

Removal of water from Mars' hydrosphere by serpentinization

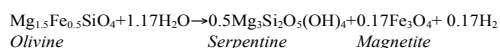
E. Chassefière (1,2) and F. Leblanc (3)

(1) Univ Paris-Sud, Laboratoire IDES, UMR8148, Université Paris-Sud, Bât. 504, Orsay, F-91405, France, (2) CNRS, Orsay, F-91405, France, (3) Laboratoire ATmosphères Milieux Observations Spatiales/IPSL, CNRS-UVSQ, Université Pierre et Marie Curie, Boite 102, 4 Place Jussieu, 75005, Paris, France (eric.chassefiere@u-psud.fr / Fax: + 33 1 69 15 49 11)

Abstract

One of the most plausible mechanisms proposed so far to explain the presence of methane in Mars' atmosphere is serpentinization of ultramafic rocks from crustal carbon [1]. This process, to be significant, requires ultramafic rocks to be present in Martian crust. Pyroxene is the most widely distributed mineral detected from the Martian orbit, covering large zones of the southern hemisphere old terrains [2]. Global maps of olivine performed by the TES spectrometer of Mars Global Surveyor show significant amounts of olivine-rich rocks at the surface of the planet [3]. Serpentine itself has been recently observed by CRISM on Mars Reconnaissance Orbiter in and around the Nili Fossae region [4], associated with alteration minerals, proving that it has been formed at some places at the surface of Mars. Serpentinization seems therefore a plausible mechanism of CH₄ synthesis in the Martian crust.

On Mars, the generation of H₂ by olivine, assuming a typical magnesium content of 75% (F_{0.75}: (Mg_{0.75}Fe_{0.25})₂SiO₄) during serpentinization can be expressed as [5]:



For 1 water molecule lost through iron oxidation, 6 molecules are involved in the hydration of olivine. As a consequence, 1 H₂ molecule released to the atmosphere is the counterpart of at least 6 H₂O molecules stored in the crust, this amount translating in 24 H₂O molecules if the released molecule is CH₄ (Fig. 1). Indeed, the oxidation of CH₄ into CO₂ (net budget : CH₄ + 2 H₂O → CO₂ + 4 H₂) results in the net release to the atmosphere of 4 H₂ molecules per released CH₄ molecule.

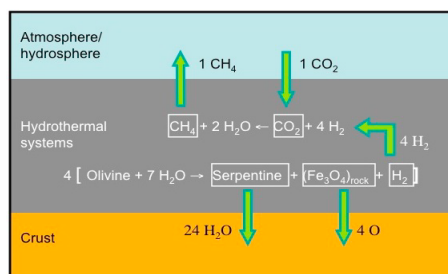


Figure 1: Schematic view of the H₂O-CO₂ cycle through serpentinization and methane formation, and related water, oxygen and carbon exchange fluxes between the crust, the hydrothermal systems and the active hydrosphere. Following this scenario, for 1 CH₄ molecule released to the atmosphere, as the result of the reduction of 1 CO₂ molecule provided by the atmosphere, 24 H₂O molecules and 4 O atoms are incorporated into crustal minerals under the form of serpentine.

Assuming that, like in some Earth's hydrothermal systems, the molar fraction of methane in the vented gas is 10%, the rest consisting of H₂, it may be calculated that, for 1 released CH₄ molecule, 78 H₂O molecules are stored in serpentine. Typically one or several hundred (if the molar fraction of methane is a few percents) H₂O molecules could therefore be stored for each released CH₄ molecule, suggesting that serpentinization could have resulted in the storage of large amounts of water in possible subsurface serpentine reservoirs.

Once released, CH₄ is converted to H₂ and CO₂ through oxidation. The release of CH₄ and H₂ results in an increase of the atmospheric H₂ buffer content, and therefore in an increase of the thermal escape flux of hydrogen, which is nearly proportional to the H₂ mixing ratio [8]. In this way, the hydrogen

released by the oxidation of the deep crust is lost to space, as imposed by the regulation of the redox state of the atmosphere by the balance between the O and H loss fluxes [9]. Crustal oxidation through serpentinization therefore results in the escape of the H atoms released by oxidation (under the form of H₂ and CH₄, and possibly other hydrocarbons), with subsequent isotopic fractionation of H. It is possible to calculate, through a simple model, the hydrogen isotopic fractionation induced by serpentinization occurring in the crust, and to estimate an upper limit of the cumulated serpentinization rate by using the present value of the D/H ratio (≈5 SMOW) as a maximum, assuming that this ratio is characteristic of the whole cryo-hydrosphere supposed to have exchanged with the atmosphere over geological times.

