THERMODYNAMIC MODELLING OF CARBONATE-PHYLLOSILICATE PARAGENESES AND IMPLICATIONS FOR ENVIRONMENTAL CONDITIONS IN NILI FOSSAE, MARS. V.F. Chevrier[1], M. Morisson[1]. [1]Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR, 72701; 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) mostly in Noachian aged terrains [1-3], often associated with lacustrine or fluvial deposits [4,5] and thus indicative of paleo-environments with abundant liquid water, a pH close to neutral and low to moderate temperatures. Despite these conditions being interesting for the global evolution of Mars [6], they remain quite vague for more localized and detailed analyses. Of all the phyllosilicate-rich regions on Mars, Nili Fossae is one of the most interesting due to the occurrence of additional phases such as carbonates or serpentine [7,8]. This interesting paragenesis at the regional scale allows thermodynamic models to be applied in order to more precisely constrain the paleo-environments and their evolution.

To this end, we use thermodynamic modelling and studied the evolution of a brine derived from a komatiitic basalt in various scenarios of temperature and geochemical conditions [9]. We focus on two important parameters: The partial pressure of CO_2, and the RedOx potential, which relates to the exitance of oxidizing or reducing conditions at the surface or in the subsurface.

Methods: The water composition data presented in Table 1 was used as an input for all the models. This composition reflects possible primary brine solutions derived from primitive basalts on Mars [10]. Al^{3+} and SiO_2 have been set up at typical terrestrial values, being determined 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 (to which berthierine and ferrihydrite were added).

Table 1. Primary concentrations and activities of dissolved species taken from [10] except for Al^{3+} which is estimated for the present work.

Ionic 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

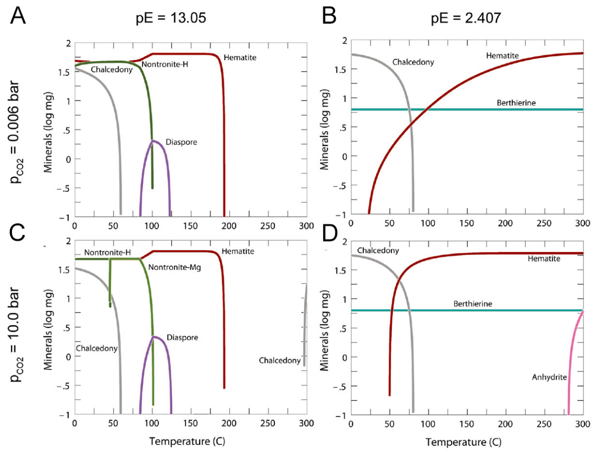

Figure 1. Evolution of the brine described in Table 1 as a function of temperature for various scenarios in open environments (so RedOx potential is constant across the simulation). A. Low CO_2 partial pressure p_{CO2} = 0.006 bar, oxidizing environment (Fe^{2+}/Fe^{3+} buffer at pE = 13.05); B. p_{CO2} = 0.006 bar, reducing conditions (S^{2-}/SO_4^{2-} buffer at pE = 2.407); C. High CO_2 pressure as on a putative early Mars p_{CO2} = 1 bar, Fe^{2+}/Fe^{3+} buffer; D. p_{CO2}= 1 bar, S^{2-}/SO_4^{2-} buffer.

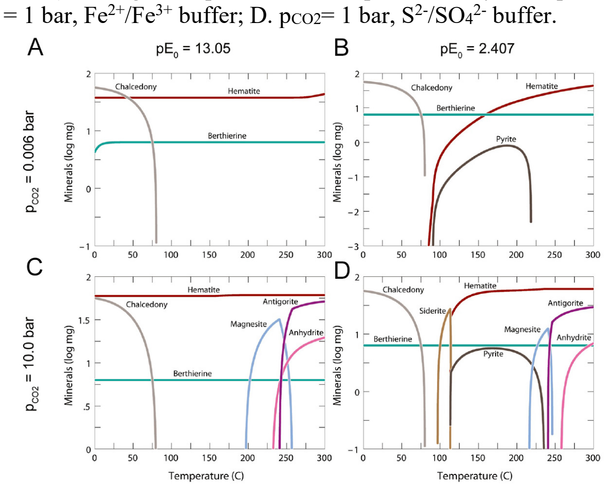

Figure 2. Evolution of the brine described in Table 1 as a function of temperature for various scenarios in open environments (RedOx potential is variable and adjusted by the model based on equilibrium phases). A, B, C and D correspond to the same conditions as in Figure 1.

Effect of temperature on brine: Two different scenarios were investigated for the effect of temperature on the precipitating parageneses: Open system like at the surface (Fig. 1) or closed system (Fig. 2) as in the subsurface. The main difference being that the open system had a fixed RedOx potential (buffered with either iron or sulfur) while the closed system's RedOx was allowed to vary according to the equilibrium phases.

