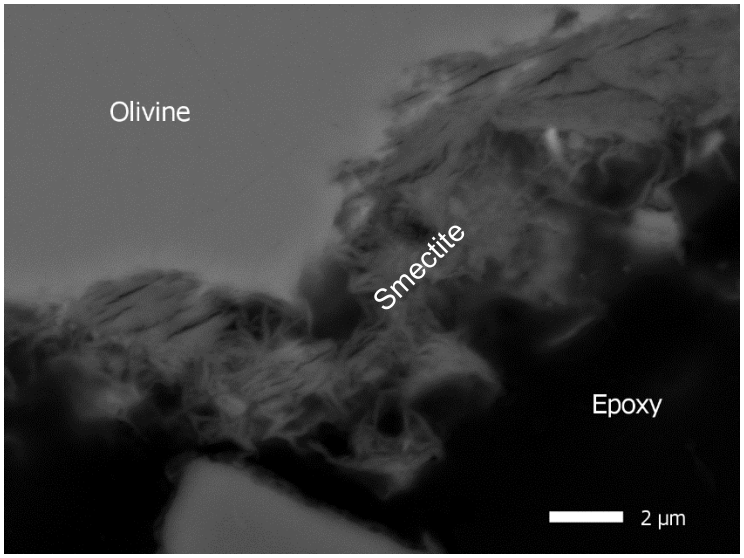
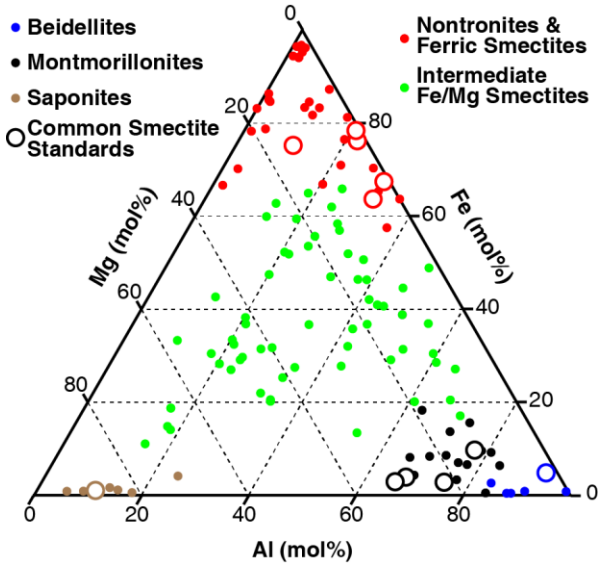
Ferrous Smectites and the Redox Evolution of Early Mars





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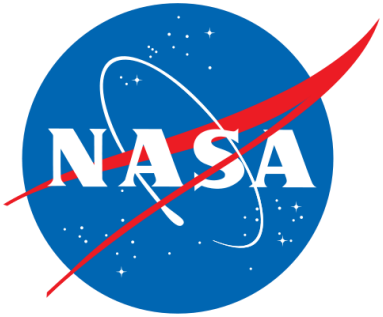
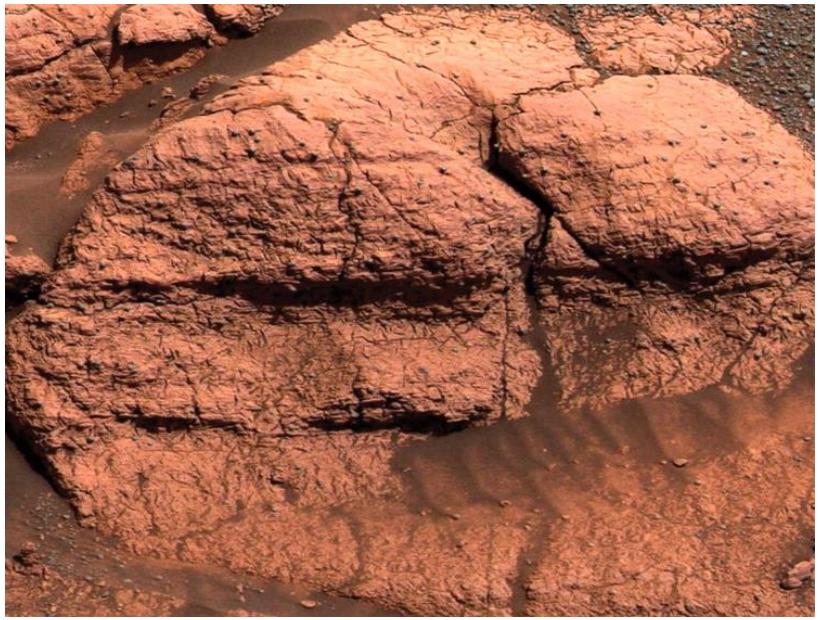
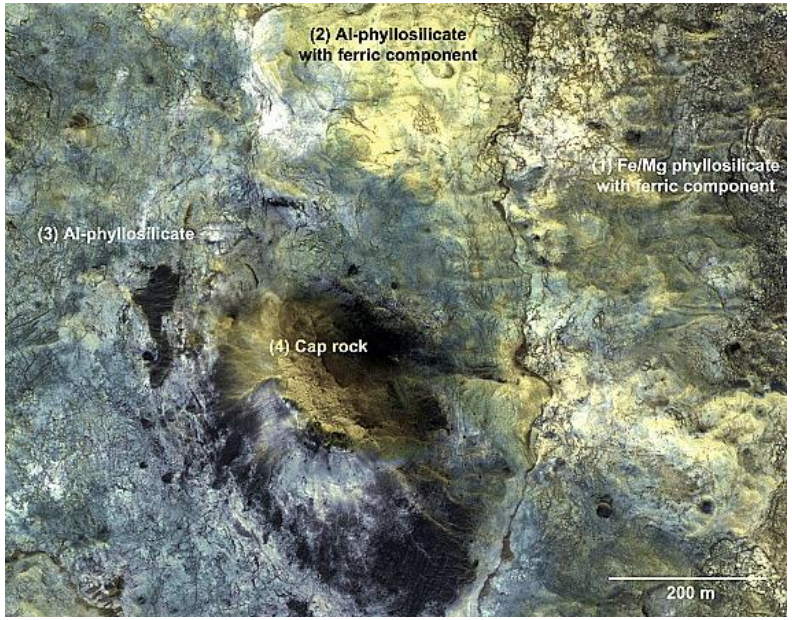


