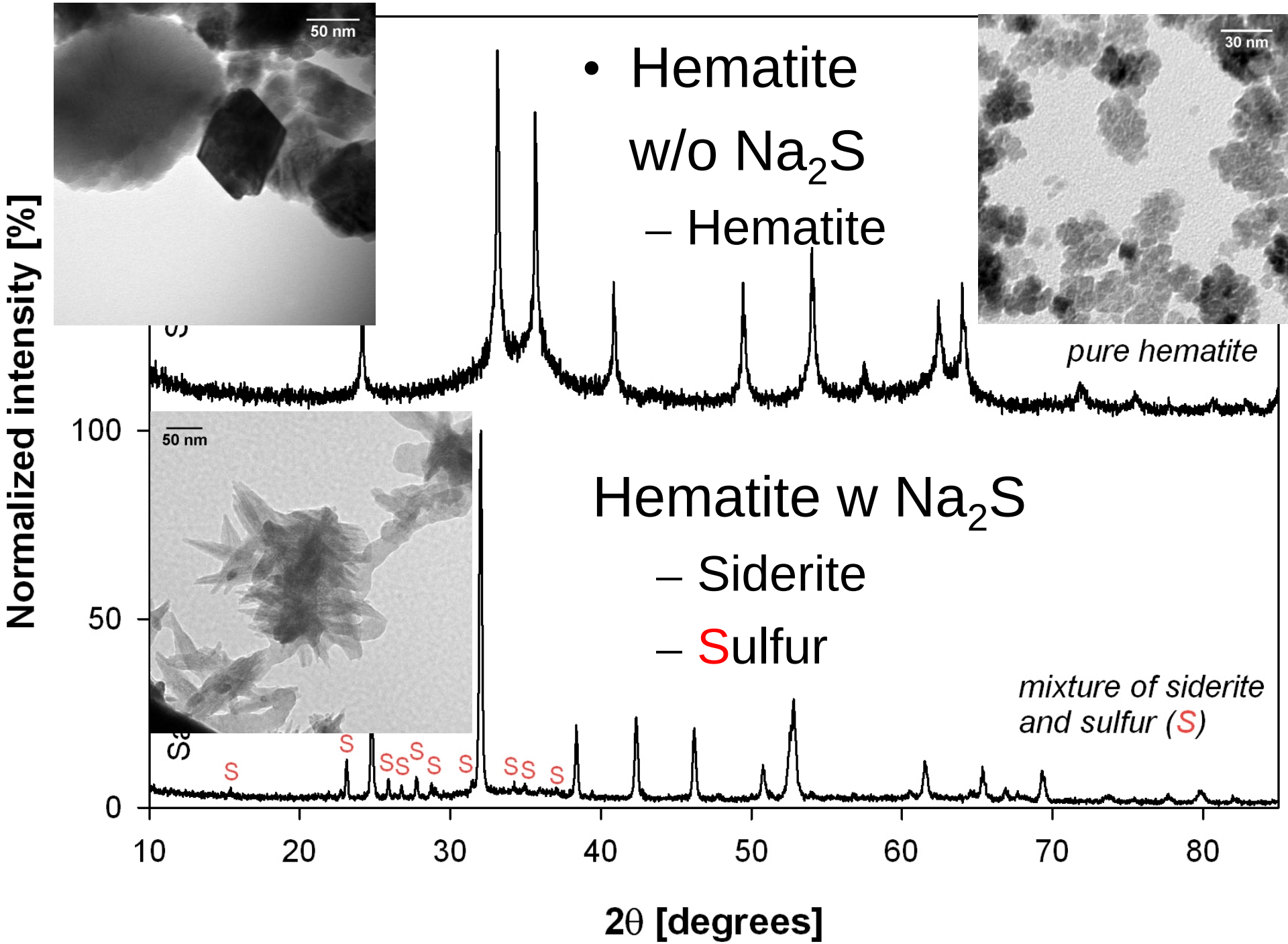
- Dependence of conversion on Temperature and H_2S partial pressure.

