Clay Minerals and the Habitability of Early Mars

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Both the rocks exposed on the surface and the ubiquitous dust are red from hematite and other iron oxides.

Widely Distributed Minerals Indicated Acidic Waters were Once Present

Jarosite Identified in Aeolian Sediments at Meridiani Planum

Fe$_2$(SO$_4$)$_3$ Beneath a Hematite Layer at Home Plate, Gusev Crater

- Iron sulfate minerals indicate pH conditions of 3 (jarosite) to <1 (ferric sulfate)

Klingelhoefer et al. (2004); Arvidson et al. (2010)
Magnesium Sulfates and Other Soluble Salts Indicate Abundant Saline Waters

Rocks Have High Sulfate Contents

- Sedimentary rocks that show aqueous activity often contain up to 40 wt.% sulfate salts
- Much of these salts are MgSO$_4$ phases, requiring salinities to form that exceed known habitable limits on Earth

MgSO$_4$ Dissolution Voids

Rieder et al. (2004) Science; Tosca et al. (2008) Science

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Southern Highland Contain Old, Complex Terrain with Craters and Fluvial Channels

- Substantial 3.7 to 4.1 Ga crust (brown) exposed on across the Southern Highlands

Map from: USGS (2014)
The Old, Southern Crust has Diverse Secondary Minerals Indicative of Past Water

Phyllosilicates (clay minerals!) and carbonates indicate neutral to alkaline conditions

Ehlmann and Edwards (2014) AREPS
Terrestrial Clay Minerals are Weathering and Alteration Products

Vertisol, a Smectite-rich Soil

Bentonite Bed (453.1 Ma) in Ordovician Limestone

Ferric Smectite (Nontronite) Vugs in Columbia River Basalt

Many Clay Units are 100s of Meters Thick, Rich in Fe and Mg, and Uniform in Mineralogy

- Thick, uniform units suggest subsurface waters and cannot be produced by acidic leaching

Ehlmann et al. (2009) JGR Planets
Clays on Mars Record the Most Ancient Geological History of the Near-Surface Environment

<table>
<thead>
<tr>
<th>Pre-Noachian</th>
<th>Noachian</th>
<th>Hesperian</th>
<th>Amazonian</th>
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<td>Large impact basins</td>
<td>Volcanic eruptions</td>
<td>High-Mg olivine, circumbasin units</td>
<td>Intermediate olivine basalts</td>
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<td>Martian valley networks</td>
<td>Martian outflow channels</td>
<td>Fe/Mg smectites, chlorites in the crust</td>
<td>Al phyllosilicates</td>
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<td>Intrabasin sulfates, chlorides, carbonates</td>
<td>Sulfate-silica diagenetic/weathering assemblages</td>
<td>Thin film weathering, oxidation</td>
<td></td>
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- Clays are important indicators of past aqueous activity in the near-surface Martian environment.
- Up to 4.1 Ga in age, older than any exposed rocks on Earth.

Ehlmann and Edwards (2014) AREPS
Earth and Planetary Sciences • Washington University
Ancient Iron-Rich Clays on Mars are Highly Oxidized

- Observed clays are primarily smectites rich in ferric iron ($\text{Fe}^{3+}$) and magnesium
- These date to early in the planet’s history: Why?

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

- Ample evidence for non-oxidizing conditions until ~2.4 Ga
  - Example: Detrital pyrite and uraninite deposited in fluvial sediments, Witwatersrand Basin
- Pre-GOE atmosphere dominated by N₂, CO₂, H₂O, possibly CH₄

Climate Models for Early Mars Require Reduced Gases to Stabilize Liquid Water

- Like today, the early atmosphere was dominated by CO$_2$
- This alone cannot provide enough greenhouse warming to explain liquid water on the surface of Mars
- The presence of small amounts of H$_2$ or CH$_4$ enhance warming
- Liquid water on early Mars appears to require a reducing, not oxidizing, atmosphere

Wordsworth et al. (2017) GRL
When was the “Mars Oxidation Event”?

