Oxidative transformations of ferrous iron smectites on Mars

S. M. CHEMTOB[1*], V. RIVERA-BANUCHI[1], S. KAMALI[2], J. G. CATALANO[3], R. V. MORRIS[4], D. G. AGRESTI[5], W. LIU[6], N. YEE[6]

[1]Temple U., Philadelphia, PA (*chemtob@temple.edu) [2]U. Tenn. Space Institute, Tullahoma, TN; [3]Washington U., St. Louis, MO; [4]NASA JSC, Houston, TX: [5]U. Alabama, Birmingham, AL; [6]Rutgers U., New Brunswick, NJ.

Fe-Mg smectites in Noachian terrains on Mars represent the products of fluid interaction with Martian basaltic crust; additionally, their iron oxidation state may help constrain the planet's trajectory of oxidative evolution. The Noachian atmosphere, like the Archean atmosphere of Earth, was likely anoxic [1]. Under such conditions, ferrous smectites are the predicted products of basalt weathering [2]; however, many orbitally detected Fe-bearing clay minerals are ferric nontronites. Possible mechanisms for producing nontronite from ferrous smectite precursors include a) Fe oxidation paired with H_2O reduction; b) UV photooxidation; c) exposure to chemically oxidizing fluids or atmosphere after Martian oxidative evolution.

We conducted experimental studies to test the plausibility of these oxidative pathways for nontronite formation from ferrous smectites [3,4]. After 7 days of exposure to air-saturated solution, synthetic ferrous smectites demonstrated incomplete Fe oxidation (24-38% Fe^{3+}) and associated contraction of the octahedral sheet. Complete oxidation was possible only after hydrothermal recrystallization, which accelerated charge redistribution in the octahedral sheet. A fraction of Fe^{3+} was ejected from the smectite structure, producing byproduct Fe oxyhydroxides or hematite. Fully oxidized ferrous smectites spectrally resembled nontronite.

Oxidative transformations were also observed in the absence of an aqueous medium. A high-Fe ferrous smectite exposed to air for 5 days had 85% Fe^{3+} and VNIR spectra consistent with nontronite. Evolved gas analyses of air-oxidized smectite show diminishment of dehydroxylation peaks at 500-600° C, suggesting major structural disruption.

In photooxidation experiments, smectite suspensions irradiated for 120 hrs with a Hg UV lamp showed modest increases (10-20% Fe^{3+}) in ferric iron content. Neoformed secondary oxides were not detected by XRD or room-temperature Mössbauer; however, MB spectra collected at 6 K show broad magnetic sextets in UV-oxidized samples, indicating changes in Fe coordination.

[1] Sholes et al. (2017) *Icarus*, 290, 46. [2] Catalano (2013) *JGR*, 118, 2124. [3] Chemtob et al. (2015) *JGR*, 120, 1119. [4] Chemtob et al. (2017), *JGR*, 122, 2469.