

**WHAT CAN CLAY MINERALOGY TELL US ABOUT ALTERATION ENVIRONMENTS ON MARS?** D.

L. Bish<sup>1</sup> and D. T. Vaniman<sup>2</sup>, <sup>1</sup>Dept. of Geological Sciences, Indiana University, 1001 E. 10<sup>th</sup> St., Bloomington, IN 47405; bish@indiana.edu, <sup>2</sup>Los Alamos National Lab, MS D462, Los Alamos, NM 87545; vaniman@lanl.gov

**Introduction:** Recent missions to Mars have provided considerable new data supporting the widespread occurrence of hydrous alteration products on the martian surface, and these observations focus new attention on hydrous environments and the minerals formed therein. In order to understand the evolution of Mars, it is useful to sample or orbitally evaluate 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. Recently, orbital data (e.g., CRISM) have begun to show in more detail not only the areal distribution of clay minerals on the surface but also the vertical distribution. By taking advantage of regions excavated by impacts, it is possible to formulate a picture of the effects of burial/depth on mineralogy, adding the valuable third dimension to our knowledge of the mineralogy of the martian surface.

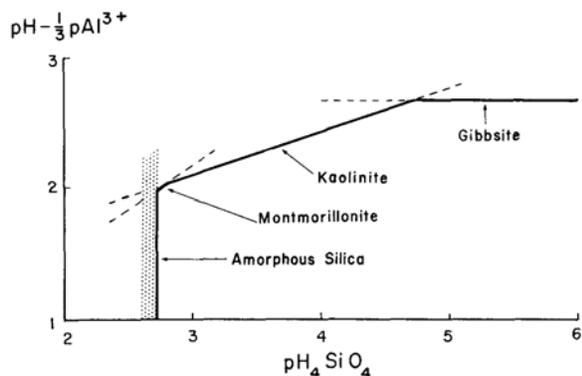
Mars' surface mineralogy holds clues to its hydrologic and geochemical histories, and we can use mineralogy to constrain past processes, including weathering, metamorphism, and hydrothermal effects, just as we do on Earth. Based on early remote IR analyses [1] and Viking XRF results [2], Fe-rich smectites or their degradation products were proposed as major constituents of martian surface soils and dusts. Gooding [3] used thermodynamic data for kaolinite and estimations 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 indirectly by Mars Odyssey results showing up to 10% H<sub>2</sub>O-equivalent H in the upper meter of the surface in equatorial regions. However, the Viking and Odyssey 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 suggest 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.

Smectites or zeolites can form from volcanic glass, depending on conditions, with smectite formation occurring in circum- 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), although a

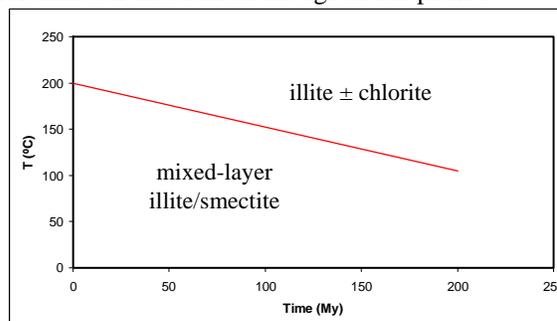


**Figure 1.** Stability diagram for minerals in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system at  $25^\circ\text{C}$  and 1 atm. Solutions are supersaturated with the respective phase to the left of or above the solid line (from [19]). The “p” in both axis labels refers to  $-\log[\ ]$ .

hydrothermal association is also common. Kaolinite, nacrite, and dickite all also commonly form under hydrothermal conditions, and kaolinite is known to transform with depth under diagenetic conditions to dickite in sandstone reservoirs. The kaolin minerals may also be accompanied by amorphous silica when formed hydrothermally, often at the expense of pre-existing volcanic rocks. In addition, they are often accompanied by  $\text{TiO}_2$  minerals such as anatase and by other hydroxides, such as gibbsite and/or boehmite, if hydrothermal leaching is more severe. On Mars, a Ti-Si association has been considered to support acid vapor alteration [14]. The generally observed relationships between intensity of weathering and resultant mineralogy show relic micas and chlorites in the least weathered/altered assemblages, smectites and kaolinite as intermediates, and oxides/hydroxides (hematite, gibbsite) as end stages. Additional information on formation conditions can be obtained from experiments. For example, nontronite has been often suggested to occur on Mars; [21] showed that nontronite can form at low temperatures only under *reducing* conditions, where Fe is soluble. If this conclusion remains sound, the occurrence of nontronite on Mars obviously has important implications for redox conditions when the clay minerals formed.

We also have the potential to learn considerable new information 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 2, 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 a possible 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 understanding of clay mineral stability and suggest that, in the absence of (plate) tectonic activity and burial, “metastable” clay minerals may be “stable” for times on the order of the age of our planet.



**Figure 2.** Time-temperature limits on clay minerals (modified from [22]).

**References:** [1] Hunt G. R. and Salisbury J. W. (1973) *Icarus*, 18, 459-469. [2] Toulmin P. et al. (1977) *JGR*, 82, 4625-4634. [3] Gooding, J. L. (1978) *Icarus* 33, 483-513. [4] Calvin W. M. (1998) *LPS XXIX*, Abstract #1162. [5] Michalski J. R. et al. (2006) *JGR*, 111, E03004. [6] Christensen P. R. et al. (2001) *JGR*, 106, 23823-23871. [7] Bibring J-P. et al. (2006) *Science*, 312, 400-404. [8] Poulet F. et al. (2005) *Nature*, 438, 623-627. [9] Milliken R. E. (2007) *EOS Trans AGU*, 88, Abstract #P12A-02. [10] Bishop J. L. et al. (2007) *EOS Trans AGU*, 88, Abstract #P13D-1559. [11] McSween H. Y. J. et al. (2003) *JGR*, 108, 5135. [12] Michalski J. R. et al. (2005) *Icarus*, 174, 161-177. [13] Ruff S. W. et al. (2007) *EOS Trans AGU*, 88, Abstract #P23A-1097. [14] Yen A. et al. (2007) *EOS Trans AGU*, 88, Abstract #P23A-1095. [15] Gooding J. L. et al. (1992) in *Mars*, 626-651. [16] Banin A. et al. (1997) *JGR*, 102, 13341-13356. [17] Hurowitz J. A. and McLennan S. M. (2007) *EPSL*, 260, 432-443. [18] Zolotov M. Y. and Mironenko M. V. (2007) *JGR-Planets*, 112, E07006. [19] Kittrick J. A. (1969) *Clays & Clay Min*, 17, 157-167. [20] Millot G. (1970) *Geology of Clays*, Springer-Verlag. [21] Harder H. (1978) *Clays & Clay Min*, 26, 65-72. [22] Velde B. (1992) *Intro. to Clay Minerals*, Chapman & Hall.