CIRCUMSTELLAR DUST WITH METASTABLE EUTECTIC COMPOSITION AS PRIMARY MATERIAL FOR CLAY FORMATION IN THE NOACHIAN TERRAINS OF MARS

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Abstract

A characteristic feature of Mars during the Noachian is the widespread presence of clay minerals, including smectites presumably formed at low temperature. The most accepted hypothesis is that crystallization of clays occurred via weathering of the primary basalt crust. This process usually requires a large volume of solution to precipitate a small amount of material, which is difficult to reconcile with the large monomineral deposits of clays encountered. Here, we analyze, as an alternative hypothesis, whether an important amount of Fe-Mg smectites may have formed by hydration of supercooled volcanic ash. We propose that dust nanoparticles may have reacted with the H_2O steam produced from ice sublimation, generating important amounts of clays in a cold and wet context. Preliminary modeling of the process show that, instead the supersaturation, the precipitation of clays can be driven by the most stable compositional term in a solid-solution where the end-members are dehydroxlated smectite and water-vapor.

1. Introduction

Disordered silicates formed at low temperature, such as smectites, are one of the major phases controlling Earth-surface environmental conditions. In Mars, the occurrence of Fe-Mg-phyllosilicates has been largely observed, mainly in terrains of the Noachian period, making the study of low-T clay formation of particular interest to understand early geochemistry of this planet. It usually thought that formation of hydrated clay minerals is the result of the reaction between Martian basaltic crust and liquid water through a process known as reverse weathering. Laboratory experiments have shown that even at highly dilute solutions, precipitation of amorphous clay precursors may take place rapidly but requires a larger volume of solutions to precipitate a few amount of bulk nanomaterials, being the time required to accumulate a detectable amount, the main issue. Furthermore, not all types of clays can be synthesized from this way.

One of the largely unknown aspect of the clay formation is the mechanism that leads to a particular structure and the importance of the composition of the starting material on this process. It has been demonstrated that the rapid crystallization from the vapor phase of silicates leads to a metastable and highly reactive eutectic mixture which is compositionally similar to the Fe-Mg-smectites found on Mars. In this work, we analyze, through geochemical modeling, the possible formation of Noachian clays by reaction of this precursor eutectic composition with a supercritical atmosphere of water and carbon dioxide, as an alternative to the conventional weathering process.

2. Supersaturation and clay crystallization.

In natural systems, the formation of clays by dissolution of the basalt bearing minerals can occur even in diluted solutions, since clays are usually very insoluble phases. Small fluctuations of concentration, provided by specific ions -like OH^- in alkaline solutions- acts as the driving force for crystallization.
However, when trying to reproduce this process in the laboratory, what actually forms, in particular at low-T, is an amorphous product. A proof of concept of this behavior was obtained by performing the dissolution of basalt in a batch crystallizer and inducing crystallization by water-loss through reverse osmosis (figure1).

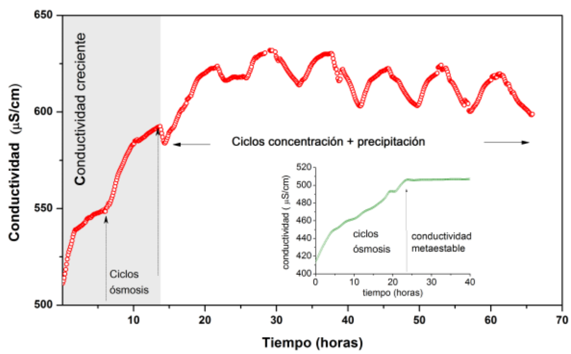

Figure 1. *Conductivity fluctuations associated to the precipitations of amorphous precursor of clays. They are obtained by cycles of dissolution-evaporation of basalt. Low-T evaporation was simulated inducing the loss of water by reverse osmosis.*

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In addition of supersaturation, a key step allowing the structural building of clay minerals is the kinetic control in the intercalation of the oxide sub-units, namely silicon or metal-oxide. The surface charges of the oxides/hydroxides units in clays are developed according with a stepped deprotonation process:

$$\text{SurfaceOH}^{2+} \leftrightarrow \text{SurfaceOH} \leftrightarrow \text{SurfaceO}^{-}$$

