

**MECHANISMS OF PYROXENE ALTERATION TO SMECTITE: IMPLICATIONS FOR INFERRING ELEMENTAL MOBILITY IN MARTIAN PALEOENVIRONMENTS.** M. A. Velbel, Department of Geological Sciences, Michigan State University, East Lansing, MI 48824-1115 U.S.A. (velbel@msu.edu)

**Introduction:** Orbiter and lander/rover studies of Mars' surface have identified and provided preliminary characterization of surficial materials including igneous and sedimentary rocks, possible volcanoclastic/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. 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. This contribution reviews what can be inferred about mineral-environment interactions from the study of parent-mineral/clay-mineral relationships produced by 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) [1-5]. Regoliths produced by weathering contain residual primary rock-forming minerals (remnant reactants) and secondary minerals (weathering products) [1-5].

In many situations of interest, the solutions left the system long ago, and it is from the surviving solids that the former processes must be inferred [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 the weathering reactions. Even on Earth, where high temperatures and abundant water facilitate 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 [1-5].

**Primary-mineral corrosion: Pyroxene:** Denticulated margins (also known in older literature as "sawtooth", "cockscorn" or "hacksaw" terminations) are a common feature of pyroxenes and amphiboles, visible in transmitted-light microscopy of grain mounts and thin-sections, and by electron microscopy. Denticles are remnants of undissolved material that formerly constituted the walls between elongate etch pits (the characteristic aqueous-dissolution form of chain-silicate minerals) [6], and occur where a grain boundary, transmineral fracture or dislocation array transects the crystal at a high angle to the  $z$ -axis [6]. Denticles occur widely in terrestrial near-surface materials that have experienced low-temperature aqueous alteration, including chemically weathered regoliths, soils in a variety of climatic and geomorphic settings, sediments and sedimentary rocks [6-7]. Ranges of dissolution forms and dimensions (commonly tens of microns in length) are identical on both pyroxenes and amphiboles in these materials [6]. Denticles are much less common on surfaces of chain-silicates altered by aqueous solutions at higher temperatures.

Denticles on weathered terrestrial chain silicates [6-7] are similar in shape and distribution to micron-scale features reported from pyroxenes in several Mars meteorites and from recent mission data [8]. The similarity of these demonstrably aqueous weathering-related terrestrial chain-silicate denticles with morphologically similar features from and on Mars supports inferences of a low-temperature aqueous origin of the Mars mineral denticles [8].

**Formation of phyllosilicates as weathering products:** There are two grain-scale mechanisms by which primary silicate minerals in general, and chain silicates in particular, weather to secondary minerals; transformation and neof ormation [1,9,10].

*Transformation.* In transformation, the bonds linking the apical oxygens of the silica tetrahedra in the chains of, for example, chain silicates are locally broken and remade, allowing single- and double-width chains to rearrange and reattach themselves laterally into extensive tetrahedral-octahedral-tetrahedral (T-O-T) sheets, the basic structural unit of 2:1 phyllosilicate minerals [3]. The earliest-formed products of transformation reactions retain large parts of the parent-mineral structure (e.g., mica to vermiculite or smectite;

pyroxene to smectite [3]). Solution composition has only modest influence on the structure and composition of the alteration product, which at least initially consists dominantly of cations and structural units inherited from the parent mineral [3,7,11-13].

**Neof ormation.** In neof ormation, destruction of primary-mineral bonding is more complete [7], and secondary minerals are formed (often at some distance from the site of primary-mineral destruction) by crystal-growth of secondary minerals from solutes. Because secondary-mineral formation by precipitation does not require any specific structural relationship with the primary reactant-mineral surface (from which precipitation may be separated by considerable distance), there is no necessary crystallographic orientation relationship between primary (reactant) minerals and their neof ormation products [7,14].

**Clay minerals and environmental conditions:**

On Earth, clays formed by weathering vary with the interplay between (1) the dissolution mechanisms and kinetics of primary minerals and (2) the leaching intensity of the weathering environment. With increased weathering, the influence of parent material on the structure and composition of weathering products diminishes, and the composition of the products is increasingly influenced by the compositions of the solutions driving the alteration. Solution composition during advanced weathering influences compositions of product minerals in terms of both the elements left behind in the products, and the elements transferred between the product-forming environment and other nearby weathering micro- and (if enough water is present) macro-environments. On Earth, leaching in wet climates removes those elements overabundant in parent minerals relative to products; in dry terrestrial environments such elements are retained in the local regolith [1-3,15]. On Mars such mobile products (esp. Si) appear not have moved far, suggesting that there was little water to carry them.

**What can parent-mineral/clay-mineral textural and compositional relationships tell us about alteration conditions on Mars?** Metastability (not thermodynamic equilibrium) is common in low-temperature mineral-water systems, even for reactive primary minerals and soluble product minerals commonly assumed to easily attain equilibrium [16], so observations of kinetically controlled textures, mineral associations, and mineral compositions are an important complement to thermodynamic approaches in detecting and interpreting evidence of alteration processes and elemental mobility [1-5,15,16].

Smectites are widely distributed on the surface of Mars [17-20]. Smectites indicate either inheritance of structure and major elements from parent material with

minimal modification by leaching (transformation) or precipitation from cation- and silica-rich solutions (neof ormation). Optical-petrographic and electron-microscope-scale textural observations are required (from Mars meteorites or returned samples) to fully distinguish phyllosilicates formed by transformation from those formed by neof ormation [6,7,11-14]. In addition to helping distinguish those situations in which thermodynamic interpretation might be simple from those in which kinetics preclude such interpretation, textural information can constrain compositional attributes and provide insight into elemental mobility. For example, during early stages of isovolumetric replacement of clinopyroxene by ferriferous nontronitic smectite in one well-studied terrestrial occurrence, Si is conserved during the transformation reaction (Si is immobile), whereas Fe must be imported (from simultaneously weathering nearby Fe-rich primary silicates) in order to account for the high Fe content of the smectite [7]. Compositional relationships between products and reactants are an observational basis for identifying mobile and immobile elements, and inferring the former conditions that facilitated the differential mobility of specific elements, even in systems in which the water that facilitated the weathering reactions is no longer present.

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