Introduction: The average rock on Mars surface is of magmatic type with a felsic composition in the northern hemisphere and a mafic composition in the southern hemisphere. The chemistry of the original rock should be one of the controls on the type of clay minerals that formed (and are still forming?) on Mars surface. However, the interplay between rock chemistry and that of the altering fluids to produce clay minerals can be rather complicated. The present contribution presents some studies of clay formation, mainly at the early stage, where several factors affecting chemical control are illustrated. They can be used to analyse what type of clay minerals can be expected to form in the several environments on Mars surface.

Rock control on clay formation: The first study reported is a hydrothermal alteration of rhyolitic glass in a wide range of temperature and water chemistry conditions (5 g of glass in 25 ml of water; NaCl/KCl molar ratio 0.01-100; total chloride concentration 0.01-1 M; other experiments used deionized water; 60-180 °C; 60-360 days). The aim was to investigate the formation of illite-smectite of different illite content. Surprisingly, the products were consistently illite-smectite with approximately 25% illite layers [1]. SEM and TEM studies with microanalysis showed that the major mechanism for illite-smectite formation was a direct transformation of the glass, with evidence of minor precipitation from solution [2]. Analysis of the aqueous activity diagrams showed that some were consistent and some inconsistent with illite-smectite formation. These results were interpreted to indicate a complete control of the glass chemistry on the composition of the neoformed clay.

In a second study (in progress) we investigated the alteration of phlogopite crystals in a matrix of phono- litic glass, from a (seemingly) pyroclastic deposit (although one author describes it as a dyke), in a karstic environment (Grotta del Cervo, Pietrasecca, Italy). Fine phlogopite crystals show alteration to mica-smectite with 1-4% smectite. SEM-EDS observation of large phlogopite crystals shows progressive in-situ alteration of mica layers towards beidellite (dioctahedral, AI-rich smectite). In this case, the almost complete loss of octahedral Mg from the phlogopite precursor and large increase in AI and Si contents indicates that water chemistry controlled the composition of the neoformed phase, even though the alteration mechanism appears to be a solid-state transformation, as in the case of the rhyolitic glass. Seemingly, the local environments where the transformation reaction takes place in the glass and the mica have different characteristics. Glass alteration starts by penetration of protons (with cation exchange) and water within the glass, which may result on the transformation process taking place within the glass grains (very near the surface) and thus, controlled mainly by glass chemistry. Alteration of the phlogopite crystals probably takes place from the outer surface (edges of the layers, primarily) and water chemistry controls the composition of the resulting phase.

Mg-rich phyllosilicates: Trioctahedral Mg-rich phyllosilicates of the 2:1 type (2 tetrahedral sheets, 1 octahedral sheet) can be easily synthesized hydrothermally. The yields are large in periods as short as several hours, depending on the method. The synthesis of Al-rich (dioctahedral) counterparts is much slower, with reactions taking months. However, Al-rich phyllosilicates are a much more common product of silicate alteration in natural environments. This is probably a reflection of the fact that Mg is less abundant than Al in silicates and of the mechanism of the alteration process, both favouring rock control. The formation of Mg-rich phyllosilicates needs high Mg contents in the rock and/or a high Mg activity in the altering fluids. Recently, a study of the early stage of amphibole weathering in a soil environment showed that Mg-rich smectite formed on some crystallographic faces and Al-rich smectite on others [3].

Our recent study of clay minerals from several submarine hydrothermal fields [4] showed talc formation on the surface of the marine sediment and in open cracks in contact with seawater, where the Si-rich hydrothermal fluids mixed with the seawater and the Mg supply from the latter is unrestricted. On the contrary, we observed the formation of talc-smectite with increasing Al content in the interior of chimney structures. In this secluded environment, the Mg supply is restricted as seawater has to penetrate through the chimney walls and the resulting phase contains more Al. Accordingly with these considerations, Mg-rich phyllosilicates are probably restricted to the southern Martian hemisphere.
**Fe-rich phyllosilicates**: Iron is abundant on Mars surface. A recent study, still in progress, of metalliferous deposits from the East Pacific Rise, off the Chilean coast, has shown a mechanism of phyllosilicate (smectite-type) formation that may be relevant to Mars.

The hydrothermal fluids in the studied region are rich in Si and Fe. At the contact between these fluids and seawater, Fe is oxidized and precipitated as very fine-grained, low crystallinity Fe oxide. Our samples from the east Pacific Rise have large amounts of biogenic calcite and lower amounts of a non-crystalline Fe-rich phase. Calcite was removed by reaction with dilute HCl. X-ray diffraction does not detect crystalline clay phases. However, SEM-EDS observation reveals numerous μm-size grains of smectite-like composition. Many of these have a high Fe content (nontronite-like) whereas others are Al-rich (montmorillonite-like). Our interpretation is that these grains correspond to “proto-clays”, particles with smectitic or near-smectitic composition in the process of maturation to acquire a crystalline structure. Reaction of amorphous Fe oxyhydroxide with dissolved silica is one of the proposed mechanisms for the formation of nontronite in submarine hydrothermal fields [5].


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