- Effect of SO_2

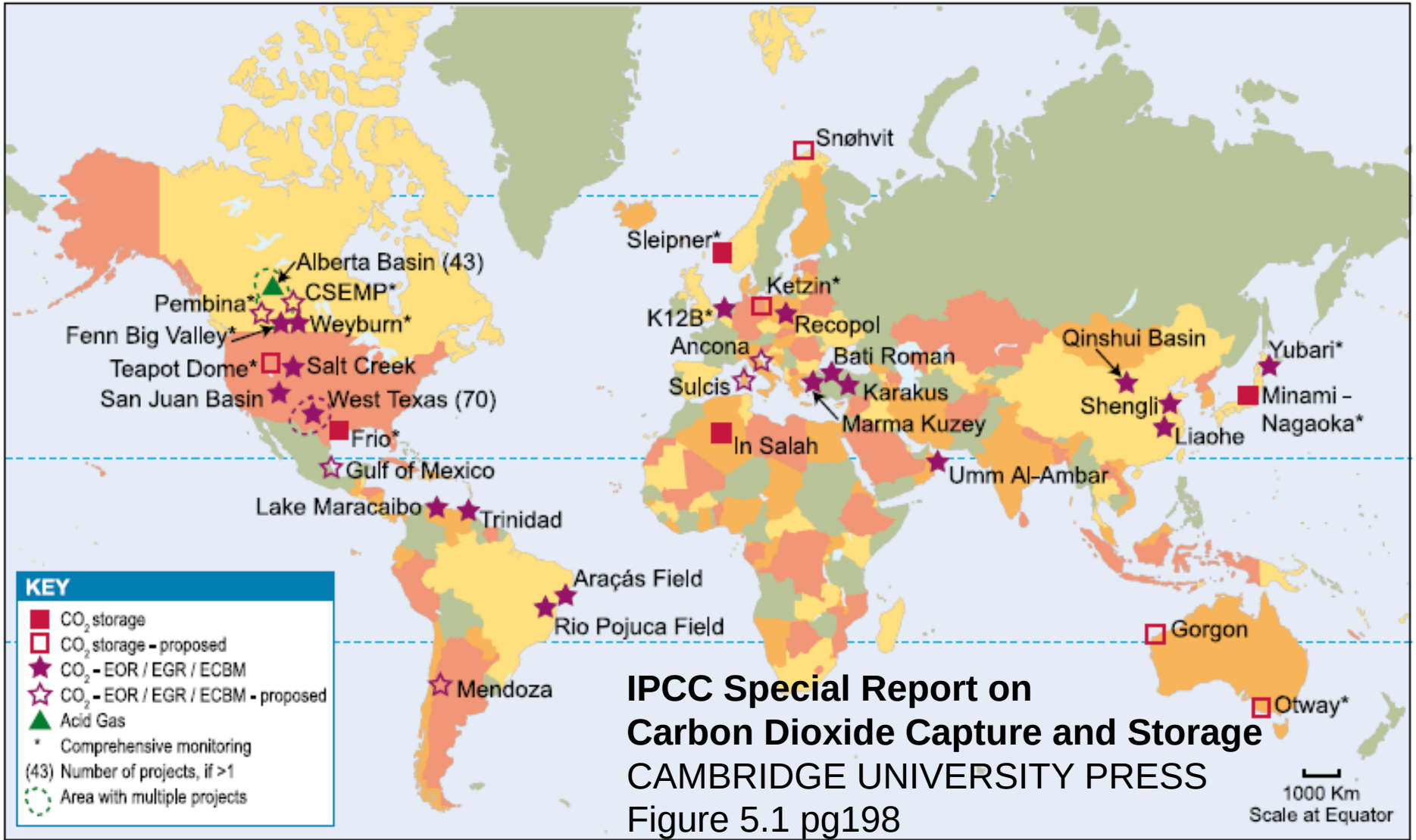
$$Fe_2O_3(\text{hematite}) + 2CO_2 + SO_2 + H_2O = 2FeCO_3 + H_2SO_4$$

(formation of siderite)


Unreacted Moenkopi Sandstone 295K
Absorption (%)
100.0
99.7
99.4
99.1
98.8
98.5
98.2
-11
-9
-7
-5
-3
-1
1
3
5
7
9
11
Velocity (mm/s)
hematite
low velocity octahedral Fe3+
high velocity octahedral Fe3+


50 nm
30 nm
• Hematite
w/o Na_2S
– Hematite
pure hematite
50 nm
Hematite w Na_2S
– Siderite
– Sulfur
mixture of siderite
and sulfur (S)
S
Normalized intensity [%]
100
50
0
10
20
30
40
50
60
70
80
2θ [degrees]

Storage is Already Occurring on a Small Scale



IPCC Special Report on Carbon Dioxide Capture and Storage
CAMBRIDGE UNIVERSITY PRESS
Figure 5.1 pg198