Serpentinization and carbonation of the Martian Crust with chlorine-rich fluids. 
B. Bultel1, F. Klein2, M. Andréani1 and C. Quantin1 1Laboratoire de Géologie de Lyon, Université Lyon 1, ENS Lyon, CNRS UMR 5271 (Laboratoire de Géologie de Lyon, Bâtiment Géode 2 Rue Raphael DUBOIS 69622 VILLEURBANNE CEDEX). benjamin.bultel@univ-lyon1.fr, 2 Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

Introduction:
Carbonates are presents in Martian meteorites as minor phases and in situ analysis of the Martian dust also reveal carbonates as a minor component [1], [2]. Only orbital detections allow the analysis of the geological context of the formation of the Martian carbonates. So far, only crustal outcrops have revealed carbonates and serpentine: in an olivine rich layers link with the ejectas of Isidis basin, or in crustal outcrops such as deep canyon or central peak of large impact crater that may have exhumed crust from depth [3], [4], [5], [6] and [7]. A systematic analysis of the alteration minerals in these central peaks of impact craters on the Noachian crust has been conducted by [4]. They demonstrate that the typical mineralogical assemblage observed in central peak of impact crater between Isidis and Hellas Basins are chlorites, Fe-Mg smectites, serpentine and carbonates. The most abundant phases in term of detection are chloride and smectite while serpentine and carbonate are rarer. A geological analysis of these detections suggests that these minerals are exhumed from depth rather than being formed at time of the impact. [8] had already pointed out that the hydration and carbonation of the martian crust lead to minor presence of serpentine and carbonates along with Mg-smectite, chloride and talc under certain conditions. This study show that it should be a fluid dominated system, with a partial pressure of CO2 (pCO2) of 1 bar and high amount of olivine should be present in the protolith (~30%).

In the present study, we used two chlorine-rich fluids to study its influence on the formation of serpentine and/or carbonates. One fluid is influenced by an ultramafic system and another by a basaltic system.

The geochemical model:
Our model was performed using the software code EQ3/6, version 8.0 [9] and [10] and a customized database for 0-400°C and 50MPa [11].

We add a pH of 1 bar in the closed system and heat the fluid at 400°C. Then, the system is studied during a cooling from 400 to 25°C with a W/R=10. The rock is composed of 30% of olivine (Fo60), 30% of pyroxene (En90,Fs10) and 40% of plagioclase (An40) what may reflect the average basaltic composition of the Martian crust as inferred from meteorites analysis as well as in situ analysis (e.g.:[12] and [13]).

Description of the fluids:
We used two different fluid. One is influenced by interaction with ultramafic system (Rainbow from [14]), the other is influenced by a more basaltic system (Menez Gwen 1997 from [15]). The ultramafic fluid is high chlorininity and low silica compare to other hydrothermal fluid ([14] and references therein). The basaltic fluid is less chlorine-rich than the ultramafic fluid (7.5x10^-1 vs 4.0x10^-1 molality). Both fluid are acidic (pH=2.8 vs pH=4.5).

Results:
The figure 1 shows the evolution of the system during the cooling from 400°C to 25°C with the fluid influenced by an ultramafic system. The %mol of the minerals in equilibrium is shown in function of the temperature. The serpentinization is predicted to occur at relatively low temperature (<160°C). The other Fe-Mg phyllosilicates predicted are beidellite at high temperature only (>345°C), chlorite (<350°C), talc (<345°C), nontronite (<160°C) and celladonite (<80°C). Quartz is predicted to be stable from 395°C to 230°C and the iron oxide (hematite) is predicted to be stable from 400°C to 105°C.

Figure 1: Percentage of mole of minerals produced from 400°C to 25°C with the fluid influenced by an ultramafic system containing 3.10^-2 mol.L^-1 of CO2 at a W/R of 10. The indication -ss indicates a solid solution.

The figure 2 shows the evolution of the system during the cooling from 400°C to 25°C with the fluid influenced by a basaltic system. The %mol of the minerals in equilibrium is shown in function of the temperature. The carbonation is not predicted to be efficient and accurs at T<220°C. The major phase are hematite
(iron oxide), saponite and nontronite (Fe-Mg phyllosilicates).

Figure 2: Percentage of mole of minerals produced from 400°C to 25°C with the fluid influenced by an basaltic system containing $3.10^{-2}$ mol.L$^{-1}$ of CO$_2$ at a W/R of 10. The indication --ss indicates a solid solution.

**Conclusion:**

Serpentinization is favor by a fluid influenced by an ultramafic system. Carbonation is favor by a basaltic fluid but the production of phyllosilicate is more efficient. The carbonation is limited by the combined low pH and low alkalinity of the systems (<20 mg/L CaCO$_3$).

If we compare our results with the one obtained in [8], the serpentinization is favored by the presence of Cl$^-$ while it disfavored the carbonation.

Synchrones serpentinization and carbonation would necessary a fluid influenced by an intermediate system between a basalt and an ultramafic rock, similar to the high-olivine basalt detected around the serpentine detection as it is at Nili Fossae [5 and 16] or Libya Montes [3].

We will compare the mineralogical assemblages predicted here with the groups of mineral associated to carbonates and/or serpentine detected on Mars [17, 18].

The detailed interpretation of our sytem concerning the exchange Fe$^{2+}$/Fe$^{3+}$ and the composition of the solid solution will be presented.

Both modelling shown here are reducing exivenissement which would favor CO$_2$ reduction to organic compounds that are proposed as potential precursors for the first building blocks of life (see review in [19]). The consequences on the habitability of the environment will so be discussed.

**References:**


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