

**X-RAY DIFFRACTION ANALYSIS OF CLAY MINERAL ASSOCIATIONS TO DETERMINE ALTERATION ENVIRONMENTS ON MARS.** D. L. Bish<sup>1</sup>, D. L. Vaniman<sup>2</sup>, D. Blake<sup>3</sup>, P. Sarrazin<sup>4</sup>, & S. Chipera<sup>5</sup>, <sup>1</sup>Dept. of Geological Sciences, Indiana University, Bloomington, IN 47405 bish@indiana.edu, <sup>2</sup>Earth & Env. Sciences, Los Alamos National Laboratory, Los Alamos, NM 87545, <sup>3</sup>NASA Ames Research Center, Moffett Field, CA, <sup>4</sup>inXitu Inc., Mountain View, CA, <sup>5</sup>Chesapeake Energy, Oklahoma City, OK.

**Introduction:** Mars' surface mineralogy holds clues to its hydrologic and geochemical histories and can provide information constraining past alteration processes. Beginning with 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 literature thermodynamic data for kaolinite and estimates of  $\Delta H^{\circ}_{298}$  and  $\Delta G^{\circ}_{298}$  of formation of the clay minerals saponite, Ca-beidellite, Na-beidellite, montmorillonite, and nontronite to conclude that the smectites were unstable relative to kaolinite. 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 through many subsequent studies and remains a major component of many surface mineralogic models in the approach to and assessment of newer data, *e.g.*, [4] and [5].

Evidence for hydrous minerals in the martian regolith is strengthened by Viking thermal analyses that show that most of the 1-1.9% H<sub>2</sub>O in martian soils is released between 200° and 500°C, a range characteristic of water evolution from many hydrous minerals but one that provides few constraints on what those hydrous minerals are. Indeed, many clay and zeolite minerals release their more strongly bonded H<sub>2</sub>O molecules over this temperature range, and recent results [6] are consistent with water loss over this temperature range. The Mars Odyssey spacecraft provided the intriguing result that extensive near-equatorial regions on Mars contain up to 10% H<sub>2</sub>O-equivalent H, also supporting, but not proving, the existence of hydrous minerals in the upper meter.

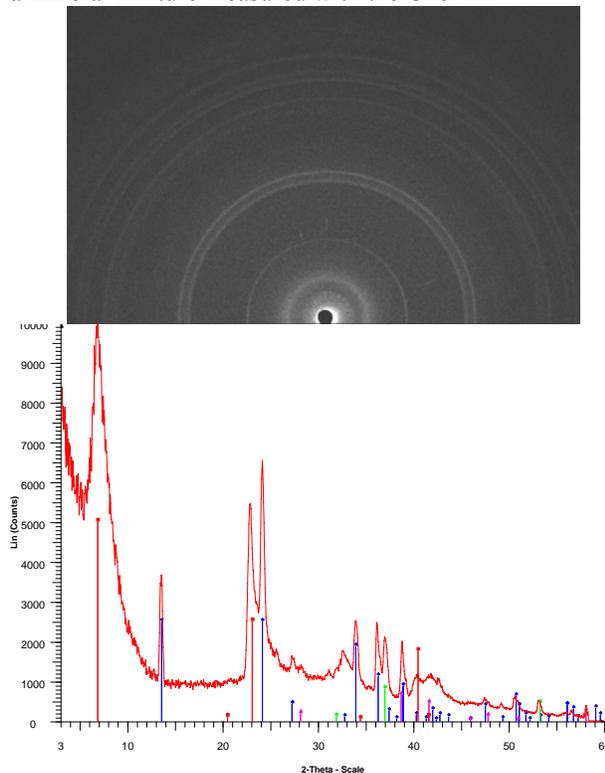
Many recent papers have summarized the surface mineralogy of Mars [*e.g.*, 5 & 7]. Rock compositions are basaltic to andesitic and contain glass and/or phyllosilicate components. Analyses of Mars Express OMEGA and MRO CRISM spectral data suggested presence of phyllosilicates in several Noachian deposits with a range of Fe, Al, and Mg bonded to structural OH [*e.g.*, 8, 9, 10, 11]. As discussed by [12], 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 substantial presence of altered volcanic material including phyllosilicates, silica, and glass, and recent work (*e.g.*, 13, 14, & 15] has suggested the presence of silica-rich deposits (*e.g.*, opal).

