Ferrous Smectites and the Redox Evolution of Early Mars

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Ample Evidence of Widespread Surface Oxidation of Mars Today

- 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 $N_2$, $CO_2$, $H_2O$

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*
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 $P_{CO_2}$
- Oxidation of these assemblages produce nontronite [Fe(III)-smectite] and hematite
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
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.

Chentob et al. (2015) JGR
X-ray absorption spectroscopy shows that H$_2$O$_2$ 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\textsubscript{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
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

- 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


Kaolinite Capping Fe/Mg Smectites in Nili Fossae

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

Earth and Planetary Sciences • Washington University
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

Chermob et al. (2015) JGR; Chermob 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 persist 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**

_H$_2$O$_2$ Image from: Encrenаз et al. (2014) A&A_