

CLAY MINERALOGY AS A GUIDE TO ALTERATION ENVIRONMENTS ON MARS. D. L. Bish¹ and D. T. Vaniman², ¹Department of Geological Sciences, Indiana University, 1001 E. 10th St., Bloomington, IN 47405; bish@indiana.edu, ²Los Alamos National Laboratory, MS D462, Los Alamos, NM 87545; vaniman@lanl.gov

Introduction: The possibility of a Mars sample return mission to continue NASA's "Follow the Water" strategy focuses new attention on hydrous environments and the minerals formed in them. In order to understand the evolution of Mars, it is useful to sample assemblages that can provide information on the evolution of the martian atmosphere, the nature of martian surface processes, and the thermal-magmatic evolution of the martian mantle and crust. Orbital and surface-derived data have greatly expanded our understanding of Mars' surface and have shown that hydrous minerals are far more common than previously imagined. Geologists traditionally "read the rocks" to interpret geologic history, and the process involves consideration of textures, assemblages, and mineralogy (and faunal and floral evidence on Earth). The focus of any sample return mission to Mars must be on locales that have the potential to maximize the return of *new* geological information and to provide data that will give us so-called ground-truth information for further interpretation of existing orbital and surface data.

Mars' surface mineralogy holds clues to its hydrologic and geochemical histories and can constrain past alteration processes. Based on early remote IR analyses [1] and Viking XRF results [2], Fe-rich smectites or their degradation products were proposed as major constituents of martian surface soils and dusts. Gooding [3] used thermodynamic data for kaolinite and estimated data for a variety of smectites to conclude that smectites were unstable relative to kaolinite. However, he also concluded that metastable formation and/or preservation could make smectites important constituents of martian dusts and soils. The inference of Fe-rich clay minerals at the martian surface has persisted and clay minerals remain a major component of many surface mineralogic models in the assessment of newer data, *e.g.*, [4] and [5]. There is also abundant evidence for hydrous minerals in the martian regolith, supported by Viking thermal analyses and also indirectly by Mars Odyssey results showing up to 10% H₂O-equivalent H in the upper meter of the surface in equatorial regions. However, these data provide few constraints on the identity of these hydrous minerals.

More definitive data on the mineralogy of Mars [*e.g.*, 5 & 6] show that rock compositions are basaltic to andesitic and contain glass and/or phyllosilicate components. Recent OMEGA and CRISM spectral data suggested the presence of phyllosilicates in several Noachian deposits with a range of Fe, Al, and Mg

bonded to structural OH [*e.g.*, 7, 8, 9, 10]. As discussed by [11], TES fits produce different results for the type-2 martian surface depending on which phyllosilicate and glass spectra are included in the end-member library. In many places, the chemistry of the martian fines is consistent with the presence of altered volcanic material including phyllosilicates, silica, and glass, and recent work [12, 13, & 14] suggested the presence of silica-rich deposits (*e.g.*, opal).

Clay Mineralogy and Alteration Processes on Mars: Mineral alteration and formation on Mars can occur via many paths, including aqueous and vapor [*e.g.*, 15, 16, 17, 18, 19], and interpreting past alteration processes is complex. However, alteration conditions on Mars can be elucidated by an understanding of alteration mineralogy. Depending on conditions, volcanic glass can alter to a variety of mineral assemblages, including zeolites, smectites, kaolin minerals, hydrated volcanic glass, and opaline silica. For example, [18] suggested that amorphous silica, goethite, and kaolinite would form early under acid alteration conditions, whereas zeolites and carbonates would form later under more alkaline conditions. Yen *et al.* [14] suggested that recently observed silica deposits could have formed from hydrothermal alteration or from acidic vapors with small amounts of liquid water. Stability diagrams can shed light on alteration conditions, and Figure 1 shows the sequence from amorphous silica through progressively less siliceous phases as silica activity decreases. The discovery of amorphous silica thus greatly constrains formation conditions.

