

**THE ROLE OF VOLCANIC SOUR GAS ON THE ALTERATION OF MARTIAN BASALT: INSIGHTS FROM GEOCHEMICAL MODELING.** G. Berger<sup>1</sup>, E. Treguier<sup>2</sup>, C. d'Uston<sup>2</sup>, P. Pinet<sup>3</sup>, M.J Toplis<sup>3</sup>, <sup>1</sup>LMTG, 14 av. E. Belin, 31400 Toulouse, France <sup>2</sup>CESR, 14 av. E. Belin, 31400 Toulouse, France ; <sup>3</sup>DTP, 14 av. E. Belin, 31400 Toulouse, France, [berger@lmtg.obs-mip.fr](mailto:berger@lmtg.obs-mip.fr)

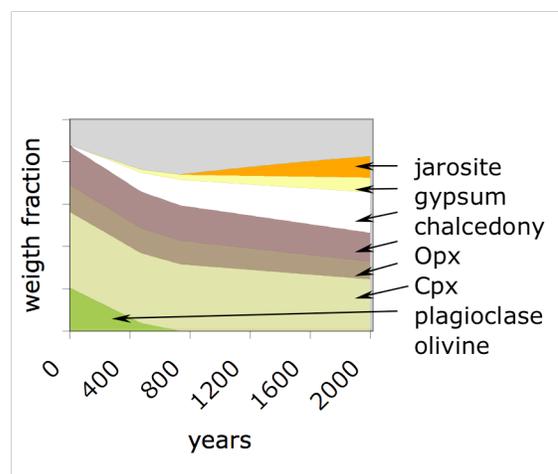
The conditions of aqueous alteration at the Martian surface have been the subject of considerable debate in the recent literature. The occurrence of layered and sulphate bearing sediments on Mars suggests the presence of water as a liquid phase during Martian geological history. Chemical models have been developed to constrain the composition of the assumed primary aqueous solution [1]. More recently, in order to explain the observations of the MER rover Opportunity at Meridiani, alternative models have favored the assumption of hydrothermal alteration of volcanic materials [2], while other authors have argued in favor of a brine/evaporite scenario [3]. Detailed geochemical modeling of the evaporation of such a brine is presented in [4], while the interaction of an acidic brine with Martian basalt has been modeled by [5].

In the present study we assess the chemical constraints of the alteration of basaltic material by a cold aqueous phase under atmospheric sour gas containing  $\text{SO}_3$ .  $\text{O}_2$  and  $\text{CO}_2$  partial pressures were assumed to be close to values currently observed in the Martian atmosphere. Water is assumed to be derived from the melting of ice, while  $\text{SO}_3$  is assumed to be provided by the dry oxidation of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in the atmosphere. It is of note that this scenario contrasts with the case on Earth, where plate tectonics and hydrothermal circulations recycle water in the lithosphere, allowing the underground aqueous oxidation of sulphur gas. In contact with near-surface water, the sour gas will dissolve extremely rapidly, producing pristine sulfuric acid capable of altering basaltic rocks at the Martian surface. Such alteration is the subject of this contribution and has been modeled using the geochemical simulator JChess [6]. In contrast to published models, we focus on gas-rock interaction, the aqueous phase, initially pure water, only acting as an agent or environment allowing the chemical reactions to proceed. The mineralogical composition of the 'pristine' basalt used in our simulations corresponds to characterizations of the Martian basalt, Adirondack from Gusev.

From a chemical point of view, preliminary models [7] show that the transformation of mafic silicates to sulphates, iron oxides and silica is controlled by the  $\text{H}_2\text{SO}_4$ /basalt ratio through a nearly isochemical reaction, with the exception of S addition. This result is of interest as APXS data from Meridiani are consistent with approximately isochemical (closed system)

alteration of the original basalt, with the exception of S addition, or accumulation of Fe-rich berries [8].

