

EARLY MARTIAN SURFACE CONDITIONS FROM THERMODYNAMICS OF PHYLLOSILICATES.

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Introduction: The Mars Express OMEGA and Mars Reconnaissance Orbiter CRISM imaging spectrometers have identified phyllosilicates (Fe, Mg, Ca-smectites, kaolinite and chlorite) in Noachian aged terrains [1,2], often associated with lacustrine or fluvial deposits [3,4]. Clay minerals usually result from long term weathering of primary minerals by liquid water at neutral to alkaline pH [5], suggesting an early environment completely different from the acidic conditions responsible for the formation of sulfate outcrops widely observed on Mars [6,7]. This also suggests a global evolution of the martian surface environment, through loss of water from the surface [5,8].

Starting from the hypothesis that phyllosilicates are formed by liquid water induced weathering of the primary basaltic outcrops, thermodynamic models are used to study the conditions on the surface during the Noachian. Focus was placed on the effect of acidic conditions and temperature using solution equilibria and thermodynamic models.

Methods: The water composition data presented in Table 1 was used as input of the models. This composition reflects possible primary solutions on Mars [9]. Al^{3+} and SiO_2 have been set up at typical terrestrial values, being generally driven by their low solubility. The Geochemical Workbench software package was used to model thermodynamic equilibria, with the *thermo_phrqptz* database, which is especially designed for solution equilibrium at ionic strength using the Pitzer model. This database was updated by including the Pitzer parameters for Fe^{2+} and Fe^{3+} as well as ferric and ferrous aqueous species [10,11]. Also included are approximately 350 silicates taken from the *thermo.com.v8.r6+* database.

Table 1. Primary concentrations and activities of dissolved species taken from [9] except for Al^{3+} and H_4SiO_4 which are estimated for the present work.

Specie	Log (Activity, $10^{-3} \text{ mol l}^{-1}$)	Concentration (mg L^{-1})
SiO_2	-4.5	60.1
Al^{3+}	-5	0.3
$\text{Fe}^{2+/3+}$	-3.1	44.7
Mg^{2+}	-3.0	24.3
Ca^{2+}	-3.3	20
K^+	-4.2	2.7
Na^+	-3.1	18.4
SO_4^{2-}	-3.7	17.3
Cl^-	-3.2	23

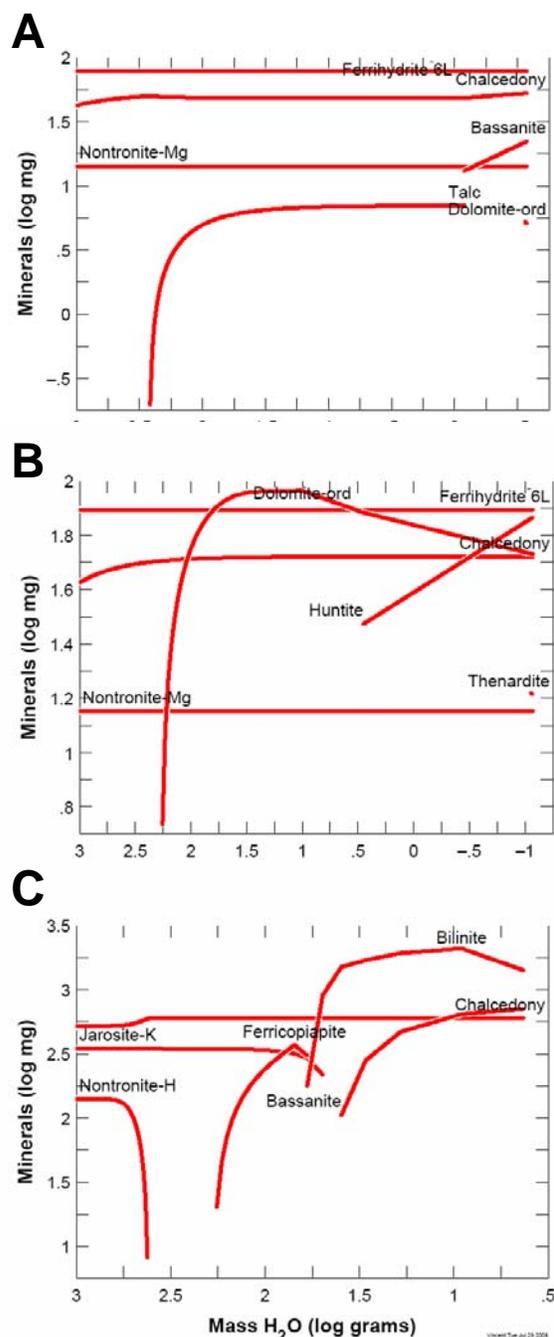


Figure 1: Three simulations of evaporation processes at 25°C using initial compositions presented in Table 1 with $p_e = 13.05$ (high oxidation level). (A) $p_{\text{CO}_2} = 0.001$ bar, $\text{pH} = 7$. (B) $p_{\text{CO}_2} = 1$ bar, $\text{pH} = 7$, $[\text{Cl}^-] = 120 \text{ mg L}^{-1}$. (C) $p_{\text{CO}_2} = 0.006$ bar, $\text{pH} = 3$, $\text{SO}_4^{2-} = 5000 \text{ mg L}^{-1}$, all concentrations are multiplied by 10 to simulate an advance state of evaporation.

Evaporation simulations: In all simulations, the evaporation paragenesis is largely dominated by ferric phases. In such a Fe-rich geochemical system, the early paragenesis (high water content) includes mostly nontronite, ferrihydrite and chalcedony (Fig. 1A&B). All these phases precipitate from the very beginning of the simulation, indicating that the early solution is supersaturated at neutral pH and high pe. The amount of precipitated phyllosilicate is largely dependent on availability of Al^{3+} .

