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Clay mineral formation on Mars: Chemical constraints and possible contribution of basalt out-gassing

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ABSTRACT

We focus on processes possibly occurring on Mars that could affect sufficiently large volumes of rocks to be detected by remote sensing techniques.

When compared with the chemical modelling of water–rock interactions, the petrographic and mineralogical characteristics of clay deposited in the prismatic joints of a lava flow from the Parana basin (Brazil) suggest that the clay fraction of lava flows may be formed at least partly during an early post-magmatic stage associated with the degassing of acid volatiles.

In view of the literature concerning other contexts, such as meteorites or experimental syntheses, we conclude that the crystallization of anhydrous mafic minerals and the formation of clay mineral are not systematically mutually exclusive phenomena. While clay formation is generally related to chemical reaction pathways, it is not necessarily due to the alteration of pre-existing silicates.

Such post-magmatic reactions, even if they are likely to represent only a minor contribution to Martian clay formation limited to early Noachian times, require much lower amounts of water compared to conventional hydrothermal alteration or weathering systems. The products of these reactions can be detected over large surface areas, as in the case of the Mars sites, thus allowing us to envisage a greater diversity of paleogeographic scenarios for Early Mars.

1. Introduction

We do not know how much liquid water existed on the surface of Mars. Even if physical conditions preclude the presence of water today, this situation may have been different in the past. This hypothesis is supported by morphological observations (incised river valleys with branched tributaries, outflow channels, etc.) as well as mineral parageneses (presence of salts, sulphates or clay minerals which are thought to be typical of water–rock interactions). The morphological features suggest huge amounts of liquid water flowed over the surface and through the subsurface of Mars in the past, and specifically inside the impact craters (Malin and Edgett, 2003; Mangold et al., 2004). The search for alteration minerals has been largely developed over the past decades through the survey of Mars' surface by several instruments: Mars Global Surveyor, Mars Odyssey and Mars Express (Wyatt and McSween, 2006 and references therein), as well as local analyses carried out by landers (Mars Exploration Rovers, Mars Science Laboratory). Apart from the large-scale sulphate deposits (Gendrin et al., 2005; Bibring et al., 2006; McLennan et al., 2005), the detection of clay minerals within Noachian terrains (Poulet et al., 2005) is of particular interest. This is because they represent the first by-products of aqueous alteration of silicate rocks, either in low-temperature surface environments (i.e. weathering) or in high-temperature hydrothermal systems. In both cases, the clay minerals result from the dissolution of pre-existing silicates by aqueous solutions infiltrating though the connected porosity of the rocks. Several studies have linked the origin of these clays to the presence of abundant surface freshwater (Greenberger et al., 2012; Marzo et al., 2009). For example, a large number of river valleys coincide exactly with the occurrence of clays, with many of these features actually cross-cutting the clay-rich outcrops and craters (Hynek et al., 2010). However, there is generally only a poor understanding of the role of erosion–transportation processes in providing the large volumes of water leading to the accumulation of clay minerals, and few studies discuss the conditions and mechanisms involved in the formation of clay minerals on Mars. By contrast, other studies, including some from the atmospheric sciences community, suggest only sporadic and transient water-related events (Kasting, 1991; Gaidos and Marion, 2003; Leshin and Vicenzi, 2006; McEwen et al., 2007; Berger et al., 2009).

But what types of clay minerals existed on Mars? Clay minerals have been directly observed in SNC Martian meteorites (shergottite, nakhlite and chassignite). These minerals have been identified

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in the iddingsite assemblage, which is typical of olivine alteration (Leshin and Vicenzi, 2006 and references herein). According to petrographic investigations, these Fe–Mg clays are considered to be of Martian origin, and likely formed by fluid rock reactions, in contrast to the Al-rich "illite-like" clays which could be formed by shock-metamorphic reactions rather than aqueous precipitation (Gooding, 1992). Moreover, Fe–Mg clay minerals are now detected on the surface of Mars by infrared reflectance spectroscopy, and the presence of such clay minerals is accepted in major units formed during the Noachian (Poulet et al., 2005; Bibring et al., 2006; Loizeau et al., 2007; Mangold et al., 2007; Bishop et al., 2008; Ehlmann et al., 2009) as well as in some specific regions on the Northern Plains of Mars (Carter et al., 2010). All these cited authors concluded that liquid water was involved in the processes leading to the formation of the observed clay minerals. However, two major questions must first be addressed:

- Does the presence of clay minerals systematically imply the alteration of pre-existing minerals; i.e. transformation of a pre-existing anhydrous mafic mineral?
- Can alteration be triggered by the circulation of stable liquid water, meteoric cold water or hydrothermal hot fluids, or can it be produced by transient steam or low-density volatiles?

To answer these questions, we need to refer to the formation processes of Fe–Mg clay minerals in comparable terrestrial rocks such as basalts.