Ample Evidence of Widespread Surface Oxidation of Mars Today



Hematite and Jarosite at Eagle Crater

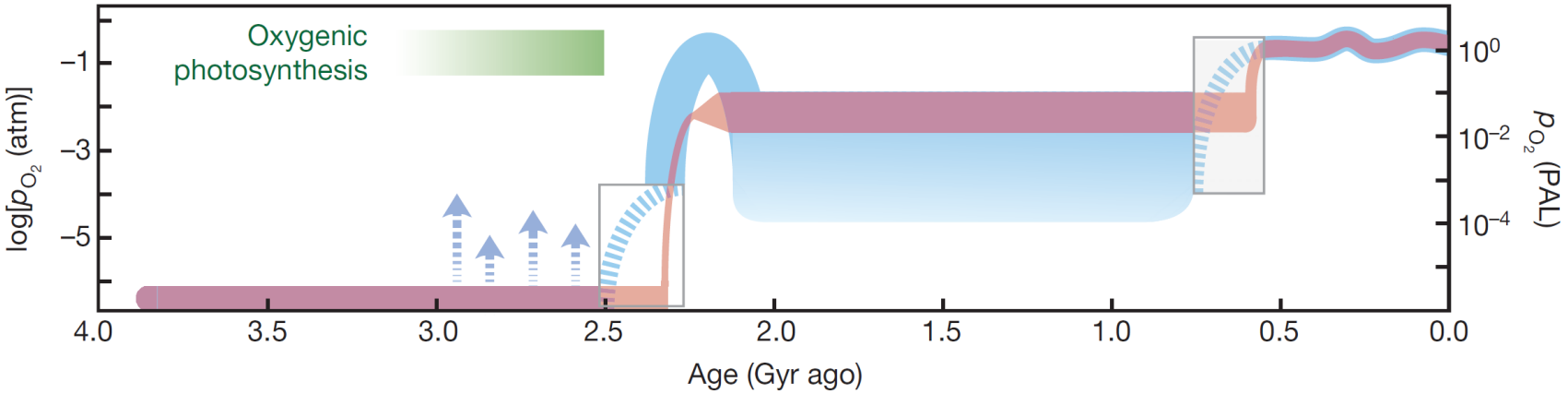


Nontronite at Mawrth Vallis

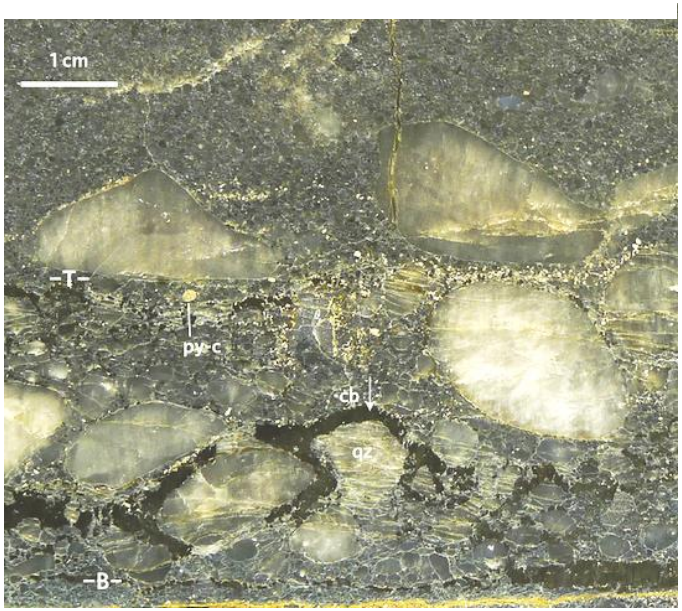
- Ample mineralogical evidence shows that the surface of Mars today is oxidized
- Ferric iron-bearing minerals is the main signature surface redox conditions
  - Hematite, jarosite, nontronite are widely observed

Images from: Squyres et al. (2004) *Science*; Muchie et al. (2009) *JGR*

Early Earth was Anoxic until the Great Oxidation Event (GOE)

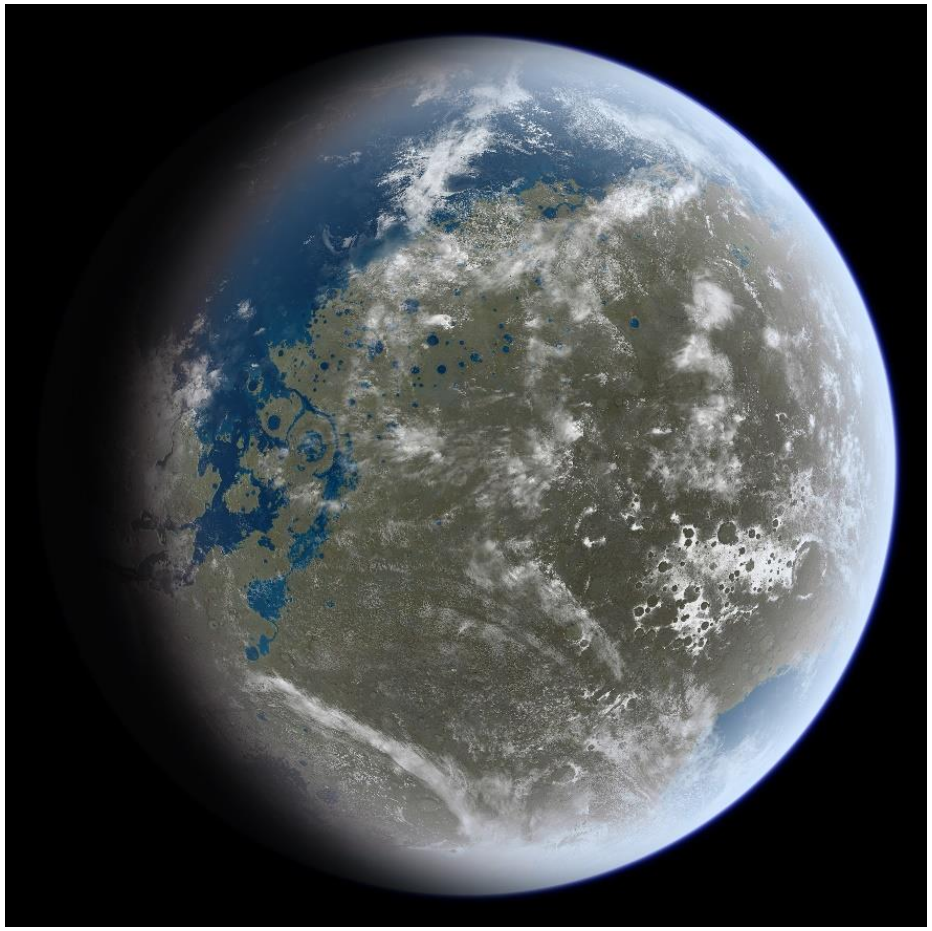


- Ample evidence for non-oxidizing conditions until ~2.35 Ga
  - Example: Detrital pyrite and uraninite deposited in fluvial sediments, Witwatersrand Basin
- Pre-GOE atmosphere dominated by N_2, CO_2, H_2O



Images from: Lyons et al. (2014) *Nature*; Heinrich (2015) *Nature Geosci.*

When was the "Mars Oxidation Event"?



