FE-SULFATES ON MARS:
Considerations for Martian Environmental Conditions, Mars Sample Return & Hazards

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Evidence for Fe-sulfates on Mars

- Fe-sulfates indicate (limited) water
- Sensitive to environmental conditions
- To preserve / unravel mineralogy during sample return we need to know how Fe-sulfates behave under different environmental conditions
Fe$^{3+}$-salts at Gusev Crater

**Variety of localities, Gusev Crater** (Johnson et al., 2007)
1. Visible-near IR – spectral deconvolution

**Paso Robles soil, Gusev Crater** (Lane et al., 2008)
2. Visible-near IR spectral matching
3. Thermal IR spectral deconvolution
4. Mössbauer spectral matching
5. Constraints from APXS... v. low K & Na

<table>
<thead>
<tr>
<th>Paso Robles (Sol 400, P2551)</th>
<th>Arad (Sol 721, P2538)</th>
<th>Tyrone (Sol 790, P2531)</th>
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<tbody>
<tr>
<td><img src="image" alt="Paso Robles image" /></td>
<td><img src="image" alt="Arad image" /></td>
<td><img src="image" alt="Tyrone image" /></td>
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**FOV**
- Paso Robles: ~25 cm
- Arad: ~60 cm
- Tyrone: ~65 cm

False-color images from Gusev Crater (blue=432 nm, green=535 nm, red=754 nm) Johnson et al. (2007)
| Fe-sulfates identified with ≥ 4 methods | ** | Ferricopiapite | $\text{Fe}^{3+} _{4.6}(\text{SO}_4)_6(\text{OH})_2\cdot20\text{H}_2\text{O}$ | (Para)coquimbite | $\text{Fe}^{3+} _2(\text{SO}_4)_3\cdot9\text{H}_2\text{O}$ | Fibroferrite | $\text{Fe}^{3+}\text{SO}_4(\text{OH})\cdot5\text{H}_2\text{O}$ |
| --- | --- | --- | --- | --- | --- |
| Fe-sulfates identified with ≥ 3 methods |  | Parabutlerite | $\text{Fe}^{3+}(\text{SO}_4)(\text{OH})\cdot2\text{H}_2\text{O}$ | Rhomboclase | $(\text{H}_3\text{O})\text{Fe}^{3+}(\text{SO}_4)_2\cdot3\text{H}_2\text{O}$ |
| Fe-sulfates identified with ≥ 1 method |  | $\text{H}_3\text{O}^+\text{jarosite}$ | $\text{H}_3\text{O}^+\text{Fe}^{3+} _6(\text{SO}_4)_4(\text{OH})_{12}$ | Bilinite | $\text{Fe}^{2+}\text{Fe}^{3+} _2(\text{SO}_4)_4\cdot22\text{H}_2\text{O}$ | Butlerite | $\text{Fe}^{3+}(\text{SO}_4)(\text{OH})\cdot2\text{H}_2\text{O}$ | Metahohmannite | $\text{Fe}^{3+} _2(\text{SO}_4)_2\text{O}\cdot4\text{H}_2\text{O}$ |
Bulk chemistry of the precipitating solution

Solutions in equilibrium with ferricopiapite-coquimbite have wt% Fe$_2$O$_3$ : H$_2$O : SO$_3$ = 8-20 : 52-60 : 25-32

Mol% Fe / SO$_4$ ~ 0.5

Modified from Merwin & Posnjak (1937)
Forming Fe-S-O-H phases

Addition of H₂SO₄ to basalt via volcanic/hydrothermal SO₂

Oxidation & hydration of Fe sulfides to produce Fe²⁺ & SO₄²⁻/HSO₄⁻

Fe²⁺-sulfates e.g. melanterite

Summarized in King & McSween (2005)
Forming Fe-S-O-H phases

note- not like Ca- or Mg-sulfates

Modified after King & McSween (2005)
Fe$^{3+}$-sulfates via dehydration-oxidation-neutralization

