HYDROLOGIC AND GEOCHEMICAL CONTROLS ON NONTRONITE FORMATION IN TERRESTRIAL COLUMBIA RIVER BASALTS AND IMPLICATIONS FOR CLAY FORMATION ON MARS. L. L. Baker,1,2 D. G. Strawn1, P. A. McDaniel1, J. P. Fairley2, and J. L. Bishop1,1 Division of Soil and Land Resources, University of Idaho, Moscow, ID 83844-2339, lbaker@uidaho.edu, 2Department of Geological Sciences, University of Idaho, Moscow, ID 83844-3022, 3Carl Sagan Center, SETI Institute & NASA-ARC, 189 Bernardo Avenue, Mountain View, CA 94043.

Introduction: Extensive layered phyllosilicate deposits have been found on Mars by orbiting spectrometers [1-5]. These deposits contain both Fe-rich phyllosilicates such as nontronite, and Fe-poor materials such as montmorillonite and beidellite, in distinct stratigraphic units. The phyllosilicate deposits are interbedded with basaltic lava flows and are observed in canyon and crater walls. The detailed stratigraphic relationships between Fe-rich clays, Fe-poor clays, and basalt are not well understood, although there appears to be compositional stratification of clays within many deposits.

It has been proposed that the stratification of these clays is due to either changing alteration conditions over time [3,5-6], in situ alteration of stratigraphic layers of different composition [3, 7-8], or surface leaching of previously altered layers [9]. Ehlmann et al. [10] argue that Martian Fe- and Mg-rich clays largely formed through subsurface alteration of basalts by groundwater, rather than by surface processes, and that these clays were later overlain by sedimentary deposits of Al-rich clays formed at the surface by higher degrees of alteration. Placing better constraints on formation conditions of clays such as nontronite will test these hypotheses, and should yield information on conditions on early Mars during the time these clays were being formed.

Mars analog clays: We are studying a terrestrial analog for this system in clay minerals formed by surface and subsurface weathering of the Columbia River basalts (CRB). Nontronite is a typical weathering product of CRB [11-13]. It is found filling enclosed spaces, such as vesicles and narrow cracks, in basalts that are only lightly weathered (Figures 1-2). Paleosols formed on more heavily weathered basalts under temperate conditions of the Miocene Climatic optimum (Figure 3), typically contain Fe-poor clays including kaolinite, halloysite, and montmorillonite, rather than nontronite. Nontronite-filled cavities (Figure 2) are found in the less weathered basalt beneath the paleosol-basalt contact.

We are investigating basalt alteration to nontronite and other clay minerals in the field and laboratory to determine how hydrologic factors (permeability, water supply, flow rate, wetting-drying cycles) and chemical and physical parameters (temperature, oxidation state, basaltic glass dissolution rates, availability of chelators) affect weathering processes and products.

Nontronite formation: The standard geochemical model of nontronite formation is that it requires conditions that are initially reducing enough for iron to remain in solution because Fe(II) is much more soluble than Fe(III). These conditions must prevail until the phyllosilicates precipitate and iron is locked into the structure, after which more oxidizing conditions are required, because most iron in nontronite is Fe(III). In the field, under conditions of poor groundwater circulation, oxidation state will be buffered largely by reaction with the basalt. However, nontronite frequently fills spaces that are in communication with the surface environment. Oxidation state in these cracks and void spaces could be increased by addition of atmospheric oxygen, subject to the relatively slow diffusion of O2 through groundwater.

Nontronite is frequently found in cracks that are open to the basalt flow surface and overlying soil. This raises the possibility that organic material from the surface may enter the cracks and influence clay formation. On fresh basalt surfaces, plants may colonize open cracks that hold water, and organic matter infill into these cracks can have significant effects on pedogenesis [15]. For example, chelation of dissolved Fe by organic matter should significantly affect the solubility of Fe (oxyhydr)oxides and possibly of nontronite. Organic acids may also influence basalt dissolution. Our experiments will investigate the effects of soil organic matter on basalt alteration and formation of Fe-rich and Fe-poor clays.

CRB hydrology: The Columbia River basalts host an extensive aquifer. Much of the porosity and permeability in this aquifer is in rubbly zones between basalt flows, with the massive flow interiors typically acting as aquitards (barriers to groundwater flow). Clay-rich sedimentary interbeds also act as aquitards. Joints and fractures in the basalts provide vertical connections between the different interflow porous zones. In the uppermost basalt flows, seasonal fluctuation of the water table surface leads to wetting and drying cycles. Clay-rich sediment layers and paleosols are present as interbeds between basalt flows and also act as aquitards. Modeling of permeability in the basalt aquifer (Figure 4) [16,17], and reaction path modeling of bas-
alt dissolution and secondary mineral precipitation, will illuminate the control exerted on nontronite formation by basalt hydrology.

**Application to Mars:** Studying clay formation in the CRB will enable more informed interpretation of the phyllosilicate occurrences on Mars and allow us to test the various hypotheses for their formation. A more thorough understanding of geochemical and hydrologic controls on nontronite formation and stability in basalts will allow for more accurate interpretations of geochemical and aqueous conditions on early Mars. Understanding the interrelationships between basalt fracture architecture and the predominant clay mineralogy may yield useful constraints on groundwater hydrology on Mars.

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Figure 1: Basalt of the Wanapum Formation showing fracture architecture at outcrop scale. Closer observation shows that mm- to cm-sized cracks are filled with green and yellow nontronite.

Figure 2: Nontronite filled void spaces in Grande Ronde basalt.

Figure 3: Lateritic weathering profile between Grande Ronde basalt flows.

Figure 4: Permeability model of basalt flow from LIDAR scanning.

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