- Clear mineralogical and geomorphic evidence for substantial past water activity on Mars
- Preservation of indicators of past redox state is less certain
  - Continued oxidant deposition today
- ***Timing of the oxidation of the Fe(II)-rich crust of Mars is unclear***

Image from: Wikimedia Commons

Importance of Clays in Exploring the Redox Evolution of Mars

- Much of the effort to understand the early history of Mars has focused on water availability
  - Water is essential for life
- Habitability also requires an energy source
  - On earth, the coupling of kinetically-slow redox reactions is the energy source for life
- Clays are important indicators of the past redox state of the near-surface Martian environment
  - Contain structural Fe that is redox-active
  - Earliest products of aqueous alteration

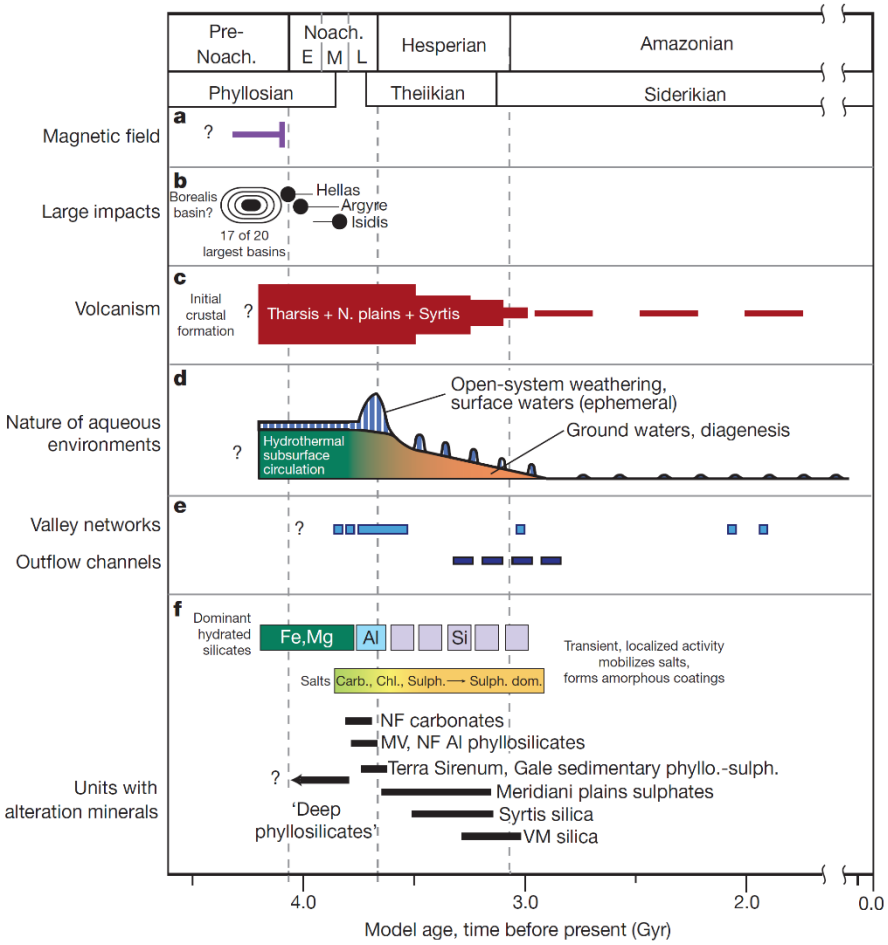
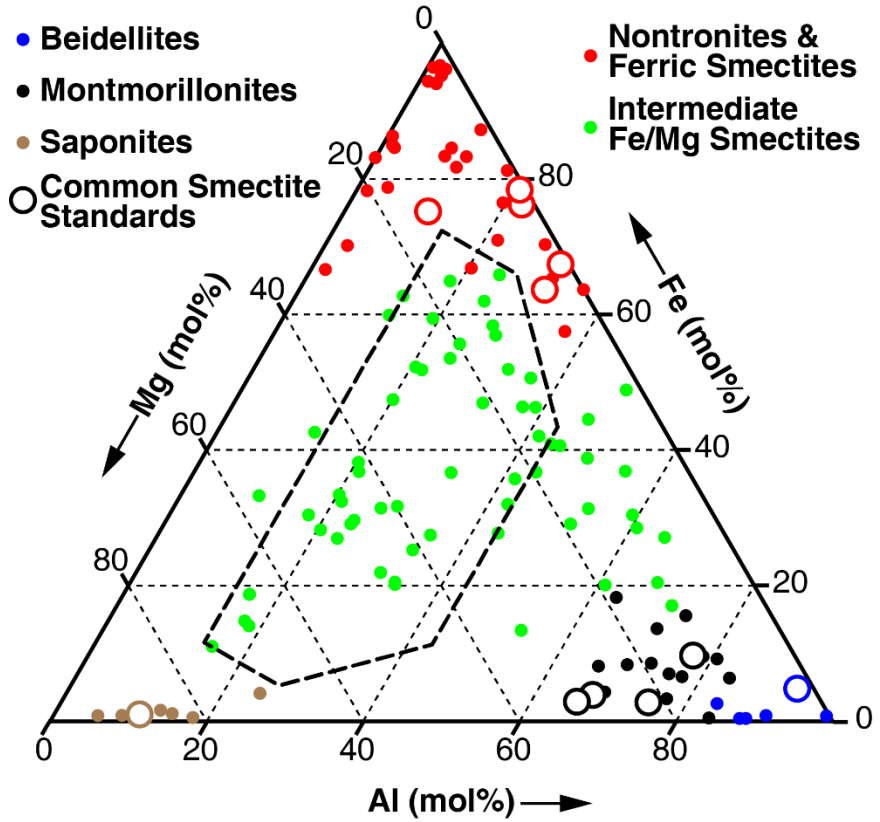


Image from: Ehlmann et al. (2011) *Nature*

Outstanding Questions in the Redox State of Clays on Early Mars

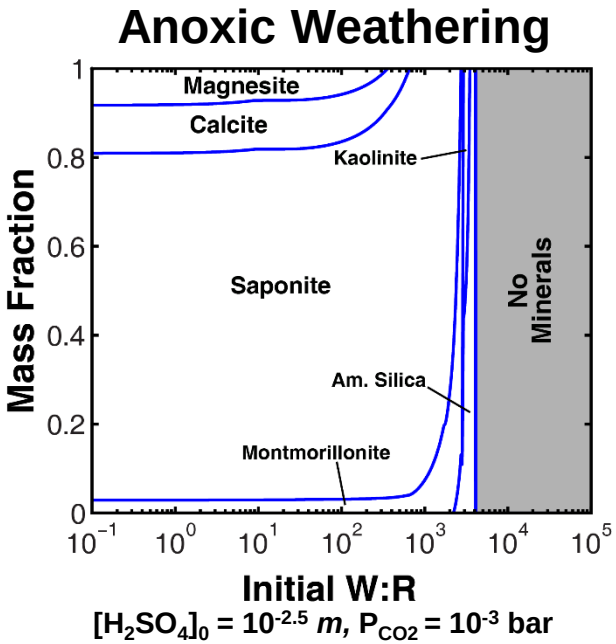
- What clays form during crustal alteration under anoxic conditions?
- What happens to these clays when they are later exposed to oxidants?
- Can the ferric clays observed today be oxidized remnants of the original phases that formed on early Mars?