Assuming that most of the present hydrogen fractionation is due to serpentinization, it is found that 330 m of water (global equivalent layer) have been trapped in subsurface serpentine, whereas 55 m of water have been involved in Fe(II) oxidation during serpentinization, with the remaining hydrogen being further lost to space by thermal escape (Fig. 2). The primitive volume of the water present at the surface of Mars after the end of the heavy bombardment, 3.8 Gyr ago, is poorly known. The volumes of the potential reservoirs for ancient ocean(s), estimated from Mars Global Surveyor images and altimeter data, correspond to a 150 m thick GEL [8], less than generally assumed to explain the formation of the ancient valley networks of the South hemisphere (500 m to 1 km).

Some authors suggested that, from the initial 150 m equivalent depth ocean, 50 m could have escaped, 20-30 m could be trapped in the present polar caps, and 80 m could have been incorporated to subsurface material [8]. According to the present scenario of serpentinization-driven storage of water in the crust, a different picture is proposed. The remaining amount of water present at the surface at the end of the heavy bombardment would have been 425 m. During later periods, 65 m would have been consumed in Fe(II) oxidation and subsequent escape of the remaining hydrogen to space (55 m due to oxidation of iron during serpentinization, <10 m due to sulfur oxidation), 330 m would have been stored in serpentine, 10 m would have escaped to space through oxygen escape, and 20 m would remain today, mainly in polar caps (Fig. 2). This scenario, which doesn't require that large amounts of water have been lost to space, suggests that most of the water still present at the end of the heavy

bombardment (330 m from 425 m, that is ~75%) could have been stored in serpentine at later stages.

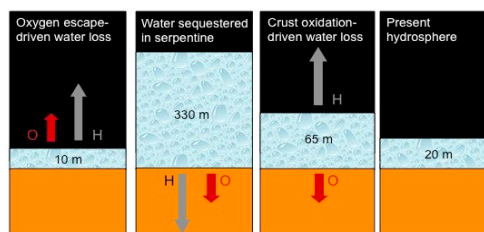


Figure 2: From the left to the right : water lost by oxygen non-thermal escape and induced H thermal escape (<10 m), water stored in serpentine (330 m), water lost by crust oxidation and induced H thermal escape (65 m) and water remaining today (20 m), assuming the SERP scenario.

Acknowledgements

This work has been supported by the interdisciplinary EPOV program of CNRS.

References

- [1] Oze, C., Sharma, M., 2005. Have olivine, will gas : Serpentinization and the abiogenic production of methane on Mars, *Geophys. Res. Lett.* 32, L10203.
- [2] Bibring, J.P., Langevin, Y., Mustard, J.F., Poulet, F., Arvidson, R., Gendrin, A., Gondet, B., Mangold, N., Pinet, P., Forget, F., the OMEGA team, 2006. Global Mineralogical and Aqueous Mars History Derived from OMEGA/Mars Express Data, *Science*, 312, 400-404.
- [3] Koeppen, W. C., Hamilton, V.E., 2008. Global distribution, composition, and abundance of olivine on the surface of Mars from thermal infrared data, *J. Geophys. Res.* 113, E05001, doi:10.1029/2007JE002984.
- [4] Ehlmann, B. L., and 13 colleagues, 2008. Orbital Identification of Carbonate-Bearing Rocks on Mars, *Science* 322, Issue 5909, 1828-1832.
- [5] Oze, C., Sharma, M., 2007. Serpentinization and the inorganic synthesis of H₂ in planetary surfaces, *Icarus* 186, 2, 557-561.
- [6] Liu, S.C., Donahue, T.M., 1976. The regulation of hydrogen and oxygen escape from Mars, *Icarus* 28, 231-246.
- [7] Chassefière E., Leblanc, F. 2010. Explaining the redox imbalance between the H and O escape fluxes at Mars by the oxidation of methane, *Planet. Space Sci.* 59, 218-226.
- [8] Carr, M.H., Head, J.W., 2003. Oceans on Mars: An assessment of the observational evidence and possible fate, *J. Geophys. Res.* 108, doi: 10.1029/2002JE001963.