In the open system, the mineral assemblages and evolution with temperature are almost identical regardless of the pressure of CO_2, but very different depending on the RedOx potential. The main phyllosilicate is nontronite in oxidizing environments (and low temperature) and berthierine in reducing environments. No carbonate is observed. In closed system, the situation is different, and this time the assemblages nature and evolution is similar between RedOx states but affected by the pressure of CO_2. Low p_{CO2} are dominated by phyllosilicates and oxides, while high p_{CO2} show the appearance of Mg-carbonates at temperatures above 200ºC and serpentine (antigorite) above 250ºC.

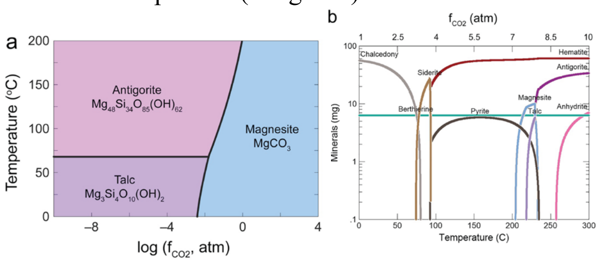

Figure 3: a. Phase diagram for Mg silicate / carbonate equilibrium; b. Evolution of the precipitating mineral parageneses as a function of temperature from 0 to 300 °C and concurrent increase of CO_2 fugacity from 1 to 10 atm, for a variable RedOx potential of initial value $pE_0 = 2.407$. Note: Antigorite is the main form of serpentine.

Implications for Nili Fossae geochemical conditions:

Carbonation on Mars: Our thermodynamic models suggest that high p_{CO2} would induce carbonation in the subsurface, especially at temperatures in the hydrothermal range (e.g. >200ºC, Fig. 2B and D). The main assemblage related to this phenomenon is the equilibrium between serpentine and talc + magnesite (Fig. 3). The identification of both magnesite and serpentine in Nili Fossae suggests that carbonation must have occurred and therefore that the CO_2 fugacity of the fluids involved was probably quite high, along with the temperature. This would also explain the limited and discrete occurrence of carbonates, and also that they are essentially Mg-carbonates. Note also that siderite can trap some of the CO_2 and iron at low temperature, if the conditions are reducing enough.

*Atmospheric implications: W*e looked into the formation of reduced gas molecules in our simulations: methane, hydrogen and carbon monoxide, as usual by-products of serpentinization and carbonation. Methane and hydrogen are of particular interest, both because they act as greenhouse gas. Methane is also of high interest for astrobiology on Mars. The most interesting result is that the pressures of gas in equilibrium with these environments is low regardless of the pressure of CO_2. In both environments, hydrogen has the highest partial pressure but only around 10^{-4}-10^{-5} bar, while methane is produced only in very small amounts, with pressures around 10^{-10}-10^{-15} bar (interestingly similar to present-day values).

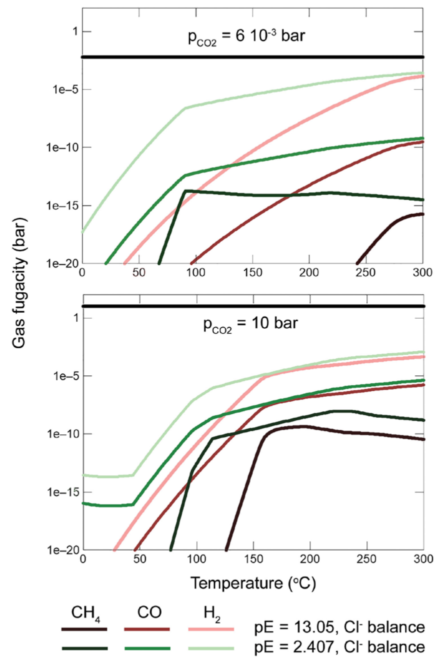

Figure 4: Evolution of the methane, carbon monoxide, and hydrogen fugacity (equal to partial pressure at low pressures) as a function of temperature for reducing (pE = 2.407, green lines) and oxidizing (pE = 13.05, red lines) conditions and different fixed CO_2 partial pressures: (A) p_{CO2} = 0.006 bar; and (B) p_{CO2} = 10.0 bar (thick horizontal line).

Conclusions: The minerals observed in Nili Fossae indicate two distinct environments. The occurrence of nontronite indicates low temperatures and oxidizing environments, probably related to weathering activity. On the other side, the occurrence of magnesite and serpentine indicate periods of hydrothermal activity, serpentinization and carbonation with fluids rich in CO_2. The concurrent secondary gas (methane or hydrogen) production is nevertheless very small. So unless widespread and extended in time, hydrothermalism was not a significant source.

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 (6), 355-358. [5] Grant J. A. et al. (2008) *Geology* 36 (3), 195-198. [6] Chevrier V. et al. (2007) *Nature* 448, 60-63. [7] Ehlmann B. L. et al. (2008) *Science* 322 (5909), 1828-1832. [8] Ehlmann B. et al. (2010) *Geophys. Res. Lett.* 37 (6). [9] Chevrier V. F., M. Morisson (2021) *Journal of Geophysical Research: Planets* 126 (4), e2020JE006698. [10] Catling D. C. (1999) *J. Geophys. Res.* 104 (E7), 16453-16469.