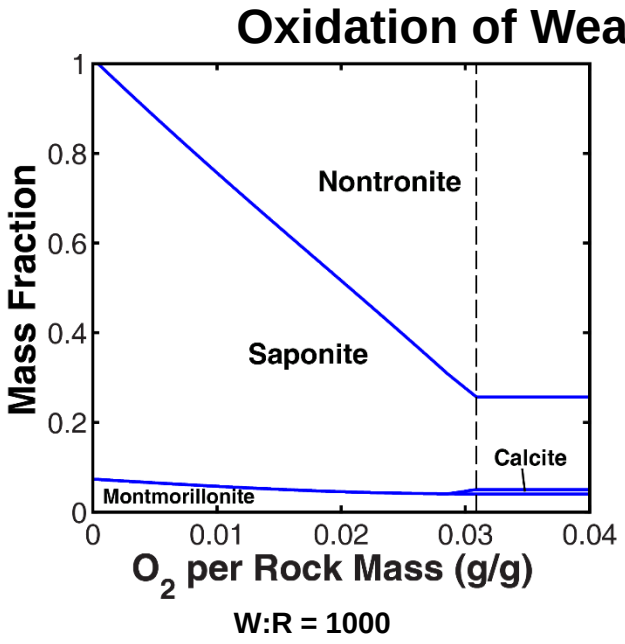


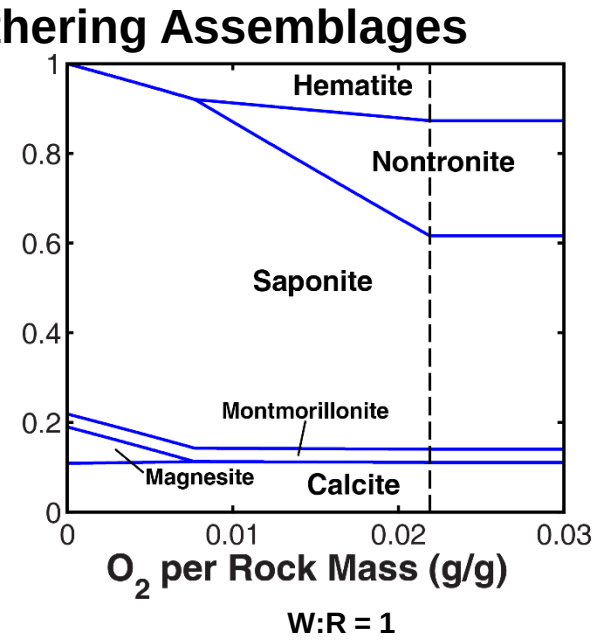
Compositional range of terrestrial smectites

The box outlines the composition of smectites observed in unoxidized altered oceanic crust

Thermodynamic Modeling Predicts Fe(II) Smectites as a Major Alteration Product Under Anoxic Conditions



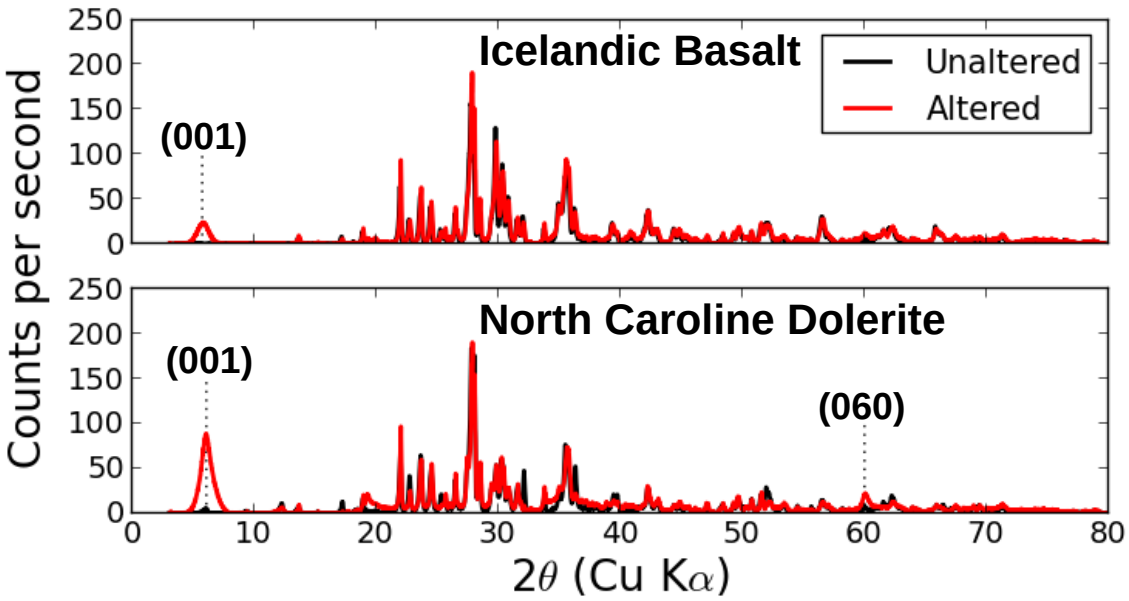


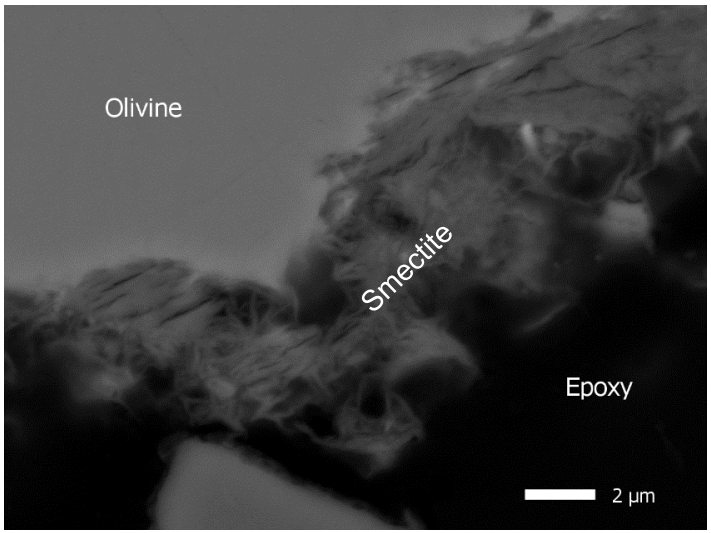


- Modeling of basalt alteration demonstrates that Fe(II)/Mg saponites are the dominant weathering product except at high P_{CO2}
- Oxidation of these assemblages produce nontronite [Fe(III)-smectite] and hematite