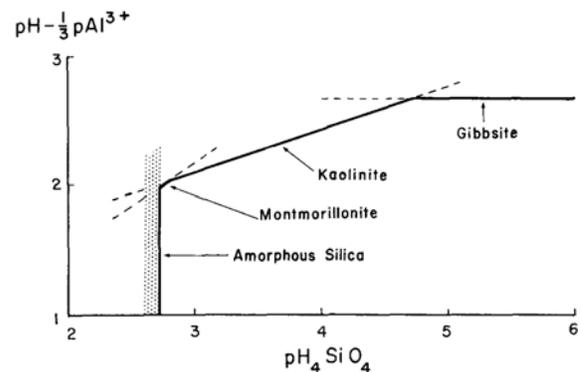


Figure 1. Stability diagram for minerals in the Al₂O₃-SiO₂-H₂O system at 25°C and 1 atm. Solutions are supersaturated with the respective phase to the left of or above the solid line (from [19]). The "p" in axis labels refers to $-\log[]$.

Either smectites or zeolites can form from volcanic ash, depending on conditions, with smectite formation occurring in near- or below-neutral pH conditions and zeolites forming under alkaline conditions. We cannot assume that basaltic volcanic ash will always alter to phyllosilicates. Detection of secondary zeolites would strongly imply the occurrence of alkaline conditions but detection of both smectites and zeolites would indicate a much more persistent and evolved hydrogeologic system. Formation of kaolin minerals would imply a reasonably distinct set of formation conditions. For example, Millot [20] emphasized that kaolin minerals form on Earth most commonly in tropical climates, usually under more-acidic conditions and with high water:rock ratios (well drained). They may also be accompanied by amorphous silica deposits when formed hydrothermally. In addition, they are often accompanied by TiO₂ minerals such as anatase. On Mars, a Ti-Si association has been considered to support acid vapor alteration [14]. Detection of 10Å hydrated halloysite, a more hydrated kaolin mineral, on Mars would imply that the mineral had never experienced dehydration after formation, as hydrated halloysite irreversibly dehydrates to a 7.2Å phase under low-RH conditions. Figure 2 summarizes the relationship between intensity of weathering and resultant mineralogy, with relic micas and chlorites in the least weathered/altered assemblages, smectites and kaolinite as intermediates, and oxides/hydroxides as end stages.

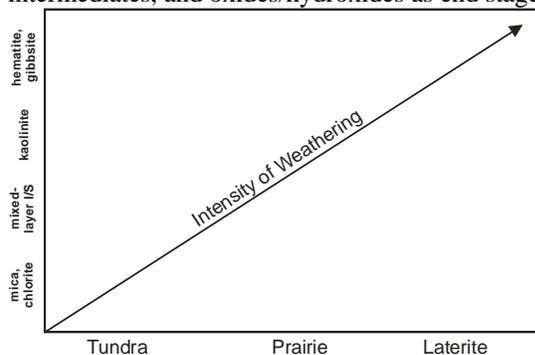


Figure 2. Mineralogy vs. intensity of weathering (modified from [21]).

Additional information on formation conditions can be obtained from experiments. For example, nontronite has been often suggested to occur on Mars; [22] showed that nontronite can form at low temperatures only under *reducing* conditions, where Fe is soluble.

We also have the potential to learn much concerning clay mineral stability from Mars' surface mineralogy. More poorly ordered clay minerals such as smectites and illite/smectites do not occur in old rocks on Earth, and it has often been assumed that these minerals gradually transform to more stable, higher-

temperature phases such as illite, micas, and chlorites. This concept is illustrated in Figure 3, which implies that mixed-layer illite/smectites are not stable over long times even at low temperatures. The discovery of smectites in Noachian terrains [7, 8] has important implications for the long-term stability of clay minerals and suggests an alternative hypothesis, namely that tectonic activity on Earth eventually results in the progressive alteration of low-temperature minerals to higher-temperature assemblages. If the existence of smectites on Mars in rocks older than 3 By is verified, these results will rewrite our understand of clay mineral stability and suggest that, in the absence of (plate) tectonic activity, "metastable" clay minerals may be "stable" for times on the order of the age of our planet.

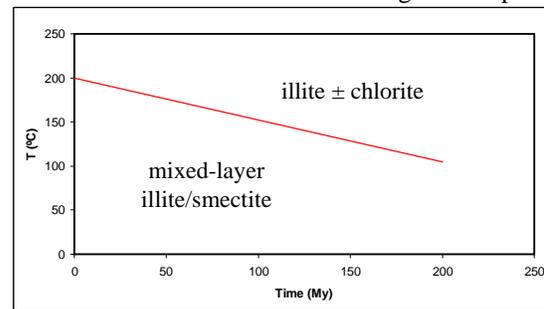


Figure 3. Time-temperature limits on clay minerals (modified from [23]).

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