- Clear mineralogical and geomorphic evidence for substantial past water activity on Mars
- The early Earth was not oxidizing, and climate models favor a reducing atmosphere
- Timing of the oxidation of the Fe(II)-rich crust of Mars is uncertain
- How did oxidized clays end up in the most ancient crust of Mars?

Or Like This?

Image from: Wikimedia Commons
Energy Sources for Life Vary with the Redox State of a Planet’s Surface Environment
The Modern Martian Surface is Highly Oxidizing

- UV light (no ozone layer), hydrogen peroxide, reactive oxygen species, and oxychlorine compounds (i.e., bleach) all readily oxidize the shallow soil
Does a Less Oxidized Mars Hide Beneath the Surface?

- Drilling at Gale Crater reveals grey sedimentary rocks a few cm below the surface.
- X-ray diffraction reveals that these contain clays.
- On Earth, the grey color seen in multiple drill cuttings generally indicates reduced sediments.

Image from: Vaniman et al. (2014) *Science*
Mixed Fe(II)-Mg smectite form in the oceanic crust under anoxic conditions, but these are poorly characterized
  – Difficult to recover without oxidizing, exceptionally rare occurrence on land

Key knowledge gaps remain: (1) **What smectite compositions form through anoxic alteration?** (2) **What is their susceptibility to oxidation?** (3) **What products form when these clays oxidize?**
Experimental and Thermodynamic Insight into Anoxic Clay Formation
Differences in Clays Between Continental and Marine Systems

Clay mineralogy often differs between continental and marine setting because it reflects the primary rock composition:

- **Granitic** to intermediate igneous rocks yield *Al-rich clays*: Montmorillonite, Beidellite, Kaolinite
- **Basaltic** compositions (like the Martian crust!) favor *Fe/Mg-rich clays*: Nontronite, Saponite

Figures from: Meunier et al. (2008) *Clays Clay Min.*; After White et al. (2001) *GCA*
Anoxic Alteration Predicted to Yield Fe(II)-Mg Smectites Except in Highly Leached Systems

- Fe(II)-Mg saponites are the dominant alteration products at moderate CO$_2$ levels
- Minor carbonate content may be overestimated in model: CO$_2$ partial pressure drops in subsurface during weathering or alteration
- High water:rock ratios, corresponding to large water volumes or limited rock reactivity, generates Al-clays

From: Catalano (2013) JGR
Experimental Clay Formation during Anoxic Basalt Alteration

- Weathering of basalts to clays takes decades: Longer than the career of a graduate student!
- Hydrothermal alteration provides a tractable route to explore clay formation in the laboratory
- Primary grains are coated in leafy rims after alteration at 200°C for 21 days under anoxic conditions

Data for North Carolina Dolerite DNC-1a

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Hydrothermal alteration under anoxic conditions produces features in X-ray diffraction patterns indicative of trioctahedral smectites.

Olivine peaks substantially decrease in intensity.

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Hydrothermal alteration under anoxic conditions produces features in X-ray diffraction patterns indicative of trioctahedral smectites.

Olivine peaks substantially decrease in intensity.
Olivine is nearly completely altered, with minor consumption of feldspar and pyroxene.
Tracking the Fate of Iron Using X-ray Absorption Spectroscopy (XAS)

- XAS is an element-specific spectroscopy conducted at a synchrotron.
- Spectra shift to the right (higher energy) as the oxidation state increases:
  - Olivine: Fe(II)
  - Hematite: Fe(III)
- Even when the oxidation state is the same, fine structure differences can indicate the element’s host: Smectite vs. olivine.
Iron in the unaltered basalts is primarily contained in olivine, pyroxene (augite), and magnetite.

The absorption edge position does not shift after alteration: Still largely Fe(II).

