KINETIC MODELING OF MINERAL SEQUENCES ON EARLY MARS USING FULLY OPEN SYSTEMS. E. R. Uceda¹, A. G. Fairén¹, C. Gil-Lozano², E. Losa-Adams², L. Gago-Duport². ¹Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain. ²Centro de Astrobiología (CSIC-INTA), Madrid 28850, Spain. ³Department of Astronomy, Cornell University, Ithaca, NY 14853, USA. ⁴Departamento de Geociencias Marinas, Universidad de Vigo, Lagoas Marcosende, 36200-Vigo, Spain.

Introduction: We have applied a reactive-transport approach to model the formation of mineral sequences known to exist on Mars, as described from lander and orbiter data [1-5], considering open system conditions both at the atmosphere-water and water-rock interfaces, and implementing a kinetic approach for the dissolution and precipitation of solid phases. We present a suite of models representing aqueous environments in systems under an early Mars atmosphere, to analyze the role of: (i) the reactive surface area of primary minerals, and (ii) the reactive transport processes through the basalt interface.

Kinetic model: We model the space-time variations of the conditions inside a basalt sediment column, where the surface water is in contact with an acidic-oxidative atmosphere at the upper interface (CO₂, SO₂, Cl₂) (as on early Mars, see [6]), and subject to a continuous loss of water by evaporation. We assume a continuous flux of gases derived from volcanic outgassing through the upper water layer, as these volatiles are the most obvious source of anions which can gradually change Eh and pH conditions. The model represents a 1-D kinetic system of evaporation + diffusion + reaction (precipitation/dissolution of mineral phases).

Oxidation is mainly driven by chlorine, through transient oxygen reactive species formed at the low pH values induced by the CO₂ and SO₂ gases [6,7]. When the upper acidic and oxidant solution starts to diffuse and mix with the interstitial alkaline water, the pH rapidly decreases with depth. The extent of pH lowering toward acidic values and increase in oxidation potential, on both time and depth, is a function of the rate of diffusion and the buffering capacity of the interstitial pore water which, in turns, depends again on the dissolution rate of the basalt forming minerals. Therefore, this model considers the two different possibilities regarding the reactive surface area of the basaltic minerals, as follows.

First, when the solution is in contact with basaltic sediments of greater size, the total amount of reactive surface area is low and, therefore, the dissolution of the basalt proceeds relatively slowly. In this case, it is expected that the input of volatiles from the atmosphere and the loss of water from evaporation are the main factors inducing variations in pe-pH conditions, and in ionic strength. In this situation the system evolves towards an evaporitic scenario, characterized by extremely acidic and oxidizing conditions. The consequence is the formation of sulfates (i.e., alunite, gypsum), more abundantly in the upper part of the sediment column, while the distribution of clays tends to follow an opposite trend in the column (Figure 1).

Figure 1: Depth profiles of the secondary mineral phases formed during aqueous reaction of a basalt column considering gases input from the atmosphere and low reactive surface area of primary minerals (cubes, L = 54 mm; Sreactive = 0.11 m²/kgw). Beidellite-Ca and gibbsite also precipitate. Both phases showed the maximum accumulation at the subsurface. Model approaches: flux of gases input: 0.1 mol/yr of CO₂(g) and 0.01 mol/yr of SO₂(g) and Cl₂(g); length of the sediment column = 20 cm; Dw = 1x10⁻⁹, f = 0.4; simulation time = 100 yrs.; linear evaporation rate =0.1 mol/yr; secondary minerals considered in the model: clays (smectite, kaolinite, beidellite and chlorite), evaporites (jarosite, alunite, gypsum, and calcite), and hydroxides (goethite and gibbsite).

And second, when the reactive surface area of the basalt increases because the basalt minerals are pervasively fractured, the dissolution of basalt occurs faster, resulting in the rapid evolution of the solution towards very alkaline values. In this scenario, sulfates do not
form, and clays are the major precipitation product in the surface layer (Figure 2a, b and c). The alkaline pH also favors the precipitation of goethite. Goethite’s precipitation front is gradually shifted towards the middle point of the column, due to the competition for ferric iron with clay minerals (i.e., nontronite) (Figure 2d).

**Figure 2:** Depth profiles of the secondary phases formed during aqueous reaction of a basalt column under the same boundary conditions described in Figure 1 but assuming high reactive surface area of primary minerals (cubes, L = 5.5 μm; Sreactive = 1096 m²/kgw). Calcite and gibbsite are also formed showing the maximum accumulation at surface and subsurface layers, respectively.

**Conclusions:** Our results are consistent with the stratigraphic sequence of Noachian phyllosilicates observed in certain locations on Mars: Fe/Mg clays (e.g., nontronite) in the lower layers, and Al-rich clays (e.g., beidellite) in the upper layers [8]. Taken together, these results highlight the importance of considering open kinetic models to reproduce the geochemical conditions on the surface of Mars. Cation removal by diffusion, together with the input of volatiles and the influence of the reactive surface area of the basalt, could play a central role in the time-evolution of the mineral sequences formed on aqueous environments on early Mars.


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