PHYLLOSILICATES, CARBONATES, METHANE AND THE HABITABILITY OF NILI FOSSAE ON EARLY MARS. V.F. Chevrier[1], [1]W.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 and Mars Reconnaissance Orbiter CRISM imaging spectrometers have identified phyllosilicates (Fe, Mg, Ca-smectites, kaolinite and chlorite) in Noachian aged terrains [1-3], often associated with lacustrine or fluvial deposits [4,5]. Carbonates have also been recently identified in similar areas [6]. Clay minerals usually result from long term weathering of primary minerals by liquid water at neutral to alkaline pH [7]. Their presence with carbonates [6] suggests an early environment completely different from the acidic conditions responsible for the formation of sulfate outcrops widely observed on Mars [8]. Although, previous results have shown that the dominance of smectites over carbonates indicates rather a CO_2-poor atmopshere (Fig. 1, [7]), where CO_2 could thus be replaced by other greenhouse gas such as methane.

Starting from the hypothesis that all secondary phases are formed by liquid water induced alteration of the primitive crust, thermodynamic models are used to study the surface conditions during the Noachian. Focus was placed on the effect of CO_2 partial pressure and temperature on the parageneses.

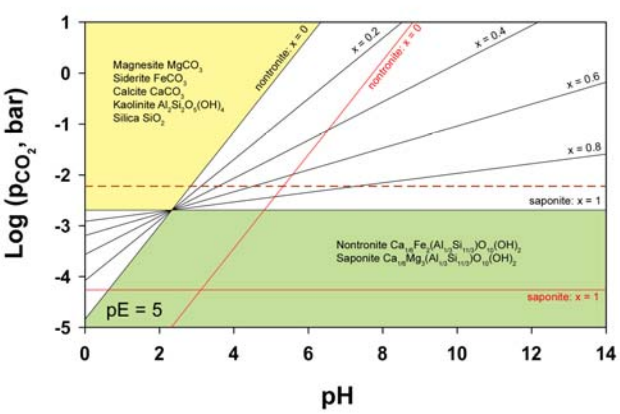

Figure 1. Equilibrium between carbonates and phyllosilicates as a function of the partial pressure of CO_2 and the pH, and for various Mg/(Mg+Fe), mol compositions. High Mg compositimons, characteristics of early Mars (as shown by the ALH84005 meteorite).

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.com.v8.r6+* database, which contains about 350 common silicates. This database uses Debye–Huckel theory for ionic activities, which is perfectly accurate to describe behavior of solutions at relatively to very low concentrations.

Table 1. Concentrations and activities of dissolved species from [9] except for Al^{3+} which is estimated in this work.

Specie	Log (Activity, 10^{-3} mol l^{-1})	Concentration (mg L^{-1})
SiO_2	-4.5	60.1
Al^{3+}	-5	0.3
$Fe^{2+/3+}$	-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

Temperature effect: the effect of temperature was tested in reducing conditions which correspond to typical terrestrial hydrothermal systems. In all cases (even at high oxidation), nontronite appears only stable at low temperatures, below 150ºC (Fig. 2). At low temperatures, siderite is present only in reducting conditions and kaolinite appears only in high p_{CO2} (Fig. 2 B). At higher temperatures, the mineralogical paragenesis is composed of diaspore, saponite and chlorite (amesite) at low p_{CO2}. At higher p_{CO2}, chlorite is replaced by serpentine (antigorite). In all cases, the excess of iron is converted into hematite. The composition in Table 1 is relatively iron-rich. Higher concentrations in magnesium, relative to iron, result in more abundant chlorite, serpentine and saponite.

Discussion: During the alteration process of olivine, two main processes occur: first the olivine is converted into serpentine:

$6\ Fe_2SiO_4 + 7\ H_2O = 3\ Fe_3Si_2O_5(OH)_4 + Fe_3O_4 + H_2$

Since this olivine is iron-rich (fayalite pole), H_2 is produced as a result of iron oxidation and reduction of water. The reacrion produces also greenalite which can be enriched in Fe^{3+}, resulting in more iron oxidized and more H_2 produced. The H_2 produced can react with CO_2 to form methane [10,11]:

$4\ H_2 + CO_2 = CH_4 + 2\ H_2O$

Alternatively, for magnesian poles, the alteration of forsterite does not produce H_2:

$2\ Mg_2SiO_4 + 3\ H_2O = Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$

Thus methane is only an ouotcome of iron oxidation. Nevertheless, a processus called carbonation occurs when serpentine formed at high temperature reacts with CO_2 to form carbonate to magnesite and talc [12]:

$$2\ Mg_3Si_2O_5(OH)_4 + 3\ CO_2 = Mg_3Si_4O_{10}(OH)_2 + 3\ MgCO_3 + 3\ H_2O$$

This reaction can occur when the temperature decreases (Fig. 3) or if the CO_2 pressure increases. Therefore, this reaction represents an alternative CO_2 sink to methane production. The similar reaction is also possible for iron phases, resulting in minnesotaite (iron pole of talc) formation