Fine-structure indicates that Fe(II) enters the neoformed smectite identified by XRD.
Clay rims yields a structural formula of a trioctahedral smectite:

$$\text{Ca}_{0.27}\text{Na}_{0.03}\text{K}_{0.01}(\text{Fe}^{II}_{1.09}\text{Mg}_{1.25}\text{Al}_{0.41}\text{Mn}_{0.02})\text{(Si}_{3.46}\text{Al}_{0.54})\text{O}_{10}(\text{OH})_{2}$$

- While olivine may nucleate smectites, it lacks Al and Ca and is too Si-deficient to form this clay by itself
  - Indicates contributions from dissolution of feldspar and possibly pyroxene
Smectites in Altered Basalts are Structurally Similar to Clays Recently Identified on Mars

- MSL Curiosity provided the first structural characterization of clays on Mars using its CheMin instrument.
- The resulting XRD patterns do not match terrestrial clay standards, but are more similar to clays produced during our basalt alteration.

XRD data from: Vaniman et al. (2014) Science
Smectites in Altered Basalt are an Imperfect Spectral Match to Mars

- Smectite clays are often characterized from orbit by their reflectance spectra
- These often show a main absorbance feature between 2.28 and 2.30 μm
- Clays in altered basalts are dominated by a feature at 2.32 μm
- Are differences related to composition (e.g., Fe content) or the lack of exposure to oxidants?

Spectra from: Michalski et al. (2015) EPSL

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Systematic Mineralogy of Ferrous Smectites
Clays identified in altered rocks on Earth show a wide compositional range poorly reflected by common clay standards.

Most studied by microanalysis, difficult to obtain bulk samples, especially without oxidizing iron in the clays.

Published sol-gel methods were thus adapted to synthesize Fe(II)-smectites representative of natural samples.
Syntheses Yield Mineralogically-Pure Smectites

- Trioctahedral smectites produced for all compositions
- XRD peak positions vary systematically with composition
- Clays C, D, and F most similar to that formed in basalt alteration experiments
- Near-complete solid solution occurs
  - All smectites are single phase except B & G

Chemtob et al. (2015) JGR
Visible and Near Infrared (VNIR) Reflectance Spectra Vary Systematically with Composition

- Bands at ~1.4 μm and 2.2-2.4 μm show systematic shifts with composition
- The (Mg,Fe)$_3$-OH band shifts from 2.32 to 2.36 μm with increasing Fe(II)
- Bands weaken with increasing Fe(II) content
  - Mg dominates spectral properties
  - Substantial Al bands also observable

Chemtob et al. (2015) JGR
Mixed Fe(II)-Mg Synthetic Smectites Similar to Smectite Formed via Basalt Alteration

- Combination bands in reflectance spectra have primary absorbance near $2.32 \, \mu m$, similar to synthetic smectite D
- (06,33) reflection ($d = 1.538 \, \text{Å}$) in XRD similar to smectite C
- Mixed Fe(II)-Mg trioctahedral smectites are the best analogue compositions for probing chemical behavior of smectites in altered basalts
Oxidation of Anoxic Clays
Reminder: Clays Observed are the Surface of Mars Appear to be Mixed Fe(III) & Mg Smectites

- The conclusion of a range of orbital studies is that smectites on Mars are mixtures of nontronite [Fe(III)] and saponite [Mg]

- But the surface is coated in reactive oxidants, and Fe(II)-rich clays may not persist without oxidizing
Extent of Fe(II) Oxidation in Smectites Varies with the Oxidant

Our synthetic smectites were reacted with oxidants known to occur on Mars.

XAS shows that H$_2$O$_2$ causes rapid, complete Fe oxidation.

Reaction with dissolved O$_2$ only causes partial oxidation, forming a mixed Fe(II)-Fe(III) clay.

