

THERMODYNAMICS OF CLAY MINERALS ON MARS: INSIGHT INTO THE GEOCHEMICAL ENVIRONMENT OF EARLY MARS. V. Chevrier¹, ¹W.M. Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701, USA <vchevrie@uark.edu>.

Introduction: The Mars Express OMEGA imaging spectrometer recently identified clay minerals (nontronite and montmorillonite) in several outcrops of Noachian age [1]. Clay minerals usually result from long term alteration of primary minerals by liquid water and on Earth are usually the products of weathering processes. The presence of clay minerals suggests a primary environment completely different from those responsible for the formation of sulfate outcrops such those observed at Meridiani Planum [1]. While these also result from aqueous processes, sulfate minerals suggest a very different geodynamical environment to those responsible for the clay minerals, involving limited action of water [2]. Here we consider the thermodynamics of clay minerals in order to help elucidate the conditions of their formation and the geochemical environment on the surface of Mars during the Noachian period.

Methods: The nontronite stability field has been determined using the water composition data in Table 1. This composition reflects possible primary solutions on Mars, with mainly a high Fe^{2+} content and relatively lower Mg^{2+} and Ca^{2+} compared to solutions commonly found on Earth [3]. The Al^{3+} has been set up at a low value, because of its low abundances in Martian rocks, and its generally low solubility. All the other diagrams are made by varying these parameters. The thermodynamic values come from [3,4]. They reflect “standard” values for clay minerals, which have variable chemical compositions, inducing changes in Gibbs free energy of formation. However, these changes are relatively small [4] and do not strongly influence the stability field of the phases.

| | concentration (mol/kg) | Log(activity) |
|--------------------------|------------------------|---------------|
| H_4SiO_4 | 1 | -3 |
| Al^{3+} | $3.2 \cdot 10^{-7}$ | -6.5 |
| Fe^{2+} | 0.8 | -3.1 |
| Mg^{2+} | 1 | -3 |
| Ca^{2+} | 0.5 | -3.3 |

Table 1. Primary concentrations and activities of dissolved species taken from [3] except for Al^{3+} which are estimated for the present work.

Results and discussion: Montmorillonite should form on Mars in relatively high activities of H_4SiO_4

and mobile cations (Ca^{2+} and Mg^{2+} , Fig. 1). Then the transition towards kaolinite and then gibbsite occurs through progressive loss of Ca^{2+} , Mg^{2+} and then silica. In this case the transformations imply increasing amounts of water leachant, but also because reactions consume H_2O , as for example for montmorillonite transformation into kaolinite:

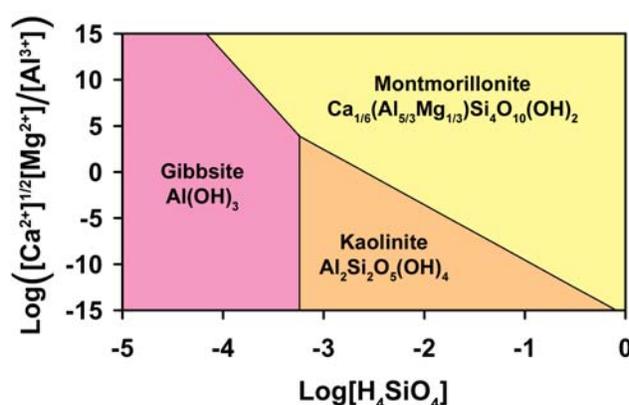
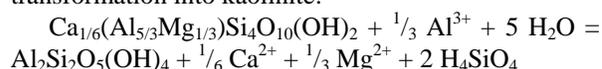


Figure 1. Stability diagram for aluminium-bearing phases in terms of H_4SiO_4 activity and ratio of the activities of mobile ions (Ca^{2+} and Mg^{2+}) to the activity of an immobile ion (Al^{3+}).

The pE-pH shows that nontronite is stable at relatively high pH (>5) and high pE (Fig. 2). These conditions are quite different from those required by the sulfate-type deposits identified by OMEGA [5] or the jarosite-bearing outcrops in Meridiani Planum [6], for which pH was probably very low [7]. Indeed relatively high pH is reached when the relative amount of water is important compared to the species susceptible to decrease the pH (i.e. CO_2 and SO_2) and/or when water has a sufficient time to react with surrounding rocks.

Nontronite can be in equilibrium with siderite if the pressure of CO_2 exceeds 10^{-4} atm. If the pressure is below this value, then the nontronite is in equilibrium with $\text{Fe}(\text{OH})_2$ or with Fe^{2+} -silicates greenalite $\text{Fe}^{2+}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and minnesotaite $\text{Fe}^{2+}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (Fig. 3). Minnesotaite should precipitate at high concentrations of H_4SiO_4 and greenalite at lower H_4SiO_4 and high Fe^{2+} concentrations, but their formation is strongly dependant on the pH (Fig. 3). In addition, as

previously discussed by Catling (1999), siderite is highly favored at higher P_{CO_2} (Fig. 4), which explains also why Fe^{2+} -silicates are favored at higher pH (or lower P_{CO_2}). Therefore the nontronite alone cannot be used to infer the CO_2 partial pressure during the Noachian. Paragenesis of nontronite is required to constrain the composition of the primary atmosphere.

