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THE IMPACT OF SUBSURFACE SOURCES AND SINKS ON THE EVOLUTION OF EARLY ATMOSPHERIC CO₂, CH₄, AND D/H. E. Chassefière^{1,2} and F. Leblanc³, ¹Univ Paris-Sud, Laboratoire IDES, UMR8148, Université Paris-Sud, Bât. 504, Orsay, F-91405, France, e-mail address : eric.chassefiere@u-psud.fr , ²CNRS, 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.

Introduction: Like Venus and Earth, Mars has been endowed with large amounts of CO₂ during main accretion. Thermal escape of carbon is expected to have removed most of the primordial CO₂, with a characteristic time to lose 1 bar of CO₂ in the range from 1 to 10 Myr : if most of Mars' CO₂ was emplaced during the main accretion phase, the entire inventory could have been lost within 40 Myr [1]. Following this loss to space of CO₂, a secondary atmosphere progressively formed through volcanic outgassing of CO₂ [2]. According to the morphological analysis, 0.3 bar of CO₂ would have been released during the last 4 Gyr [3]. Crust formation modelling suggests that a total ≈ 1 bar of CO₂ have been outgassed, mostly during the Noachian [2]. The present CO₂ pressure is 7 mbar, showing that most of the atmospheric CO₂ present at the late Noachian has been removed during subsequent periods, either by escape to space, or by trapping in the subsurface, or both.

Mars has been similarly endowed with large amounts of water during accretion, equivalent to the content of several Earth oceans, corresponding to a several 10 km thick Global Equivalent Layer –GEL– [4]. The present total inventory of water on Mars has been estimated to correspond to a 35 m thick GEL [5]. The mega-regolith capacity is large, with up to ~ 500 m potentially trapped in the cryosphere, and hypothetically several additional hundreds of meters (up to ~ 500 m) of ground water surviving at depth below the cryosphere [6]. A ~ 500 m thick GEL is generally assumed to be required to explain the formation of outflow channels [7]. The fate of this water is unknown. It may have escaped to space, and/or be trapped in the subsurface under the form of hydrated minerals, water ice or, at large depth, liquid water.

The fate of CO₂ (several hundred mbar up to several bar) and H₂O (several 100 m thick GEL) present in the atmosphere and at the surface (or in the close subsurface) at the late Noachian is poorly constrained, and remains mysterious. Non-thermal escape of carbon and oxygen, driving the losses of, resp., CO₂ and H₂O, is not efficient enough to have removed hundred millibars of CO₂ and a several hundred meters thick GEL of H₂O [8,9]. Trapping of these volatiles in the crust under the form, resp., of carbonates and hydrates could have been the major process at the origin of Mars desertification.

A long-term carbon cycle involving CO₂, CH₄ and carbonates: The recent discovery of methane in the Martian atmosphere at a typical 10 ppb level [10,11] suggests that CH₄, rapidly oxidized to CO₂ in the atmosphere (or the regolith), could have been an important contributor to the atmospheric carbon inventory, in addition to volcanic CO₂ [3]. If CH₄ is the result of serpentinization in crustal hydrothermal systems [12], the carbon in the released methane could originate from subsurface carbonates that were decomposed by hydrothermal fluids. Alternatively, CH₄ may originate in magmatic CO₂ converted to CH₄ through fluid-rock interaction in deep hydrothermal fluids [13]. Assuming that the hydrothermal activity has remained proportional to the extrusion rate of volcanic lava, estimated from existing geomorphological analysis of the Martian surface [3], an upper limit on the cumulated amount (from the late Noachian to the present time) of CO₂ resulting from CH₄ release in the range from 0.2-2 bar, of the same order as the volcanic CO₂, has been proposed [8]. Because non-thermal escape cannot have removed more than ≈ 10 mbar of CO₂ since the late Noachian [8], it may be thought that atmospheric carbon has been significantly cycled to the crust at late Noachian, Hesperian and Early Amazonian through subsurface hydrological activity. In this way, the production of CO₂ through CH₄ release and further oxidation, and the removal of CO₂ from the atmosphere, could have a common origin and be two facets of a currently, although progressively damping with time, active hydrological system.