Catalano (2013) *JGR*

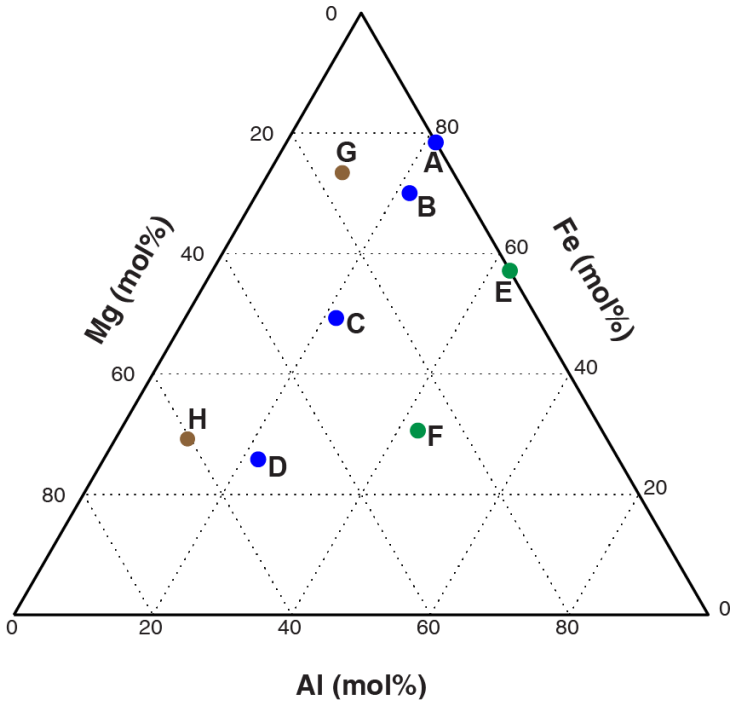
Experimental Hydrothermal Alteration of Basalt Produces Fe(II)-Bearing Trioctahedral Smectites

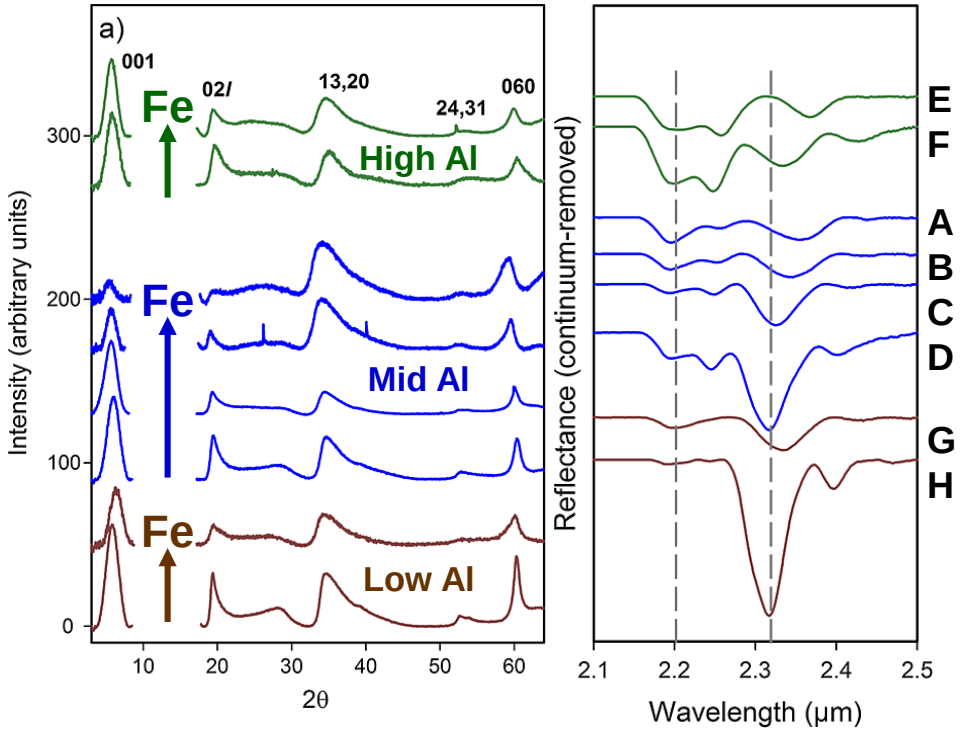




- Hydrothermal alteration of terrestrial basalts generate trioctahedral Fe(II)/Mg smectites (Fe:Al:Mg ~45:20:35)
  - Greater FeO content of Martian basalts would produce a smectite with more Fe and less Mg
- Alteration predominantly consumes olivine

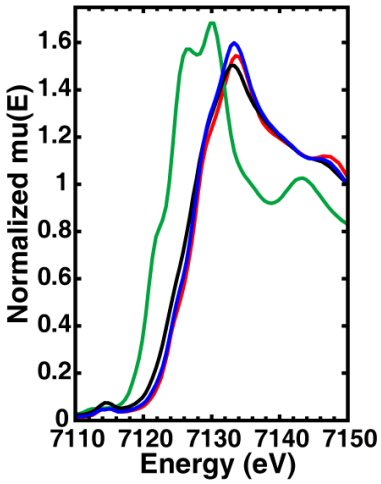
Systematic Mineralogy and Spectral Properties of Fe(II) Smectites

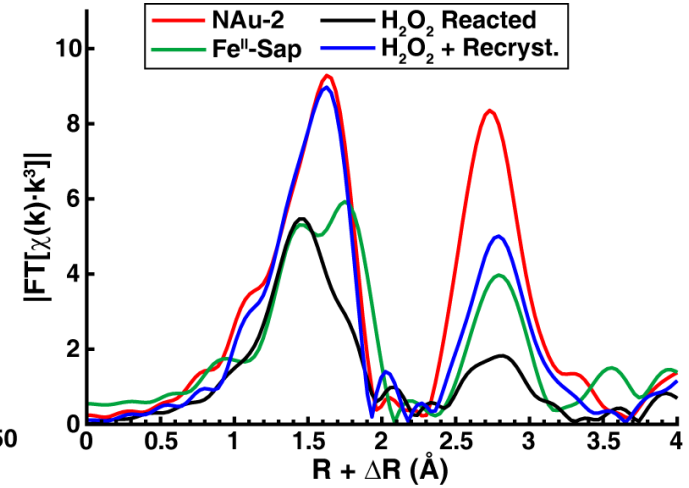


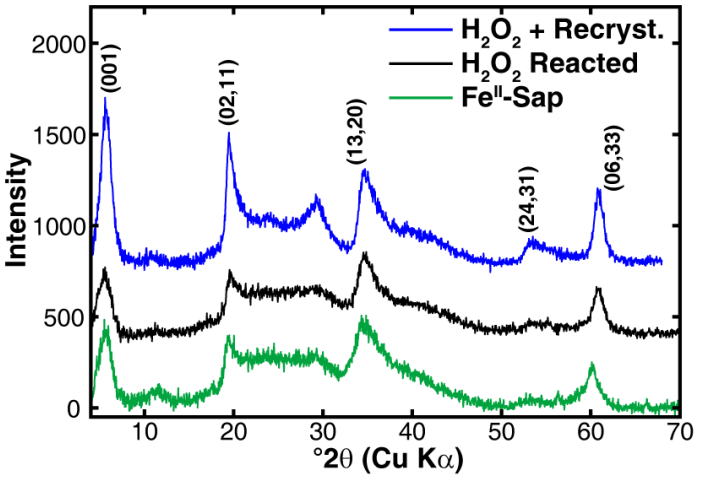


- Fe(II) smectites were synthesized to span the range of compositions observed in unoxidized altered oceanic crust
- XRD peak positions and VNIR metal-OH bands vary systematically with compositions
  - Fe(II) smectites have weaker reflectance spectral features than Mg smectites

