Experimental Studies of Iron Smectite Oxidative Alteration

- An Fe(II)-saponite was synthesized using a sol-gel method and then oxidized by O₂ or H₂O₂ sub- samples were hydrothermally recrystallized.
- The initial clay had a formula of: Ca₂⁺Na₂⁺Mg⁺⁺Fe³⁺⁺Al⁺⁺₂(Al⁺⁺,Si⁺⁺)₂O₃(OH)₆
- Oxidation by H₂O₂ was rapid but structurally disruptive.
- H₂O₂ oxidized >90% of the structural Fe(II) (Fig. 1)
- EXAFS spectra (not shown) demonstrate that much of the oxidized Fe was ejected from the smectite structure, although the outer sheet structure was preserved (Fig. 1)
- Recrystallization produced an Fe-bearing dioctahedral smectite (Fig. 1)

- Oxidation by O₂ was slower and incomplete but maintained the structure.
- 21% of the structural Fe(II) was oxidized in 1 day and 37% in 6 days (Fig. 2)
- Oxidation preserved the saponite structure with little apparent change in lattice parameters (Fig. 2)
- Recrystallization resulted in the exsolution of a dioctahedral smectite, with the extent of exsolution correlated with the fraction of Fe(II) that was oxidized (Fig. 2)

- These studies show that Mars-relevant oxidants are capable of oxidatively altering precursor ferrous smectites into ferric smectites (Fig. 3)
- Complete oxidation without allowing the structure to relax is disruptive and appears unfavorable in the absence of a strong oxidant.
- The lack of octahedral vacancy sites in trioctahedral smectites appears to limit the extent of oxidation or, if complete oxidation is forced, results in Fe ejection.
- Structural relaxations that accompany recrystallization appear to be important in generating ferric smectites through oxidation; complete oxidation and conversion to ferric smectites is likely possible if given enough time for the structure to accommodate the smaller, high charge Fe(III) cation.

Thermodynamic Modeling of Clay Formation During Basalt Alteration and Oxidation

- Basalt weathering under oxic conditions produced hematite at high W:R, nontronite at intermediate W:R, and Mg-saponite, and hematite mixtures at lower W:R
- Minor kaolinite, montmorillonite, or calcite form under limited conditions
- Weathering under high (0.1 bar) CO₂ conditions (not shown) trapped Mg in carbonates, preventing saponite formation; nontronite formation was unaffected.
- Oxidation of weathering products formed under anoxic conditions produced mixtures of nontronite and Mg-saponite
- Hematite was predicted to form under some conditions
- While oxidative weathering of basalt can produce smectite clays consistent with the compositions identified on Mars from orbit, other pathways also produce similar assemblages.

Conclusions

- Observation of ferric smectites in Noachian-aged deposits via remote sensing does not demonstrate that the early Martian atmosphere was capable of extensive iron oxidation.
- Thermodynamic modeling predicts that later oxidative alteration of precursor ferrous iron phyllosilicates, formed through either anoxic weathering or hydrothermal alteration, can produce such ferric smectites.
- Experimental analogue studies show that ferrous saponites, the product of basalt weathering under anoxic conditions, can be oxidatively altered into ferric smectites by Mars-relevant oxidants.
- Ferric smectites observed today may thus be poor indicators of conditions on early Mars; if ferric smectites can be found than these would likely be unaltered Noachian-aged weathering products.

References


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