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Chemtob et al. (2017) JGR Planets
Rates and Products of Fe(II)-Mg Smectite Oxidation Vary with Oxidant and Composition

- Oxidation in air-saturated water partially converts structural Fe$^{2+}$ to Fe$^{3+}$ after 1 week
  - No oxides, including magnetite, are produced, all Fe remains in smectite
  - Likely greater, yet still incomplete, oxidation after longer reaction times
- Peroxide causes rapid, complete oxidation
  - Yields an Fe(III)-bearing smectite plus hematite nanoparticles

Chemtob et al. (2017) JGR
Diffraction and Spectral Features Associated with Oxidation

- Partial oxidation by dissolved O$_2$ produces little change in XRD reflection and VNIR absorbance bands
- Complete oxidation by H$_2$O$_2$ causes clear structural and spectral shifts, producing features similar to a mixture of Fe(III) and Mg smectites

Chemtob et al. (2017) JGR
Clays Formed via Basalt Alteration and Subsequent Oxidation Reproduce the Range of Spectral Features of Mars Clays

- Main absorbances in reflectance spectra of oxidized clays range from 2.285 to 2.320 μm.
- This mirrors the spectra seen from orbit in clay-rich terrains on Mars.

Spectra from: Michalski et al. (2015) EPSL
Non-Coeval Formation and Oxidation of Clays on Mars Allows for a Complex Atmospheric History

- Oxidation preserves the smectite structure but generates substantial ferric iron in the clay
  - Resulting spectra are consistent with orbital observations
- Our experimental studies demonstrate that clay formation and iron oxidation need not be coeval, and possibly could be separated by large gaps in geologic time
- Oxidized clays in ancient terrains on Mars thus do not indicate that an oxidizing atmosphere was present ~4 Ga
Possible Concurring Observations and Implications
Multiple Alteration Events in Gale Crater
Sedimentary Rocks

- Lacustrine mudstones in Gale Crater contain diverse secondary minerals
- The assemblages found are often clearly out of equilibrium
- This suggests multiple alteration events, with oxidation occurring late

Mineralogy from: Vaniman et al. (2014) Science
K-Ar dating of the jarosite-bearing Mojave 2 samples in Gale Crater yield a young (2.12 Ga) and old (4.07 Ga) component
- ~2 Ga age attributed to the jarosite, older component consistent with feldspar

Even after accounting for possible Ar loss, the data indicates that jarosite formed long (>500 Myr) after the lake dried up and sediments were buried

Consistent with oxidation being a late process in the aqueous history of Mars

Martin et al. (2017) *JGR Planets*
Leaching Profiles Suggest Weathering Under Anoxic Conditions

Comparison of leaching profiles on clay stratigraphies on Earth and Mars suggest different redox conditions

- Deccan Traps: Weathering produces Al-clays plus iron oxides
- Nili Fossae, Mars: Al-clay horizons are depleted in iron

Low Fe abundance cannot occur under oxidizing conditions: $\text{Fe}^{3+}$ and $\text{Al}^{3+}$ have similar solubility
The Mars 2020 rover will explore a large delta complex in Jezero Crater that contains abundant Fe/Mg smectites.
Implications: Anoxic Early Mars may have Generated Substantial Hydrogen Gas

**H₂ from Serpentinization and Radiolysis**
Tarnes et al. (2018) *EPSL*

**Groundwater-Lake Water Mixing Produces Magnetite and H₂**

- Serpentinization, radiolysis, and magnetite precipitation may have produced copious quantities of hydrogen gas in groundwater and lakes
Anaerobic Life Strategies: Focus of Our Search for Biosignatures on Mars

- Metabolisms on the early Earth were dominated by anaerobic processes.
- Genomic evidence suggests the most ancient pathways for energy production involved H₂.
- If early Mars was anoxic, then the search for past life on Mars should focus on biosignatures of H₂-based metabolisms.
Potential Timing of the “Mars Oxidation Event”?  

- The atmospheric pressure of early Mars was higher  
  - Large fraction of gases have been lost to space*
- Photodissociation of H$_2$O vapor forms H atoms that escape the atmosphere, desiccating the surface
- This leaves behind O-bearing oxidants
- The drying of Mars and the rusting of Mars may thus have been coeval
- Such an event would have substantially altered the habitability of early Mars

*See: Jakosky et al. (2018) Icarus