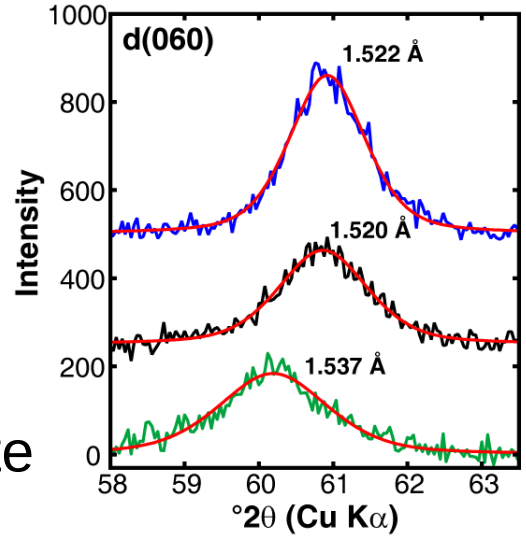
Fate of Fe(II)-Smectites Upon Exposure to Hydrogen Peroxide



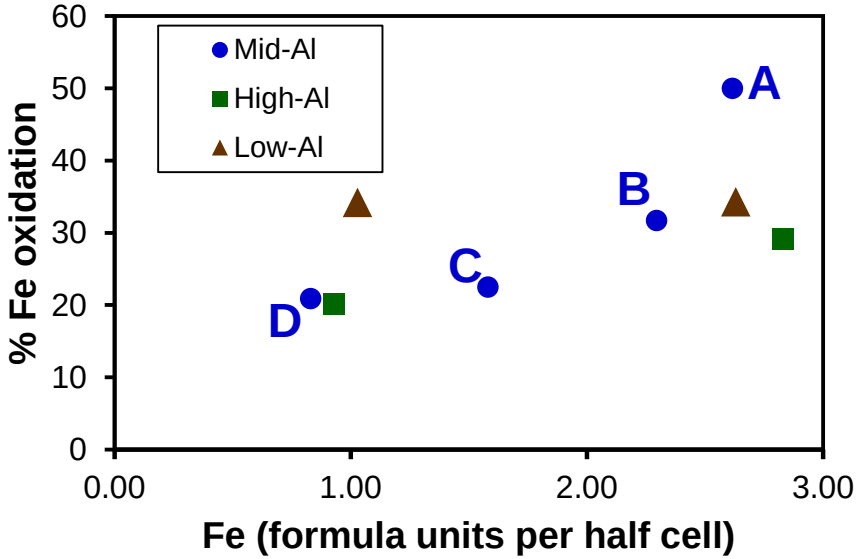




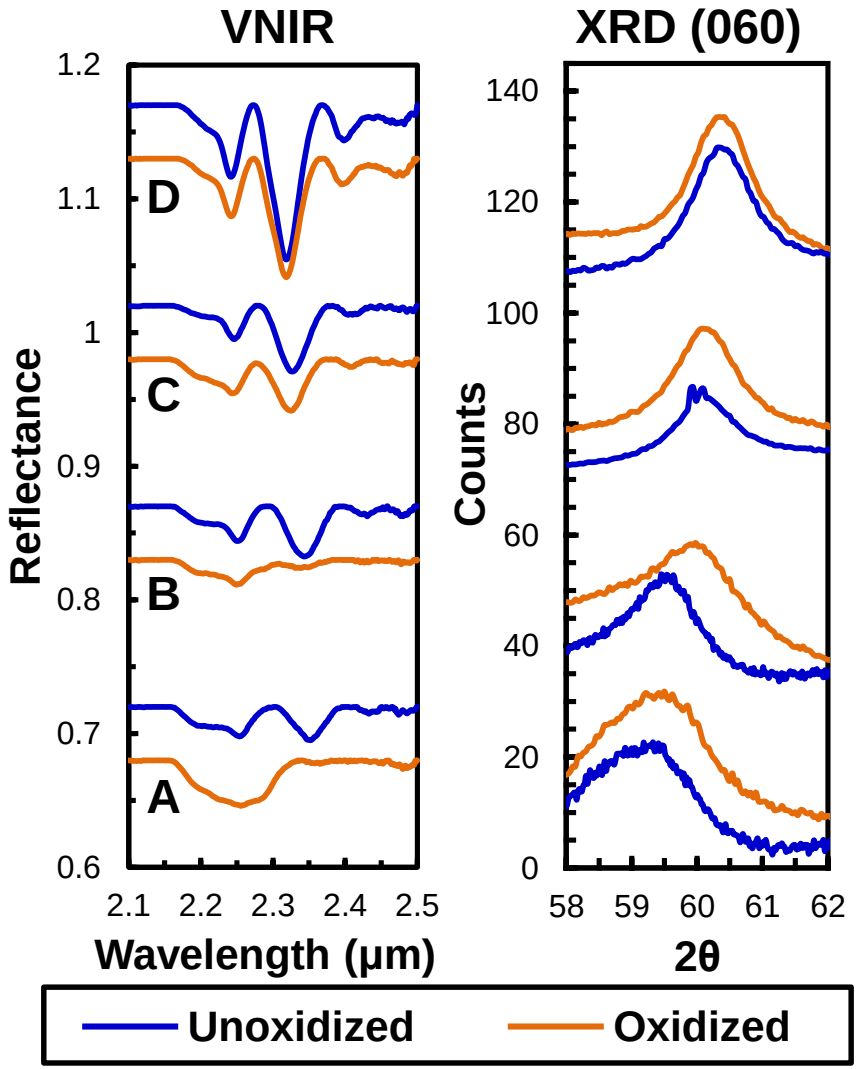
- X-ray absorption spectroscopy shows that H_2O_2 causes rapid, complete Fe oxidation
  - About half of Fe is ejected from octahedral sheet, likely forming ferrihydrite nanoparticles
  - 2:1 smectite structure is always maintained
- Recrystallization produces an Fe(III)-smectite