Our aim here is to focus on the processes that could take place on Mars besides conventional alteration, which might affect sufficiently large volumes of rocks to be detected by remote sensing techniques. Considering the prevalence of basaltic material at the surface of Mars, representing relics of an early volcanic history, we can test the hypothesis of possible clay formation during magma degassing by analyzing terrestrial analogues, as well as reviewing the literature on other contexts such as meteorites or experimental syntheses. Among these analogues, we pay particular attention to the petrography and mineralogy of clay coatings in the prismatic joints of a lava flow from the Parana basin (Brazil). The deposition sequence at this locality has been discussed in terms of hydrothermal alteration by Gonçalves et al. (1990), and is re-interpreted here using quantitative chemical and thermodynamic models. Other examples as well as a literature review corroborate the hypothesis of an eventual early formation of clay minerals from deuteric water.

2. Chemical constraints for clay formation

In general terms, clays are mainly produced on Earth by two contrasted mechanisms: bio-mediated alteration of silicate bedrocks by soil formation processes or abiotic thermoactivated hydrothermal alteration. A third process should be mentioned here: the devitrification of marine volcaniclastic sediments. Owing to the amorphous state and large specific surface area of the starting materials, this latter process leads to the formation of large and massive clay deposits (Schiffman et al., 2000). At the microscopic scale, these parageneses are the result of a large number of chemical processes, so many different pathways need to be considered. From the chemical point of view, alteration is essentially controlled by kinetic constraints, in particular the dissolution rate of the source minerals involved in the first step of the alteration process. Most mafic minerals are composed of a silicate network, whose lattice is dominated by covalent bonds between O and Si or Al. The breaking of these bonds by the water molecule is difficult, and hydrolysis is promoted either at high temperatures due to the lowering the energy barrier by thermal agitation, or by the action of protons or other catalysts that modify the surface charge of the minerals, and hence also the strength of the neighbouring Si,Al–O bonds. Therefore, a source of protons is a necessary precondition for low-temperature alteration. Kinetic constraints are even more severe in the case of the crystallization of a well ordered structure, so we cannot use simple thermodynamic equilibria to predict/infer the paragenetic sequence associated with dissolution and precipitation reactions during alteration. The conversion of smectite to illite is a well known example of this kinetic complexity in a sedimentary context (Velde and Vasseur, 1992, Lanson et al., 2002; Berger et al., 1999).

The second type of constraint is thermodynamic. The basalt-forming minerals can be regarded as oxide mixtures with alkaline properties, due to the concentration of alkali and alkaline earth elements in the solid phase. When it comes into contact with an acid fluid, the fluid-rock system is unstable and acid–base reactions produce the conjugate acid of the rock (clays and other alteration minerals) along with the conjugate base of the fluid (brine). By contrast, alkaline solutions do not drive any significant alteration process. So, the conditions that promote alteration are generally related to the production of acidic compounds.

The final constraint is based on the electrical balance of the solution. The consumption of protons during alteration is compensated by a release of labile cations from the rocks. These cations equilibrate the electric charge of the anions initially associated with the protons. The major anions HCO^-, $SO_4^-$and Cl^- determine the amount of cations that can be transferred from the rock to the fluid, depending on the solubility of the corresponding salts.

These fundamental constraints may help to determine whether certain reactions are probable or unlikely, in particular on Mars where observations are scarce. Since bio-mediated alteration remains somewhat speculative in the Mars context, we focus here on inorganic reactions. The weathering of the Martian regolith likely produces radically different by-products when compared to the Earth, where humic and fulvic acids facilitate the development of soil profiles associated with the persistence of confined horizons. According to the constraints outlined above, the prolonged exposure of silicate rocks to abundant water is comptatible with the wet and warm climate assumed for Early Mars. However, the availability of water does not appear as a sufficient condition for clay formation, while other studies propose more arid conditions (McEwen et al., 2007). Hence, we need to determine the pH conditions that prevailed. Under near-neutral conditions, the alteration rates of mafic minerals are slow. Hence, pure dissolution is the most likely process affecting the Martian soil, or at least the precipitation of secondary oxy-hydroxide minerals, but probably not clays. By contrast, under acidic conditions driven by high CO_2 pressure during Early Mars history (Fairén et al., 2004; Fernandez-Remolar et al., 2001), the chemical conditions would be more favourable for clay formation. Even on the Earth during Precambrian times, when abiotic conditions are supposed to be dominant, the occurrence of paleosoils (Erikson and Cheney, 1992; Yang and Holland, 2003; Beukes et al., 2002) can be related to the high CO_2 concentration in the atmosphere (Hoffman et al., 1998) with the notable formation of nahcolite ($NaHCO_3$).

With increasing temperature, the kinetic control on the nucleation and growth of phyllosilicates becomes less important, and the dissolution rate of the source material is slower, promoting thermodynamically stable clay assemblages, in contrast to the metastable poorly crystallized phases formed at low temperature. The assumption of hydrothermal clay formation on Mars is supported by several observations. The majority of clays detected are trioctahedral smectites (Fe–Mg rich) associated with impact craters (Mangold et al., 2007, Mustard et al., 2008, Fairén et al., 2010, Ehlmann et al., 2011a). Chlorite and mixed-layer clays are