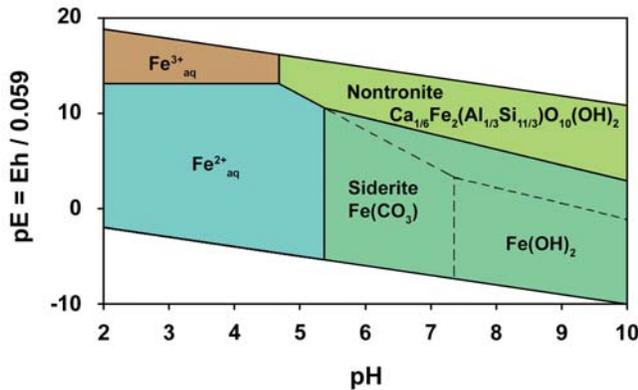


Figure 2. pE-pH stability diagram of nontronite in primary Martian conditions. The dark green area corresponds to siderite stability field calculated for $P_{\text{CO}_2} = 1$ atm. The dashed lines correspond to the equilibrium between nontronite, Fe^{2+} and $\text{Fe}(\text{OH})_2$ (or Fe^{2+} -silicates), if $P_{\text{CO}_2} < 10^{-4}$ atm.

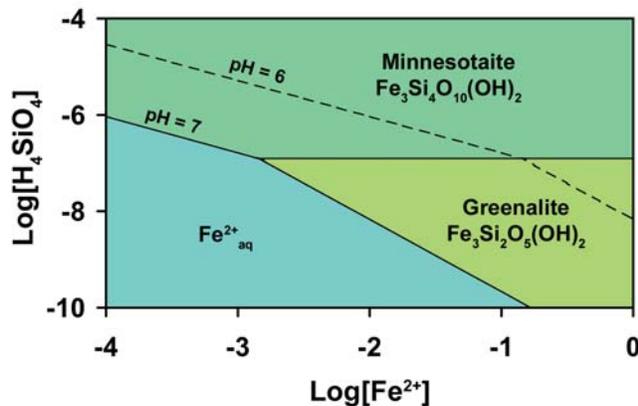


Figure 3. Stability diagram of Fe^{2+} -silicates greenalite and minnesotaite, calculated at $\text{pH} = 7$. The dashed line correspond to the same equilibrium but at $\text{pH} = 6$. The equilibrium line between minnesotaite and greenalite is independent from the pH .

Alternatively, the potential absence of Fe^{2+} phases has important consequences on the primitive environment on Mars. Indeed, it is generally stated that early conditions on the surface of telluric planets are reducing, as evidenced by siderite on the Earth [8]. Therefore, the apparent absence of Fe^{2+} phase implies that surface conditions became oxidizing very early. However the possible oxidants effective at this epoch are

quite limited. H_2O_2 has probably always remained a minor or even a trace species in the atmosphere, and thus is unlikely to be an important oxidation agent on the surface. O_2 is usually invoked in alteration models. On Earth its high abundance is widely accepted to be a result of photosynthesis which requires the presence of life. The last potential oxidant on Mars is H_2O followed by the escape of H_2 . Such mechanisms have been previously evoked to explain the rise of photosynthetic O_2 on the Earth [9]. Here the irreversible oxidation of early Mars occurs through out-of-equilibrium oxidation, H^+ being used as the main oxidant, providing a sink for oxygen in oxidized species and explain the loss of water from Mars [10].

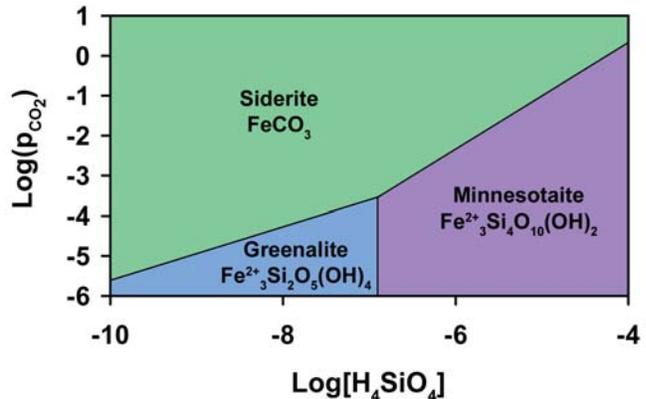


Figure 4: Stability diagram of Fe^{2+} -silicates and siderite as a function of H_4SiO_4 activity and CO_2 partial pressure.

Conclusions: Thermodynamic calculations show that nontronite and montmorillonite have formed on Mars in the presence of abundant water, and near neutral pH. Such environment is very different from the sulfate-acidic media of Meridiani Planum and related formations. In addition the presence of nontronite suggests that conditions became oxidizing early in the Martian history. Alternatively detection of Fe^{2+} -phases such as silicates / siderite, if present, could bring important insights into the primitive conditions during the Noachian, propice to the emergence of life.

References: [1] Poulet F. et al. (2005) *Nature*, 481, 623-627. [2] Goetz W. et al. (2005) *Nature*, 436, 62-65. [3] Catling D. C. (1999) *J. Geophys. Res.*, 104, 16453-16469. [4] Gooding J. L. (1978) *Icarus*, 33, 483-513. [5] Gendrin A. et al. (2005) *Science*, 307, 1587-1591. [6] Squyres S. W. et al. (2004) *Science*, 306, 1709-1714. [7] Madden M. E. E. et al. (2004) *Nature*, 431, 821-823. [8] Ohmoto H. et al. (2004) *Nature*, 429, 395-399. [9] Catling D. C. et al. (2001) *Science*, 293, 839-843. [10] Lammer H. et al. (2003) *Icarus*, 165, 9-25.