Modified after King & McSween (2005)
Thermodynamic modeling

• Thermodynamic database & compositions chosen have strong influence on results

• We used
  39 minerals & species, plus
  • $a_{Fe}=0.3$, $a_{HSO_4^{-}}=a_{SO_4^{2-}}=0.08$ based on Paso Robles soils
  • Fe-S-O aqueous species *not* suppressed
Oxidation-dehydration diagram, pH = 1

Ferricopiapite - with 20H$_2$O
- only stable at high $\log a$H$_2$O
- fO$_2$ has a minor effect on its stability

Ferricopiapite: Fe(SO$_4$)$_2$
Oxidation-neutralization diagram, \( \log aH_2O = 0 \)

- Ferricopiapite
  - \( pH \sim 0.5 \) to 2

If \( HSO_4^- \) or \( SO_4^{2-} \) increased:
  - S-mineral fields extend to lower pH
  - + Melanterite
  - + Rhomboclase
Oxidation-neutralization diagram

\[ \log a_{H_2O} = 0, \text{ oxides suppressed} \]

- Ferricopiapite
  - pH ~ 0.5 to 2.5

- SUITES of minerals help us to better determine environmental conditions

- Addition of K & P stabilizes K-jarosite & strengite

- Ferri-copiapite
- Schwertmannite
- Bilinite
- FeSO\(_4\)
- FeSO\(_4\)\(^+\)
- FeSO\(_4\)\(^{++}\)
- FeHSO\(_4\)\(^{++}\)
- Fe\(^{++}\)

25°C
Summary of Fe$^{3+}$-sulfate stability with Paso Robles composition solutions

**Ferricopiapite**
$pH<2.5$, $RH>~90\%$, $logfO_2>-30$

*(Para)coquimbite* difficult to form

Fibroferrite & *(para)butlerite* no thermodynamic data, we know $logaH_2O/pH$, but we don’t know the lines’ intercepts

Rhomboclase forms at more acidic, S-rich conditions
Temperature effects on a dehydration-neutralization diagram.
Recommendations for Fe-sulfate return

**Sample Containment**
- Fe	extsuperscript{2+}-(Fe	extsuperscript{3+})-sulfates: fO	extsubscript{2} variations important
- Fe	extsuperscript{3+} sulfates - fO	extsubscript{2} variations not v. important
- Relative humidity: seal samples in containers on Mars
  (know moles of O\textsubscript{2} + aH\textsubscript{2}O, calculate volume of martian air needed to keep minerals stable using PV = nRT). Understand that changes may occur, but know how to account for it.
- Temperature dependence of reactions: limited C\textsubscript{p} data- need more
- Sulfates may get “sticky” or “clump”, form acids, or Fe-oxides/hydroxides/oxyhydroxides
- Engineering & cost concerns aside:
  - Put samples in separate containers
  - Use acid-resistant materials
  - Use lids & insulation
  - Enclose a T-RH-P data logger
To maximize information from returned Fe-sulfates we need to

**Understand Environmental Conditions**
- Need to be able to characterization small Fe-sulfates, so we can determine environmental conditions
- Understand reaction kinetics of small particles (with high surface/volume)
- Have more thermodynamic data for Fe$^{3+}$-sulfate & phosphate phases & possible gels/deliquescence products
- Understand that disequilibrium may have occurred

**Unravel Habitability**
- Need to know effects of solution bulk composition, pH, fO$_2$ & aH$_2$O on life
- Understand radiation shielding properties of Fe-sulfates in protecting any life
Summary

• Thermodynamic models are useful for constraining environmental conditions & optimal conditions for sample return, especially if suites of Fe-sulfate minerals are identified.

• Ferricopiapite, if present, occurs at pH<2.5, RH>~90%, logfO₂>-30

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Fe-sulfate hazards

Fe\(^{2+}\)-sulfates - not very toxic

Fe\(^{3+}\)-sulfates - toxic

- Overall, likely insufficient volume to be extremely hazardous (see abstract)
- Acid Fe-sulfates may produce irritation if ingested, inhaled or touched

\[\text{Fe}^{3+}(\text{H}_2\text{SO}_4)(\text{OH})(\text{SO}_4).3\text{H}_2\text{O} \rightarrow \text{rhombooclase}\]

\[\text{H}^+ + 2\text{SO}_4^{2-} + \text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{acid}\]