In low p_{CO_2} , nontronite dominates along with silica (chalcedony) and ferrihydrite (Fig. 1A). If the CO_2 pressure becomes high, then carbonates become predominant (Fig. 1B). However, siderite does not appear because the conditions are too oxidizing.

Finally, in the presence of sulfur (in this case SO_4^{2-} , resulting from sulfides or SO_2), the evaporite assemblage is dominated by ferric sulfates (jarosite, ferricopiapite and bilinite). This case shows the lowest stability of nontronite, which dissolves very early in the evaporation sequence as a result of conditions becoming strongly acidic. In most simulations, smectites did not last in acidic conditions, with the exception of kaolinite which can precipitate down to pH ~ 2.

Temperature effect: Two different scenarios were investigated for the effect of temperature on the precipitating parageneses. In the first one, the conditions are oxidizing ($pe = 13.05$) which can simulate the effect of increasing the temperature on the surface, for example by volcanic activity. In this case, nontronite appears remarkably stable, destabilizing only at temperature above 190°C.

In the second scenario, conditions are strongly reducing ($pe = -5$). This corresponds to typical terrestrial subsurface hydrothermal systems. In this case the mineralogical paragenesis appears very complex, with several assemblages of Fe^{2+} and Fe^{3+} phyllosilicates evolving with the temperature. Globally, carbonates and nontronite are stable up to ~50°C. Other iron silicates are present up to 75°C, including minnesotaite and cronstedtite. At higher temperature, iron phyllosilicates are not stable any more and are replaced by magnetite + saponite. At temperatures higher than ~140°C, chlorite (clinochlore) becomes stable.

Conclusions: These simulations confirm previous results concerning low- CO_2 pressure during the Noachian [5]. Nevertheless, while some specific conditions could lead to clays-carbonates associations (high pH, low pe, low temperature), these minerals appear mutually exclusive with sulfate deposits.

Thermal results indicate that chlorite identified by CRISM [2] formed in localized reducing conditions. However, the general abundance of Fe,Mg-smectites still suggests an overall oxidizing environment.

Further study will focus on the variability of smectite silicates (Fe, Mg, Al) to constrain primary solutions and the relationship with bedrock and atmosphere.

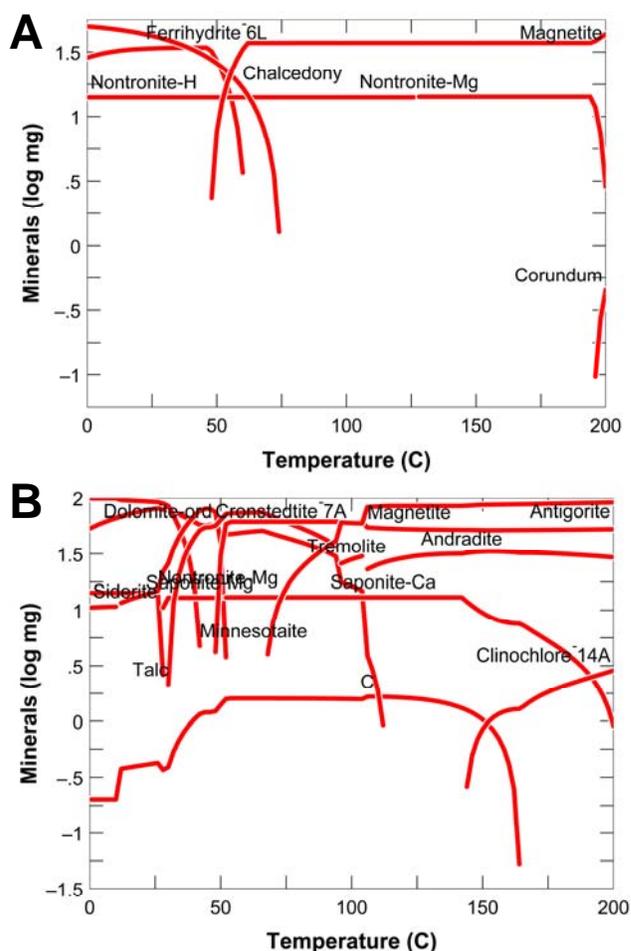


Figure 3: Evolution of the secondary paragenesis as a function of the temperature of the system. (A) pH = 7 and $pe = 13.05$. (B) more reducing conditions with pH = 7 but $pe = -5$. Nontronite is much more stable at high pe, but the conditions need to be reducing for chlorite to precipitate.

References: [1] Poulet F. et al. (2005) *Nature* 431, 623-627. [2] Mustard J. F. et al. (2008) *Nature* 454, 305-309. [3] Ehlmann B. L. et al. (2008) *Nature Geosci.* 1, 355-358. [4] Grant J. A. et al. (2008) *Geology* 36, 195-198. [5] Chevrier V. et al. (2007) *Nature* 448, 60-63. [6] Gendrin A. et al. (2005) *LPSC XXXVI*. [7] Squyres S. W. et al. (2004) *Science* 306, 1709-1714. [8] Bibring J. P. et al. (2006) *Science* 312, 400-404. [9] Catling D. C. (1999) *J. Geophys. Res.* 104, 16453-16469. [10] Marion G. M. et al. (2008) *Geochim. Cosmochim. Acta* 72, 242-266. [11] Tosca N. J. et al. (2007) *Geochim. Cosmochim. Acta* 71, 2680-2698.