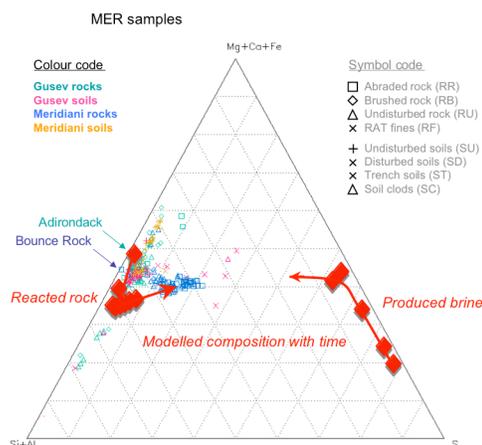
To extend the results of the preliminary data, more complicated reaction pathways have been considered to simulate the context of embedded dunes involving fresh basalt, pure water (ice melting) and atmospheric  $\text{SO}_3$ . The conditions of temperature,  $\text{CO}_2$  and  $\text{O}_2$  pressure, are those used previously. Several  $\text{SO}_3$ /basalt mass ratios and different dissolution kinetics laws have been tested. Given the acidic conditions of the modeled environment, the kinetics of dissolution may be expected to decrease in the order, magnetite, then olivine, then the other rock forming minerals. The nucleation and growth kinetics of the stable secondary phases are assumed to be immediate for carbonate, silica and sulphate. For the short term reactions considered here we have assumed the precipitation of goethite rather than hematite, chalcedony rather than quartz and excluded the precipitation of magmatic mafic and ultramafic minerals. For the precipitation of clay minerals, we selected rate constants symmetric to the dissolution of plagioclase, a typical aluminosilicate. Figure 1 shows the changes in mineralogy as a function of time of a 0.5 m thick basalt layer exposed to a 200 m high Martian atmospheric column, with an initial overpressure of 100 millibars  $\text{SO}_3$ . The nature of the secondary phases is consistent with the observations of the MER rovers, and the progressive disappearance of the mafic minerals mimics the variation of Fe-mineralogy (derived from Mössbauer) as a function of sulfur abundance (derived from APXS) observed at Meridiani.



**Figure 1.** Mineralogical changes with time.

Assuming evaporation of the fluid phase under the low pressure conditions of the Martian sub-surface, the final chemical composition of the system is a mixture of altered basalt and the precipitated brine. An additional variable affecting the final composition of the rock is thus the mobility of the brine: does brine leave the altered zone before evaporating? does it evaporate where it formed?, or can brine accumulate before evaporation by migration from a neighboring area?

To assess this issue results of our modeling have been compared to a compilation of APXS data collected by the MER rovers (Fig. 2), reported in the (Mg+Fe+Ca)-(Si+Al)-S ternary diagram already used by [2, 3]. This comparison suggests that the sulphate rich rocks at Meridiani can be derived from the overlying basalt sand by the sole action of water and  $\text{SO}_3$ , with minor influence of the mobility of brine. On the other hand, we note that within the framework of the modeling presented here, the occurrence of Fe-oxide spherules observed in basaltic sand and rock outcrops [9] could represent the product of the earliest stages of acidic alteration, without in-situ evaporation of the resulting brines.



**Figure.2:** modeled composition (red symbols) for the altered basalt (left) and the brines (right) as a function of elapsed time (arrow)

**Reference :** [1] King, P.L. et al. (2004), *G.C.A.* 68, 4993-5008. [2] McCollom, T.M. and B.M. Hynek (2005), *Nature* 438, 1129–1131. [3] Squyres, S.W. et al. (2006), doi:10.1038/nature05212. [4] Tosca, N.J. et al. (2005), *EPSL* 240, 122-148. [5] Zolotov, M.Y. and M.V. Mironenko (2007), *JGR*, doi: 10.1029/2006JE002882. [6] Van der Lee, J. and L. de Windt, (2002), Users manual LHM/RD/02/13. [7] Tréguier, E. et al., *JGR-planets* submitted [8] Tréguier, E. et al. (2007), 38<sup>th</sup> LPSC, Abs. #1730. [9] Squyres, S.W. et al., (2006), *JGR* 111, E12S12, doi:10.1029/2006JE002771.