**Alteration Processes on Mars:** Mineral alteration on Mars can occur via many paths, including aqueous and vapor [*e.g.*, 16, 17, 18, 19, & 20], and unraveling past alteration processes is difficult. However, the nature of past alteration on Mars' surface can be elucidated by a better 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, [19] 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. [15] suggested that recently observed silica deposits could have formed from hydrothermal alteration or from acidic vapors with small amounts of liquid water. Formation of both smectites and zeolites from volcanic ash is common, with smectite formation occurring in below-neutral pH conditions and zeolites forming under alkaline conditions. Thus, 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. Kaolin minerals usually form under more-acidic conditions, often with high water:rock ratios (well drained), and they may be accompanied by amorphous silica deposits when formed hydrothermally. In addition, they are often accompanied by TiO<sub>2</sub> minerals such as anatase, an association that was considered to support acid vapor alteration [15]. Detection of 10Å hydrated halloysite 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.

**Detection of Clay Minerals And Associated Phases by XRD:** Although orbital and landed instruments have provided tantalizing clues regarding alteration mineralogy on the martian surface, the optimum method for analyzing mineralogy, particularly clay mineralogy, is X-ray diffraction (XRD). CheMin is such an instrument, now being built for the 2009 Mars Science Lander. As many clay minerals have large

diagnostic repeat distances in their structures, it is crucial that any XRD instrument be capable of detecting low-angle (large d-spacing) diffraction peaks. Figure 1 illustrates the 2-D and conventional XRD patterns for a mineral mixture measured with the CheMin



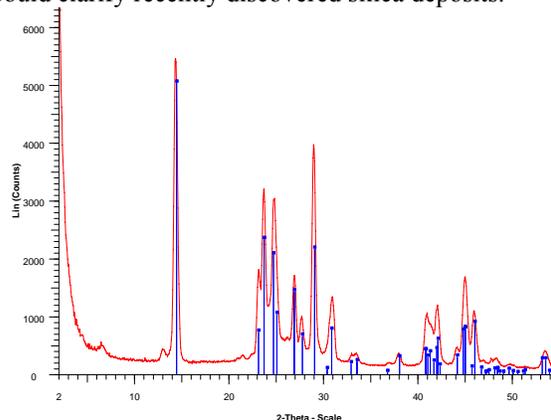
**Figure 1. CheMin CoK $\alpha$  XRD pattern of nontronite (61 wt%, red), gypsum (25 wt%, blue), halite (8.7 wt%, green), & hematite (5.3 wt%, purple).**

instrument. This figure shows that the  $\sim 15\text{\AA}$  d-spacing from nontronite is easily resolved. With this performance, CheMin can identify and distinguish a number of clay minerals, although the variety of treatments used in terrestrial laboratories will not be accessible on Mars (e.g., saturation with ethylene glycol vapor). The lowest-angle diffraction peak from  $10.1\text{\AA}$  hydrated halloysite occurs at  $\sim 10.2^\circ 2\theta$  with Co radiation and is easily detectable, although the mineral may dehydrate inside the CheMin instrument. However, dehydration within the CheMin instrument could be used to advantage in discriminating between different phyllosilicate minerals such as kaolinite (Figure 2) from smectite. Comparison of figures 1 and 2 also illustrates the ease of discriminating between kaolinite and smectite.

#### **Discrimination of Amorphous Phases by XRD:**

Although amorphous phases do not diffract X-rays, they scatter them in a well-defined manner that allows distinction between different compositions and facilitates quantitative analysis of samples containing amor-

phous components. For example, basaltic glass can be distinguished from opal-A or opal-CT, a capability that could clarify recently discovered silica deposits.



**Figure 2. CheMin XRD pattern of kaolinite (blue lines: kaolinite CoK $\alpha$  peaks). Peak at  $\sim 6.5^\circ$  is due to Kapton window and other peaks are kaolinite CoK $\beta$  peaks.**

**Summary:** Detection of and discrimination between different alteration minerals, such as clay minerals and even amorphous phases, is crucial to allow interpretation of past alteration events on Mars. Clay mineralogy can shed considerable light on alteration mechanisms and, when taken together, the entire mineral assemblage can greatly constrain processes responsible for today's martian mineralogy.

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