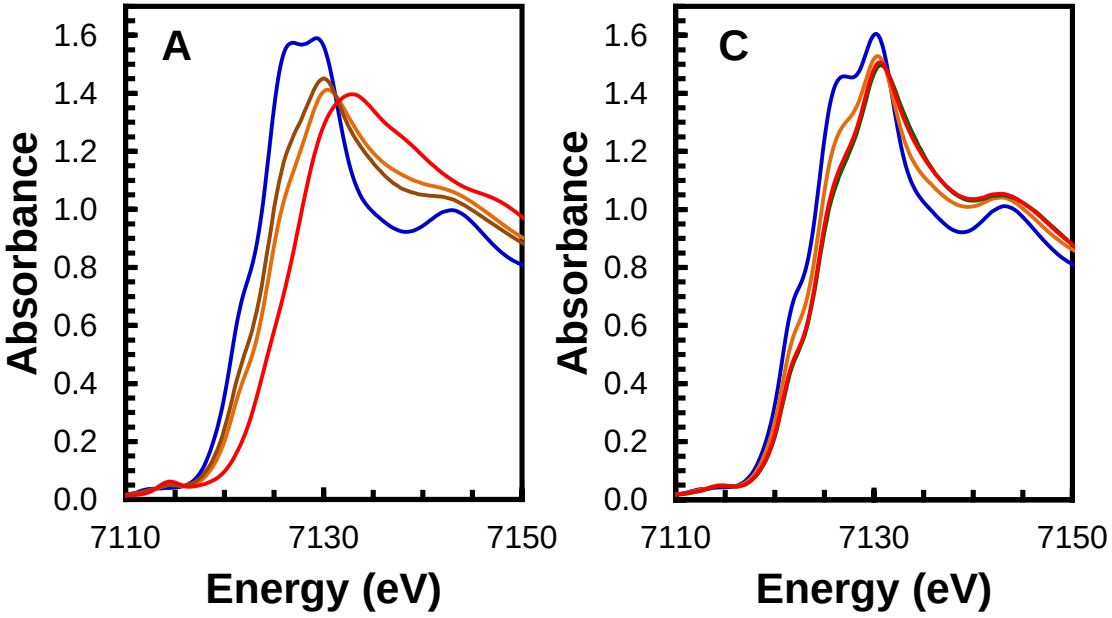
Fate of Fe(II)-Smectites Upon Exposure to Molecular Oxygen: Initial Oxidation

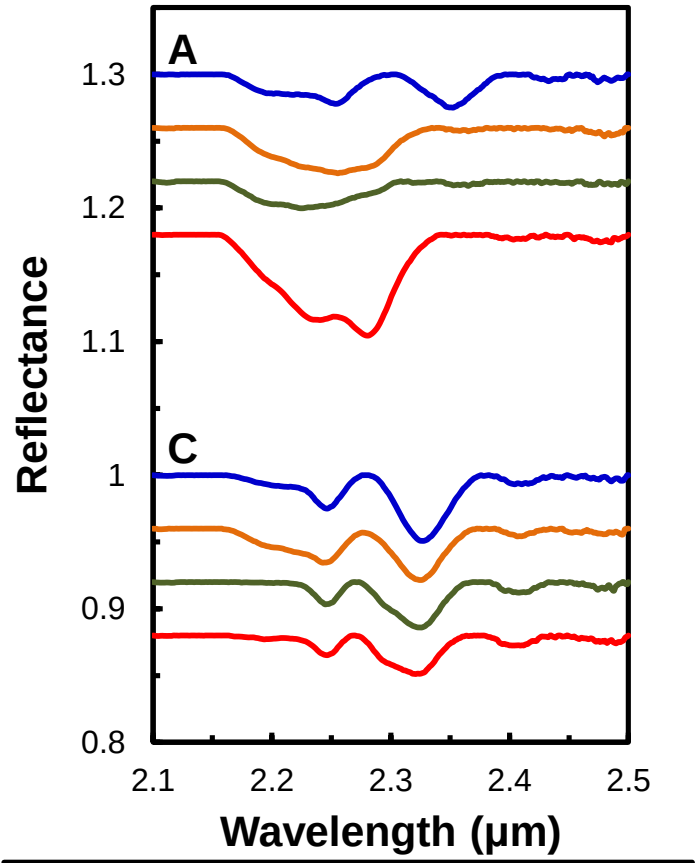


- Exposure to dissolved O_2 for 1 week only partially oxidizes clay
  - Most of this oxidation occurs in 1 day
- Smectite structure preserved
  - Lattice parameter shifts and changes in VNIR reflectance spectra limited to high Fe clays



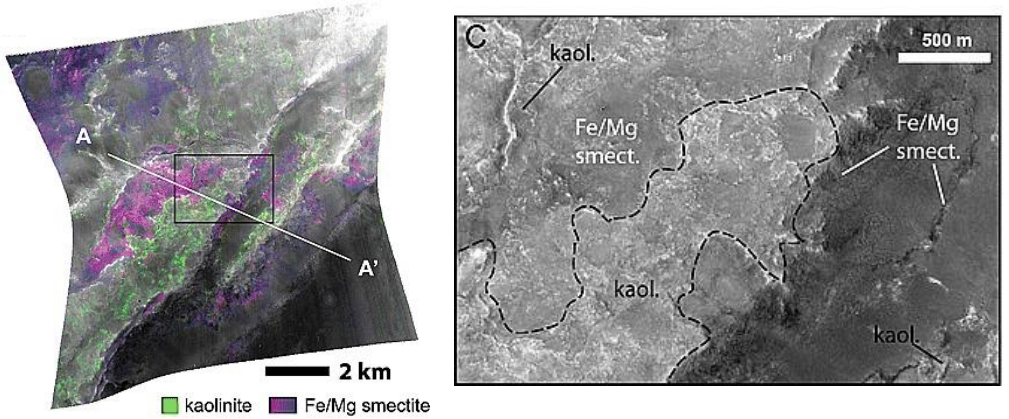
Fate of Fe(II)-Smectites Upon Exposure to Molecular Oxygen: Aging Effects





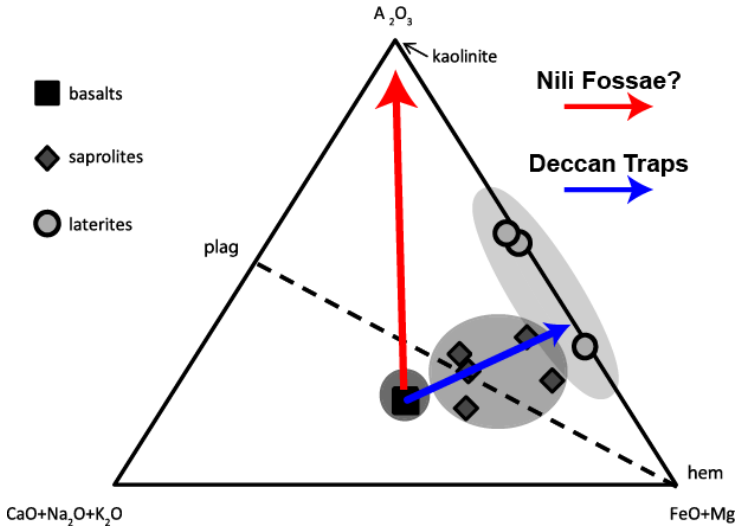
- Recrystallization of Fe(II)-smectites relaxes the structure, allowing further oxidation
- Smectites with higher initial Fe(II) content show greater total oxidation
  - VNIR changes only seen in high-Fe clays

