MASSIVE SULFATE DEPOSITS ON MARS COULD BE REMOBILIZED NOACHIAN SALTS. M. Yu. Zolotov[1] and M. V. Mironenko[2], [1]School of Earth and Space Exploration, Arizona State University, Tempe AZ 85287-1404, USA, E-mail: zolotov@asu.edu. [2] Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia.

Introduction: Orbital spectral observations of the Martian surface indicate uneven occurrences of aqueous minerals in geological formations of different ages. Secondary minerals seen in the Noachian terrains are dominated by phyllosilicates, while the Hesperian formations are characterized by massive deposits of layered sulfates seen in the Valles Marineris trough system, related depressions, and other places [1-4]. The initial interpretation of these data suggested deposition of phyllosilicates from Noachian alkaline solutions and formation of sulfates from acidic fluids related to volcanism in the Hesperian epoch [1].

Fe-Mg phyllosilicates (smectites, chlorites) are the most abundant clay minerals on Mars [2-4]. Typically, Fe-Mg phyllosilicates are located at lower stratigraphic layers than Al-rich clays such as montmorillonite and kaolinite. As an example, in the Mawrth Vallis region, minerals are observed within the following stratified sequence of layered rocks (from the top): silica and kaolinite, montmorillonite-like Al-rich clays, a Fe^{2+} phyllosilicate, Mg/Fe smectites, and sulfates [5-8]. Sulfates are also seen in the middle part of the stratigraphic sequence.

The composition and occurrence of phyllosilicates and salts could be used to constrain ancient aqueous environments. This requires understanding of effects of solution chemistry, *pH*, *Eh*, temperature, and duration of processes on composition of precipitated minerals. In addition to terrestrial analogs and laboratory data, the formation and fate of secondary minerals could be evaluated with numerical physical-chemical models. We have modeled rock alteration by percolating aqueous solutions to constrain origins of observed minerals.

Modeling of weathering profiles with phyllosilicates and salts: Alteration has been modeled through calculation of chemical equilibria in multicomponent systems with non-ideal aqueous, solid, and gas solutions. These models consider solubilities of solids and gases in aqueous solution and constrain conditions of mineral saturation. Additional procedures quantify *pH*-dependent rates of mineral dissolution coupled with chemical equilibria in solution [9] and percolation of fluids. With these models, formation and compositional evolution of secondary minerals could be linked to a specific stage and/or setting of water-rock interaction. The models tie the composition and *pH* of solution with the mineralogical assemblage, which may contain secondary phases together with unaltered minerals.

Our models demonstrate sequential formation of phyllosilicates (kaolinite then smectites), low-solubility salts (gypsum), and salt-bearing solutions through neutralization of initial acidic fluids interacting with martian basalt (Figs. 1-3). Modeling of percolation of acidic fluids through basalts predicts formation of the vertical sequence of dominated minerals (from the top): amorphous silica - kaolinite and/or montmorillonite – a ferrous chlorite - Fe-Mg smectites. Zeolites and Fe^{2+}-chlorites occur with smectites, and Fe^{2+} chlorite-bearing rocks form between layers rich in montmorillonite and smectites. This series reflects leaching of elements and neutralization of fluids with depth, and is similar to the succession observed in the Mawrth Vallis region [5-8] and several other areas, including walls of the Valles Marineris canyon system. The minerals observed in the upper part of some Martian profiles (silica and ferric phases, Fig. 2) agree with an open-system alteration in acidic conditions.

The results show that phyllosilicates form together with sulfates, and clay-sulfate assemblages (except kaolinite-rich or jarosite-rich cases) do not indicate acidic environments. Smectite-sulfate assemblages form in contact with neutralized fluids at depth. Much high-solubility salts (Mg and Na sulfate and chlorides) remained in neutralized solution. These results suggest that alteration solutions rich in high-solubility salts