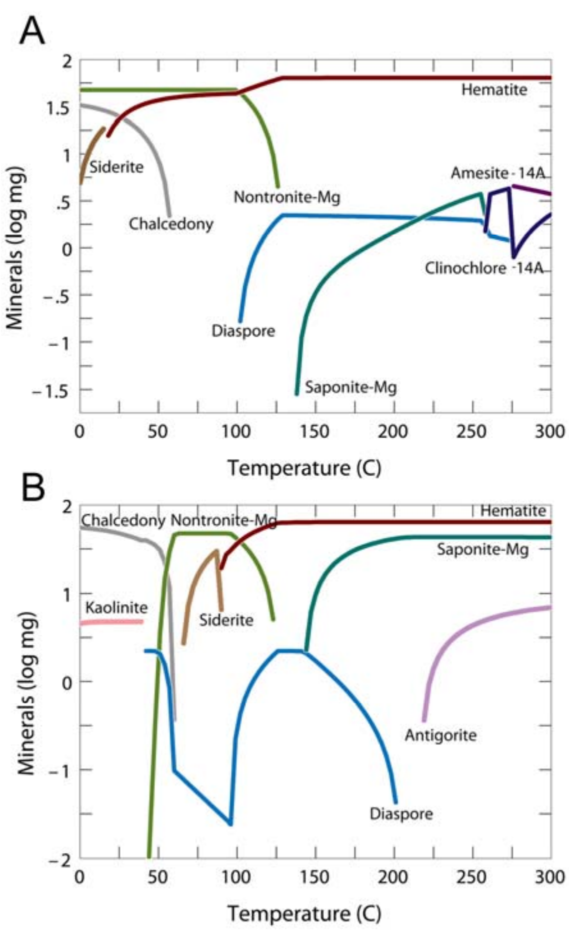

Figure 2. Evolution of the secondary paragenesis as a function of the temperature of the system in reducing conditions (pe = 0)0. **(A)** Low p_{CO2} = 0.006 bar. **(B)** High p_{CO2} = 1 bar. High temperatures favor the formation of chlorite phases at low p_{CO2}. Talc and saponite form at higher p_{CO2}.

Conclusions: These results confirm that the Noachian parageneses are controlled by the CO_2 partial pressure and temperature, rather than pH or water abundance [7]. The observation of serpentine in Nili Fossae [13] indicates hydrothermal alteration of olivine, although the presence of magnesite shows that carbonation processes and thus reaction with CO_2 probably occurred at relatively high temperature, preventing its release in the atmosphere. Then the presence of nontronite indicates that conditions probably evolved from early hydrothermalism at the end of the emplacement of the primitive crust, to surface weathering and evaporation in low CO_2 partial pressure (Fig. 1).

The presence of magnesite indicates that CO_2 reacted with the basement rocks and if some iron-bearing phases were present, they probably oxidized, resulting in methane formation, although no secondary iron-rich phyllosilicate (greenalite, minnesotaite) has been indentified in this region. This would however provide an ideal environment for life. On Earth, methanogen bacteria uses the process of iron oxidation, facilitating the conversion from H_2 and CO_2 to CH_4. Thus iron-rich phases would provide a better environment than just magnesium, providing the energy source for archea. But the most important conclusion is that the presence of methane suggests a geologically active environment, necessary to life to appear and persist over time.

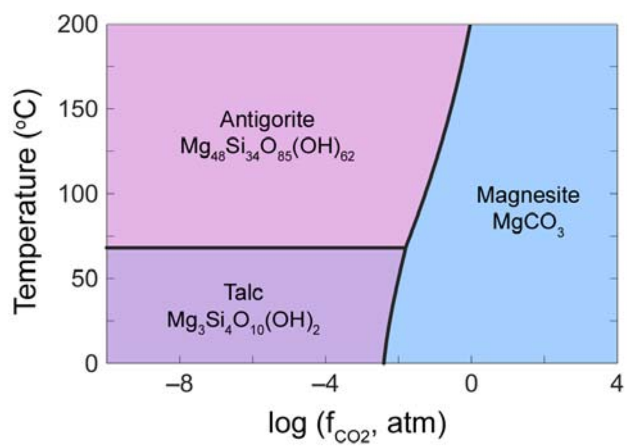

Figure 3. Equilbrium between magnesium silicates (serpentine and talc) and carbonate as a function of temperature and p_{CO2}. This diagram illustrates the processus of carbonation.

References: [1] Poulet F. et al. (2005) *Nature* 481, 623-627. [2] Mustard J. F. et al. (2008) *Nature* 454, 305-309. [3] Bishop J. L. et al. (2008) *Science* 321, 830-833. [4] Ehlmann B. L. et al. (2008) *Nature Geosci.* 1, 355-358. [5] Grant J. A. et al. (2008) *Geology* 36, 195-198. [6] Ehlmann B. L. et al. (2009) *Science* 322, 1828-1832. [7] Chevrier V. et al. (2007) *Nature* 448, 60-63. [8] Bibring J. P. et al. (2006) *Science* 312, 400-404. [9] Catling D. C. (1999) *J. Geophys. Res.* 104, 16453-16469. [10] Lyons J. R. et al. (2005) *Geophys. Res. Lett.* 32. [11] Oze C., M. Sharma (2005) *Geophys. Res. Lett.* 32. [12] Hansen L. D. et al. (2005) *Canadian Mineralogist* 43, 225-239. [13] Ehlmann B. L. et al. (2009) *LPSC* XL, #1787.