

INTRODUCING FULLY OPEN SYSTEMS IN THE KINETIC MODELING OF DIVERGENT MINERAL SEQUENCES ON MARS. A. G. Fairén^{1,2}, C. Gil-Lozano¹, E. Losa-Adams³, L. Gago-Duport³, E. R. Uceda⁴, J. A. P. Rodríguez⁵, ¹Department of Planetology and Habitability, Centro de Astrobiología (CSIC-INTA), Madrid 28850, Spain (agfairén@cab.inta-csic.es). ²Department of Astronomy, Cornell University, Ithaca, NY 14853, USA. ³Departamento de Geociencias Marinas, Universidad de Vigo, Lagoas Marcosende, 36200-Vigo, Spain. ⁴Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain. ⁵Planetary Science Institute, Tucson, AZ 85719, USA.

Introduction: Most geochemical models of aqueous mineral precipitation on Mars often assume either (i) static closed system conditions only, or (ii) semi-open system conditions (i.e., open to the atmosphere but closed in the basal interface) allowing ionic exchange between the gas phases (H_2O , CO_2 , Cl_2 , SO_2) and the solution through the water-atmosphere interface. In both types of models, the fraction of ions derived from the weathering of primary minerals, either cations (mostly Fe, Mg, Ca, Al, Na) or anions (particularly Si), is forced to remain constant in the form of dissolved species or to precipitate as secondary minerals (i.e., clays and salts).

While closed system models can be useful to describe the equilibrium balance between primary and secondary mineral assemblages, when applied to ancient martian sediments the net balance between ions released after the dissolution of basalt and the total ions incorporated into clays results in a residual amount of cations in solution that cannot bind to clays due to the stoichiometric restraints imposed by the limited availability of the silicate anion. Provided the existence of an alternative source of anions, mainly derived from volatiles, it is expected that these ions would have reacted to form salts; however, in most localities on Mars, salts are commonly absent in clay-dominated sediments, and there is no evidence for later dissolution or separation of salts through physical processes on the surface, including dissolution, transport, and re-precipitation in younger terrains [1].

Our aim here is to help understand the sedimentary mineralogy on Mars, where mineral sequences show that salts generally do not appear together with clays.

Methods: We use geochemical models of secondary mineral precipitation considering open conditions both at the atmospheric and basal interfaces, and implementing a kinetic approach for the dissolution-precipitation of solid phases. To the best of our knowledge, this is the first work that models the formation of mineral sequences on Mars considering both open system conditions and kinetic evolution. All the geochemical calculations presented hereafter were done with the Phreeqc software [2].

Model set up: flux of gases input: 0.02 mol/yr of $CO_2(g)$ and 0.001 mol/yr of $SO_2(g)$ and $Cl_2(g)$; length

of the sediment column = 20 cm; $D_w = 1 \times 10^{-9}$, $f = 0.4$; simulation time = 100 yrs.; linear evaporation rate = 0.02 mol/yr; secondary mineral considered in the model: clays (smectite, kaolinite, beidellite and chlorite), salts (jarosite, alunite, gypsum, and calcite) and hydroxide (goethite and gibbsite).

Results: Our models show that, starting from a solution in equilibrium with basalt at circumneutral pH, the rate of mineral dissolution is initially controlled by the reactive surface of primary minerals. In fractured basalt (Fig. 1), mineral dissolution is counter-balanced by the precipitation of clays and the downward diffusion of cations through the basal interface, and therefore the precipitation of salts in surface waters is restricted.

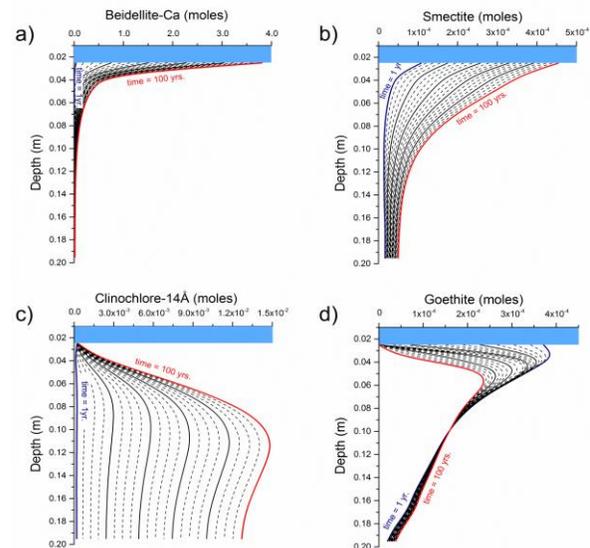


Fig. 1: Deep profiles of the secondary mineral phases formed during aqueous reaction of a basalt column considering gases input from the atmosphere and high reactive surface of primary minerals (cubes, $L = 5.5$ mm; $S_{reactive} = 1096$ m²/kgw). Calcite and gibbsite are also formed showing the maximum accumulation at surface and subsurface layers, respectively.

