**CLAY MINERALS IN RETURNED SAMPLES AND ALTERATION CONDITIONS ON MARS.** Michael A. Velbel, Department of Geological Sciences, 206 Natural Science Building, Michigan State University, East Lansing, MI 48824-1115, velbel@msu.edu.

**Introduction:** A Mars Sample Return Mission will further understanding of the geologic history of Mars, by enabling direct study of surficial materials. The history of chemical interactions between Mars' crustal materials and the planet's fluid envelopes are recorded in igneous and sedimentary materials presently exposed on Mars' surface. The known history of vigorous surficial fluvial and aeolian activity on Mars suggests that much of the surficial material available on the surface of Mars has been modified by exogenic processes involving physical and/or chemical interactions with Mars' atmosphere, and with any hydrosphere which existed at different times during Mars' natural history. However, the extent of any chemical/mineralogical alteration, the relative importance of physical and chemical processes, the timing of any chemical alteration that may have occurred, and what information the surficial materials contain about the chemical history of Mars' surface and atmosphere are all matters of continuing research interest.

Orbiter and lander/rover studies of Mars' surface have identified and provided preliminary characterization of a range of surficial materials available for sampling, including igneous and sedimentary rocks, possible volcaniclastic/pyroclastic rocks, and unconsolidated sediment. Some surfaces expose unaltered anhydrous silicates (militating against extensive interactions with water), but most results (including studies of Mars meteorites) indicate at least minor aqueous alteration of exposed surface materials.

Clay minerals form by deuteric and hydrothermal alteration of igneous parent materials; weathering of any parent-rock type; and diagenesis of sediments (including volcaniclastics). This contribution reviews what can be determined about mineral-environment interactions from the study of the clay-mineral products of mineral-water interactions, emphasizing low-temperature surface phenomena (weathering).

**Rock and mineral weathering**. During weathering, primary rock-forming minerals react with solutions and/or volatiles. Reactants (minerals and mobile species) are consumed through processes governed by interactions among structure, composition, surface properties, and solute composition (the latter itself influenced by the history of the solution, including its origin and other reactions the solution participated in prior to arriving at the current reaction site). Weathered regoliths produced by weathering reactions contain residual primary rock-forming minerals (remnant reactants), secondary minerals, and solutions and/or volatiles of altered composition. On Earth, clays formed by weathering vary with the interplay between (1) the dissolution kinetics of primary minerals that release silica and cations to solutions and (2) the leaching intensity of the weathering environment.

In many situations of interest, the solutions left the system long ago, and it is from the surviving solids that we infer the former processes [1-5]. Although reactant and product solutions and volatiles may no longer exist, considerable insight into their nature, abundance, and properties can be achieved by examining the reactant and product minerals. The compositional and textural relationships among reactants and products record mineral stability and elemental mobility, which in turn result from the thermodynamics and kinetics of reactions in the weathering system (including its volatiles). Even on Earth, where high temperatures and abundant water facilate relatively rapid kinetics (at least in comparison with present conditions on Mars), the mechanisms of weathering reactions often prevent the attainment of thermodynamic equilibrium. Most naturally weathered materials therefore represent various intermediate stages between unaltered parent materials and the ultimate weathering products.

Multiple analytical methods are required to identify, characterize, and reconstruct weathering factors, processes, and conditions (including atmospheric composition and the solute characteristics of any liquid water) that may have existed when the weathering reactions took place in these transitional materials. Some analyses can be performed *in situ*, but the complete array of methods available in terrestrial laboratories is not readily transported off-planet. Also, robotic missions are constrained to use instruments that were available when the mission was designed. As the Stardust mission recently reminded us [6,7], sample-return missions allow use of the instrumental state-of-the-art available at sample return and thereafter.

**What do clay minerals tell us about alteration conditions?** For most of Mars' natural history, Martian environments of aqueous alteration (surface and shallow subsurface environments like those sampled by Mars meteorites) were likely characterized by low fluid-rock ratios, negligible leaching, and highly reactive (mafic) parent materials. Weathering in such systems may resemble the earliest stages of weathering of terrestrial mafic volcanic rocks. Rapid reaction rates of the mafic silicates and negligible leaching produce

conditions more similar to closed-system conditions than in most other terrestrial weathering environments. Consequently, much analysis of Mars-surface mineralogy assumes that thermodynamic equilibrium adequately describes parent-product mineral relationships of weathered planetary surface materials [8-10]. However, metastability (not thermodynamic equilibrium) is common in low-temperature mineral-water systems, so observations of kinetically controlled textures and mineral associations are more likely than thermodynamic modeling to detect evidence of processes and reaction paths [1-5].

*Elemental transfer during alteration.* Unlike whole-landscape (orbiter) and whole-sample (lander/rover) mineral and chemical data, returned samples will allow a variety of observations at spatial scales comparable to those at which chemical mineral-water interaction processes operate. These include textures at the interfaces between reactant and product minerals (that preserve information about the geochemical kinetics of the reactions; [11]); compositions (structural formulae, trace elements, isotopes) of reactant and product minerals and genetically related reactant-product assemblages; and compositional relations of products with mineral phases elsewhere in the regolith/landscape other than the local "parent mineral".

Structural relationships between naturally weathered chain-silicates and their alteration products indicate that the T-O-T (tetrahedral-octahedral-tetrahedral) "I-beams" of the chain silicates are transformed with minimal rearrangement of bonds into 2:1 T-O-T sheets [5,12-15]. While these structural relationships are well understood, less is known about compositional aspects of these reactions. Where primary- and secondary-mineral compositions are known from electron microprobe analyses, (isovolumetric) pseudomorphic replacement of primary chain-silicates by secondary sheet-silicates requires export of some elements and import of others. For example, one recent case study finds that clinopyroxene weathering to smectite conserved Si in the conversion of pyroxene to clay, lost Mg, and required import of Fe from faster-weathering Fe-bearing minerals nearby [16]. On Earth, leaching removes those elements overabundant in parent minerals relative to products; on Mars such mobile products may not have moved far in those cases where there was little water to carry them. Recent studies of within-regolith redistribution of major mineral-forming elements during terrestrial weathering [16] will serve as a model for future studies of major-, minor-, and trace-element redistribution at various spatial scales during clay-mineral formation in both terrestrially and extraterrestrially weathered rocks.

*Primary-mineral corrosion textures and clay-mineral textures.* Olivine subjected to terrestrial weathering of Mars-meteorite finds corrodes in the same manner as terrestrially weathered terrestrial olivine [17] and small-scale corrosion features on weathered terrestrial chain-silicates resemble features in Mars meteorites [18], indicating that insight from terrestrial weathering of mafic silicates is transferable to interpreting the alteration of silicates in samples from Mars.

Pyroxene surfaces are unaffected by relative humidity changes during sample handling and examination [11,16], whereas the smectite formed as the weathering product of the same pyroxene is strongly modified by environmental excursions during sample handling [16]. Preservation of clay-mineral textures in returned Mars samples will be challenging; like other hydrous phases, variations in temperature and relative humidity will drive hydration-dehydration and changes in the volumes and textures of hydrous phases. Corrosion and replacement textures at the surfaces of anhydrous igneous minerals (including contacts with alteration products and exposed surfaces) will be much less vulnerable to modification by the sample recovery-return process. Compositional attributes of clays are more robust than textures and will better survive sample return.

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