Fig. 1. The water-rock (*W/R*) ratio as a proxy for depth in a weathering profile of Adirondack martian basalt. Upper layers are altered at higher *W/R* ratios.
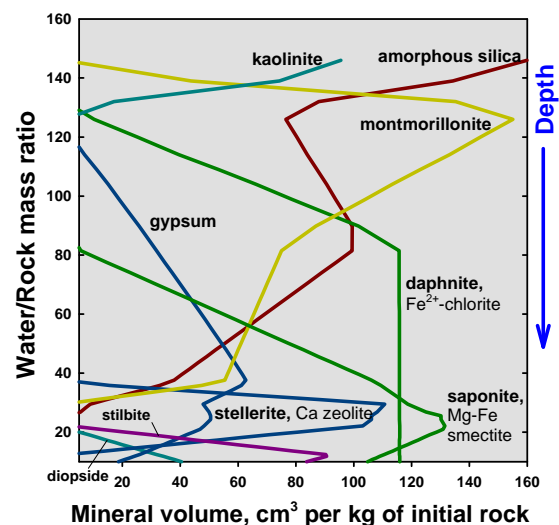
Fig. 2. The modeled evolution of the surface basalt layer affected by parcels of O_2-saturated acidic fluids. The increasing number of solution parcels corresponds to alteration progress.
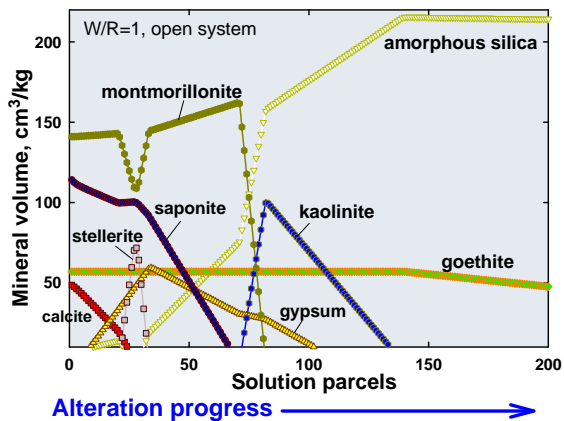
could have accumulated at depth in pore spaces and subjected to freezing, evaporation, and subsurface migration and remobilization throughout history.

Modeled weathering by neutral fluids also leads to a stratified sequence of Al-rich (top) and Fe-Mg clays (bottom). However, formation of a 100 m weathering profile requires tremendous volumes of neutral or slightly acidic (CO_2-saturated) fluids and does not look feasible. These models do not produce abundant salts and are inconsistent with observations. These results may indicate formation of Noachian phyllosilicates by initially acidic solutions [c.f., 9].

Discussion: The modeled formation of phyllosilicates together with salts imply formation of abundant salts in the Noachian epoch (see also [9,10]). These rock alteration models are consistent with the detection of Noachian sulfate-phyllosilicate assemblages [e.g., 11,12] and possible chloride deposits [13]. Several vol. % of sulfates could be present in Noachian clay-rich formations but may not be detected with orbital methods. A formation of interior layered sulfate deposits through acidic alteration of silicate rocks in the Hesperian epoch [1] should have led to formation of vast phyllosilicate and/or silica deposits, which are not observed.

We advocate for a scenario that includes aqueous alteration of mafic rocks by transient fluids generated by Noachian impacts related to the Late Heavy Bombardment. Acidic fluids generated by impacts [9] were neutralized through alteration of rocks followed by precipitation of phyllosilicates and low-solubility Ca sulfates. Neutralized fluids rich in high-solubility Mg and Na sulfates and chlorides have accumulated in ground waters. Subsequent freezing of subsurface flu-

ids led to deposition of these salts in the pore space and accumulation of subfreezing brines in the megaregolith. Some cold chloride-rich brines could have released to the surface, consistent with observations [13]. A Hesperian remobilization of high-solubility sulfates and chlorides could have been caused by melting of crustal ice related to an enhanced heat flow, and by basaltic magmatism and volcanism. Subsurface drainage of neutral and reduced (Fe^{2+}-bearing) fluids into depressions (e.g., Valles Marineris and other chasmata) was followed by the formation and evaporation of sulfate-rich lakes. Oxidation of Fe^{2+} ions by atmospheric O_2 in canyon lakes led to deposition of ferric oxides/hydroxides in somewhat acidic and salt-rich environments. This scenario does not exclude a near-surface formation of sulfates and opaline silica by transient acidic aerosols and rains, and other fluids related to volcanic and impact events in the Hesperian and Amazonian epochs.

Fig. 3. The modeled weathering profile of Adirondack basalt formed through percolation of acidic fluids from above. The plot on the right shows neutralization of fluids at depth. The results agree with observations in the Mawrth Vallis region.
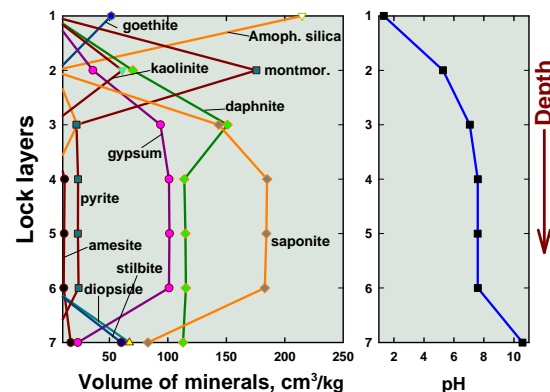
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