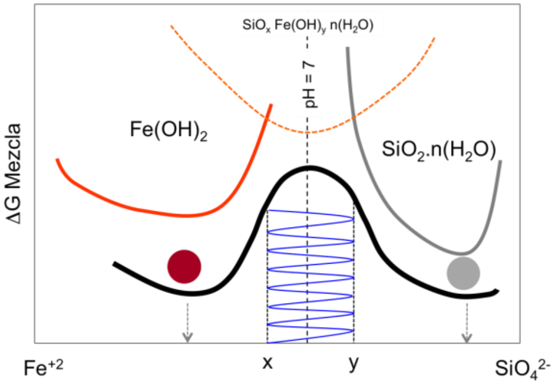

Figure 2*. Compositional dependence of Gibbs Free energy during the molecular mixing of oxides to form clays*.

Where silicon oxides are generally negatively charged, while aluminium and iron oxides are amphoteric with positive or negative charges depending upon the pH, and concentration of different the ions in solution. Factors that that should be included in the geochemical the models in order to estimate the probability of transformation of this amorphous material on true clays.

3. Geochemical scenarios for the formation of Noachian clays in Mars.

In situ weathering of basalt. (i.e. the so-called “reverse weathering “) usually does not lead to the formation of deposits of great thickness, due to the formation of passivating layers that prevents the advance of the reaction in depth. However, there are Noachian deposits of more than hundreds of meters that are not reached on Earth even in tropical climates. To solve this problem, several alternatives have been proposed. Most of them are associated with early magmatic and hydrothermal processes. [1], [2].
A different possibility would be the formation of clay minerals from "circumstellar" volcanic dust. This material, either true interstellar material present during the formation of the crust or derived from supercooled volcanic ash (different of aeolian dust formed by mechanical attrition of basalt), because supercooled ash has a fixed compositions, called *metastable eutectics composition* (figure 3) that exactly matches the composition of some clays in a dehydroxylate state. [3].

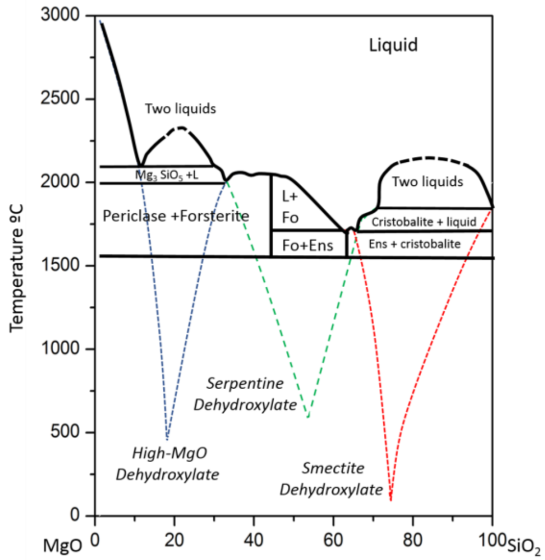

Figure 3*. Metastable eutectics with composition of “dehydroxylated clays” forming during the rapid cooling of volcanic dust. [3].*

We have modelled the reaction between dust nanoparticles and $H_2O_{(g)}$ resulting either from volcanic outgassing or ice sublimation by the *solid-solution* algorithm in the PHREEQCI geochemical code. We used the metastable eutectic dehydroxylated smectite and $H_2O_{(g)}$ as end-members of a solid solution and we consider the following hydration reaction:

$$\textit{Smectite (Dhx)} + m\, H_2O(l) = \textit{Smectite } (m\, H_2O)$$

The main outcome is that this type of reaction allow form the whole suite of clays observed in the Noachian soils of Mars (i.e.: montmorillonite, beidellite, saponite, talc and also kaolinite in a lesser amount.

4. Conclusions.

Kinetically controlled gas-to-solid condensation of Mg–SiO–Fe-Al--H_2–O_2 vapors gives in the formation of chemically ordered solids with predictable metastable eutectic compositions. The hydration of these nanoparticles, could generate very thick mono-mineral deposits of clays similar to those observed in Mars during the Noachian. The use of proxies (i.e: Li-isotopes) to determine the true residence time in solution could help to elucidate the aqueous origin of the clays formed in the earliest periods of Mars.

5. References

[1] Meunier et al (2012) Nature Geoscience **5** 739-743*.* [2] Cannon et al (2017).Nature ***552****, 88–91.* [3] Rietmeijer et al (2008).Icarus **195**:493–503.