Relevance to Observations on Mars



Kaolinite Capping Fe/Mg Smectites in Nili Fossae

Grey Sheepbed Drill Cuttings

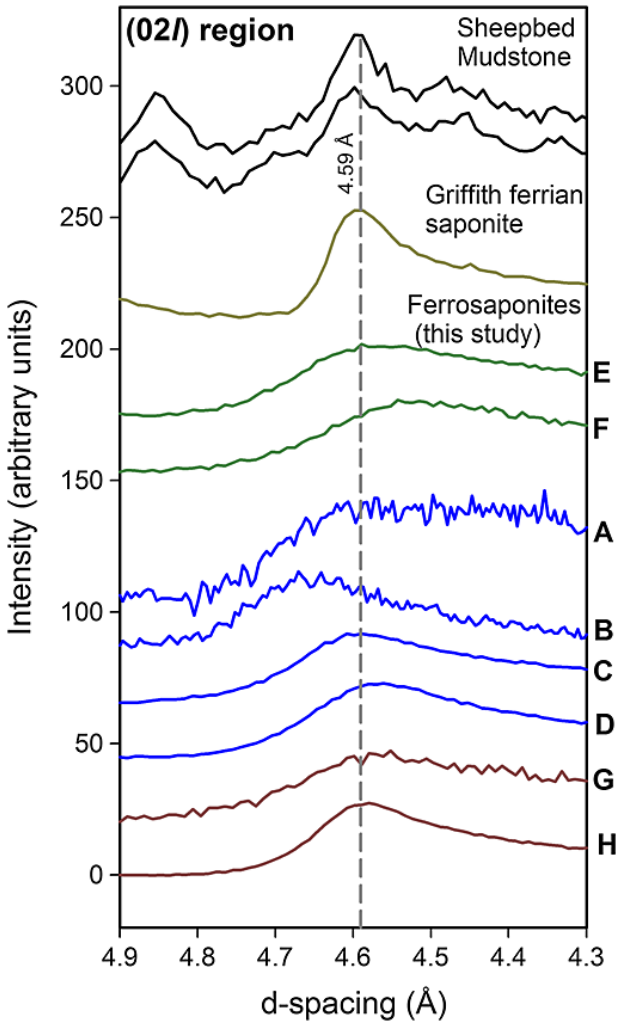


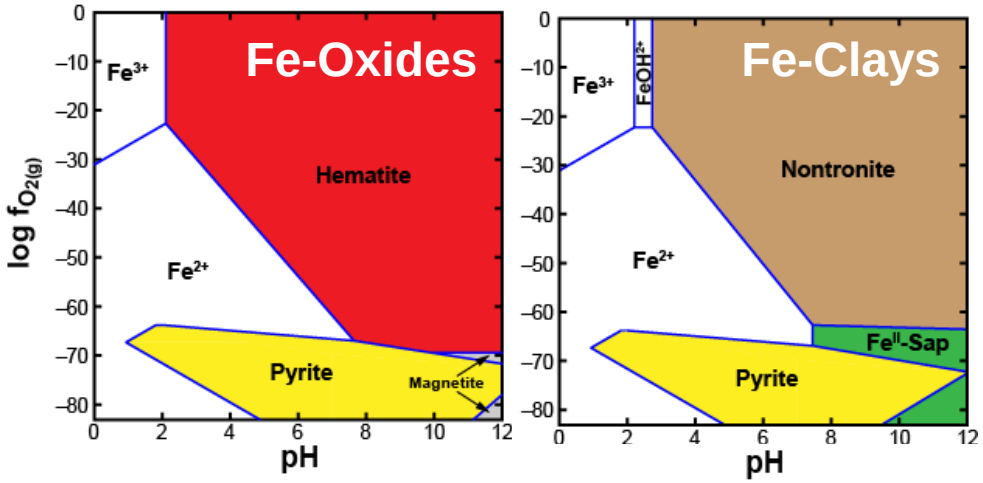
Possible Distinct Chemical Trend in Weathering in the Deccan Traps versus Nili Fossae

- Al-clay horizons overlying Fe/Mg smectite units may indicate anoxic leaching
  - Leaching at Deccan Traps produces abundant Fe oxides
  - Suggests distinct weathering pathway
- Gray drill cuttings from Sheepbed Mudstone suggest reduced Fe

Images from: Ehlmann et al. (2009) *JGR*; NASA
After: Greenberger et al. (2012) *JGR*

Comparison to and Assessment of Clays in the Sheepbed Mudstone





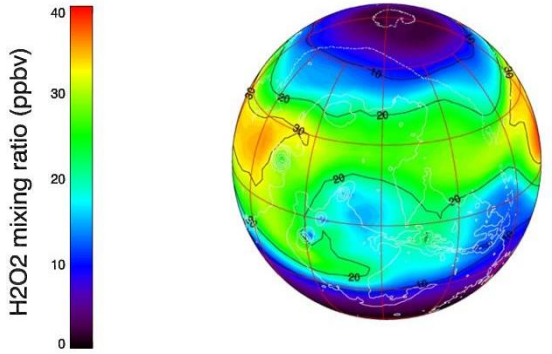
- Smectites observed by ChemMin at Gale Crater need not be oxidized to explain XRD features
- A mineral assemblage containing Fe sulfides and magnetite is in the Fe(II)-saponite stability field
  - Griffithite is not thermodynamically stable versus Fe(II)-saponite or nontronite
- The Sheepbed mudstone may have been formed under anoxic conditions

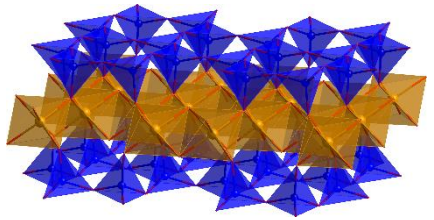
Chemtob et al. (2015) *JGR;* Chemtob et al., in preparation

Widespread Clay Formation on Mars May Predate Planetary Oxidation

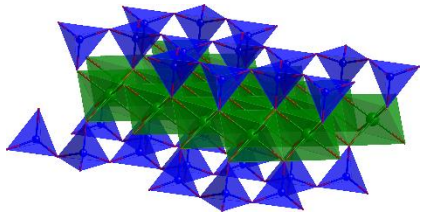
- Anoxic alteration of basalt produces Fe(II)-smectites
- Mars surface experiences substantial oxidation today (H_2O_2 deposition, 0.14% O_2 in atm.)
  - Fe(II)-smectites cannot persists if exposed at the surface; Oxidize to Fe(III)-smectites
- Fe(III)-smectites observed today do not indicate oxidizing conditions in the past
  - Orbital and rover observations can be explained by anoxic conditions at time of deposition/alteration
- The past redox state of Mars cannot be assessed by examining surficial materials
  - Reflectance spectroscopy senses top few microns; Biased towards oxidized materials
- ***An accurate geologic record of past conditions is likely only accessible in the subsurface***

July 3, 2014 – Ls = 156°
GCM H_2O_2/CO_2 mixing ratio





Ferric Clays on Surface



Ferrous Clays in Subsurface?

H_2O_2 Image from: Encrenaz et al. (2014) *A&A*