In contrast, although mineral dissolution of less fractured basalt (Fig. 2) would proceed slowly, evaporation and long-term interaction with volatiles will increase the concentration of cations and favor the evolution toward more acidic and oxidizing conditions, leading to salt precipitation in surface waters.

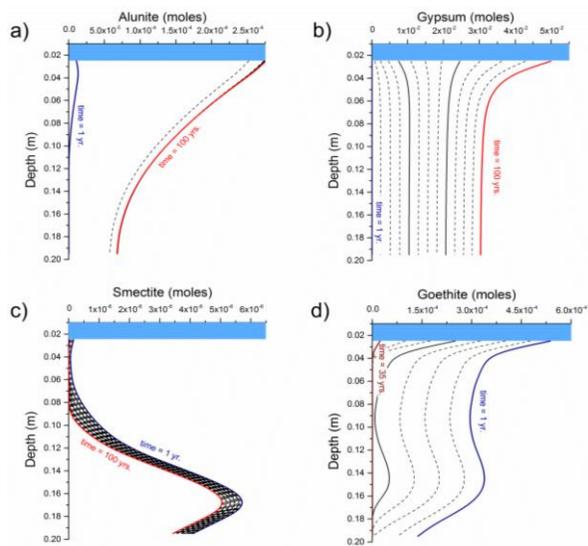


Fig. 2: Deep profiles of the secondary mineral phases formed during aqueous reaction of a basalt column considering gases input from the atmosphere and **low** reactive surface of primary minerals (cubes, $L = 54 \text{ mm}$; $S_{\text{reactive}} = 0.11 \text{ m}^2/\text{kgw}$). Beidellite-Ca and Gibbsite also precipitated. Both phases showed the maximum accumulation at the subsurface.

The contrasting weathering behavior of massive basalts versus basaltic detrital sediments influences the secondary mineral products that may have resulted from aqueous interaction on early Mars. Although the variation in the total reactive surface of basalt does not change the pH dependencies for the dissolution of the individual minerals, the different ratios of release of cations may be significantly modified. The interplay between this contrasted dissolution behavior with ion removal by vertical diffusion transport, in an aqueous scenario undergoing evaporation and open to the input of volatiles, can help to understand the stratigraphic sequences of secondary minerals observed on Mars, and also provide insights into the dissolution behavior of multi-phase rocks.

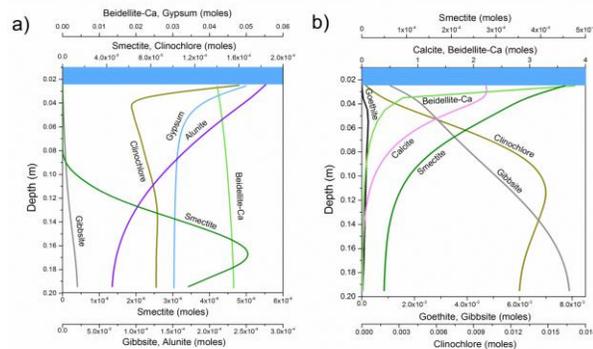


Fig. 3: Distribution of the mineral assemblage from the models shown in Figs. 1 and 2, after 100 years of simulation: a) with high reactive surface, and b) with low reactive surface.

Our results show that cation removal by diffusion, together with the input of volatiles and the influence of the reactive surface of the basalt, could play a central role in the time-evolution of the mineral sequences formed on aqueous environments on early Mars (Fig. 3).

Conclusions: Our results help explain the observed trends in the mineral record on Mars, highlighting the contrasting weathering behavior of massive basalts versus basaltic detrital sediments, and its influence on the secondary mineral products that may have resulted from aqueous interaction on early Mars. In a scenario of highly fractured basalt with a large reactive surface, the small grain-size basaltic silicates would dissolve fast, forming clays; conversely, in a scenario of massive basalt deposits (i.e., non-fractured) with a small reactive surface, dissolution of silicates would have been slower, resulting in the precipitation of salts after the evaporation of water in contact with atmospheric volatiles.

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References: [1] Milliken, R. E., Fischer, W. W., Hurowitz, J. A. (2009) Missing salts on early Mars. *Geophys. Res. Lett.*, 36: L11202, doi:10.1029/2009GL038558. [2] Parkhurst D. L., Appelo C. A. J. (1999) User's guide to PHREEQC (Version 2)--a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, ed. *U.S. Geological Survey, Water-Resources Investigations Report 99-4259*, 312 p.