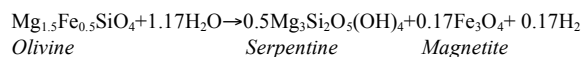
Such a long term carbon cycle, with a progressive net removal of CO₂ from the atmosphere and subsequent carbonate deposition in the subsurface, would explain the present low value of the amount of CO₂ contained in the atmosphere (7 mbar) and polar reservoirs (4-5 mbar [14]), compared to the ≈ 1 bar CO₂ secondary atmosphere produced by volcanic outgassing. Because a C atom could have been cycled several times through the crust since its release from the mantle by volcanism, the cumulated CH₄ released rate (up to 0.2-2 bar) must not be interpreted as the content of an isolated subsurface reservoir. It rather suggests that an efficient carbon cycle has been maintained by hydrothermal processes, with a substantial fraction of the volcanic outgassed carbon being cycled one or several times through crustal carbonates. Contrary to the steady state carbon cycle at work on Earth, a progressive damping of the carbon cycle has occurred on Mars due to the

absence of plate tectonics and the progressive cooling of the planet.

The scarcity of carbonates detected at the surface of Mars [15] doesn't contradict this view. At the end of the Noachian, the surface was probably the less favorable place where they could form because of acidic conditions [16]. Most of carbonate deposition may have occurred in the subsurface where conditions could have been more alkaline and neutral. An active subsurface liquid water hydrosphere, leading to substantial crust alteration, could have been present in the close subsurface at the time of the Noachian-Hesperian transition. If most of alteration processes at the origin of the dissipation of the atmosphere occurred in the subsurface, signatures found today at the surface don't necessarily constitute the most relevant record of climate evolution at this time.

Removal of water by serpentinization and impact on the D/H ratio: 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 [12]. Such rocks, like pyroxenes and to a lesser extent olivines, have been detected in large amounts at the surface of Mars [16,17]. Serpentine has been recently observed in the Nili Fossae region [15] associated with alteration minerals.

On Mars, the generation of H_2 by olivine, assuming a typical magnesium content of 75% ($Fe_{0.75}(Mg_{0.75}Fe_{0.25})_2SiO_4$) during serpentinization can be expressed as [12]:



For 1 water molecule lost through iron oxidation, 6 molecules are involved in the hydration of olivine. As a consequence, 1 H_2 molecule released to the atmosphere is the counterpart of at least 6 H_2O molecules stored in the crust, this amount translating in 24 H_2O molecules if the released molecule is CH_4 [9]. Assuming that, like in some Earth's hydrothermal systems, the molar fraction of methane in the vented gas is 10%, the rest consisting of H_2 , 78 H_2O molecules are stored in serpentine for 1 released CH_4 molecule [9]. Typically ≈ 100 H_2O molecules are therefore expected to be stored for each released CH_4 molecule, suggesting that serpentinization could have resulted in the storage of large amounts of water in subsurface serpentine.

Once released, CH_4 is converted to H_2 and CO_2 through oxidation. The release of CH_4 and H_2 results in an increase of the atmospheric H_2 buffer content, and therefore in an increase of the thermal escape flux of hydrogen, which is nearly proportional to the H_2 mixing ratio. 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 [18]. Crustal oxidation through serpentinization therefore results in the escape of the H atoms released by oxidation (under the form of H_2 and CH_4 , 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 value [9]. Assuming that most of the present hydrogen fractionation is due to serpentinization, it is found that a 330 m thick GEL of water may have been trapped in serpentine, whereas a 55 m thick GEL has been involved in Fe(II) oxidation during serpentinization, with the remaining hydrogen being further lost to space by thermal escape [9]. According to this scenario, the GEL of water present at the surface at the end of the heavy bombardment would have been ≈ 425 m thick, that is about of the right order to explain the formation of outflow channels [7]. This scenario, which doesn't require that large amounts of water have been lost to space (only a 10 m thick GEL according to this model), suggests that most of the water still present at the surface of the planet at the end of the heavy bombardment (330 m from 425 m, that is $\sim 75\%$) could have been stored in serpentine at later stages.

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