TRAPPING OF VOLCANIC SULFUR IN CLATHRATE HYDRATES ON EARLY MARS.

E. Chassefière[1], E. Dartois[2], J.-M. Herri[3], F. Tian[4], F. Schmidt[1], O. Mousis[5,6] and A. Lakhlifi[6], [1]GEOPS, Université Paris-Sud, CNRS, France (eric.chassefiere@u-psud.fr), [2]IAS, Université Paris-Sud, CNRS, France, [3]Centre SPIN, ENS des Mines de Saint-Etienne, France, [4]Center for Earth System Sciences, Tsinghua University, Beijing, China, [5]Center for Radiophysics and Space Research, Space Sciences Building, Cornell University, Ithaca, NY 14853, USA, [6]Institut UTINAM, Université de Franche-Comté & OSU THETA de Franche-Comté, France.

General approach and main results: It is generally agreed that a dense CO_2-dominant atmosphere was necessary in order to keep early Mars warm and wet. However, current models have not been able to produce surface temperature higher than the freezing point of water. Most sulfate minerals discovered on Mars are dated no earlier than the Hesperian [1], despite likely much stronger volcanic activities and more substantial release of sulfur-bearing gases into Martian atmosphere during the Noachian. Using a 1-D radiative-convective-photochemical model [2], we have shown [3] that clathrate formation during the Noachian would have buffered the atmospheric CO_2 pressure of early Mars at ~2 bar and maintained a global average surface temperature ~230 K. Because clathrates trap SO_2 much more favorably than CO_2, all volcanically outgassed sulfur would have been trapped in Noachian Mars cryosphere, preventing a significant formation of sulfate minerals during the Noachian and inhibiting carbonates from forming at the surface in acidic water resulting from the local melting of the SO_2-rich cryosphere.

The massive formation of sulfate minerals at the surface of Mars during the Hesperian could be the consequence of a drop of the CO_2 pressure below a ~2-bar threshold value at the late Noachian-Hesperian transition, which would have released sulfur gases into the atmosphere from both the Noachian sulfur-rich cryosphere and still active Tharsis volcanism. A lower value of the pressure threshold, down to ~0.5 bar, could have been sufficient to maintain middle and high latitude regions below the clathrate formation temperature during the Noachian and to make the trapping of SO_2 in clathrates efficient. Our hypothesis may explain the formation of chaotic terrains and outflow channels, and the occurrence of episodic warm episodes facilitated by the release of SO_2 to the atmosphere. These episodes could have played a role in the formation of valley networks and the degradation of impact craters, but it remains to be confirmed by further modeling.

Thermodynamic modelling of CO_2-SO_2 clathrates in Martian atmospheric conditions: The Van der Waals and Platteeuw model [4] describes the equilibrium of hydrate phases by means of a convergence between a statistical thermodynamics approach implementing Kihara parameters and a classical approach with reference state parameters. Using this approach, we have extrapolated existing data to low temperatures on the composition of CO_2-SO_2 clathrates [3]. At 200-220 K, the enrichment factor of SO_2 in the clathrate with respect to gas has been found to be very large, in the range from ~100-500.

General scenario of Mars early evolution: If during the Noachian the atmospheric CO_2 pressure exceeded ~2 bar due to an efficient Noachian volcanism, the CO_2 in excess of 2 bar could have been stored in the cryosphere under the form of CO_2 clathrates. Indeed, due to the increasing albedo of the atmosphere through Rayleigh scattering for increasing CO_2 pressure above 1 bar, the surface temperature induced by a p>~2 bar CO_2 atmosphere is smaller than the equilibrium temperature of clathrates, resulting in a saturation of CO_2 and its condensation under the form of clathrates. Such a clathrate buffer would have maintained the CO_2 pressure close to ~2 bar, and the surface temperature close to 230 K, resulting in a cold Mars at the Noachian. The cryosphere would have trapped all the sulfur released by volcanism under the form of sulfur-rich CO_2-SO_2 clathrates, yielding the trapping of the equivalent of a pure SO_2 atmosphere of several tens to hundreds millibars.

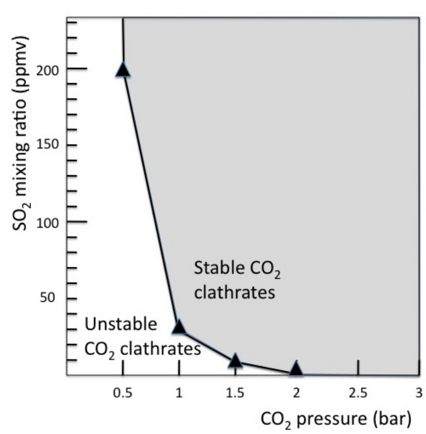

Fig. 1. Equilibrium SO_2 mixing ratio as a function of CO_2 pressure.

For a surface pressure <2 bar and progressively decreasing, atmospheric sulfur is no longer trapped in clathrates (Fig. 1), and an increasing fraction of the atmospheric SO_2, up to 10 ppm at p_{CO2}=1.5 bar, and 30 ppm at p_{CO2}=1 bar, can remain in the atmosphere.

If the amount of atmospheric SO_2 exceeds these thresholds, the cooling effect of sulfate aerosols results in a decrease of surface temperature below the clathrate equilibrium temperature and the condensation of the SO_2 in excess in CO_2-SO_2 clathrates. During this period, significant amount of SO_2 was converted into sulfate aerosols, which further settled down to the surface and possibly led to the formation of sulfate minerals. This sulfur may have been released, not only by volcanoes but also (and more continuously) by the SO_2-rich cryosphere formed when p_{CO2}>~2 bar. Through this mechanism, the cryosphere may have lost at this stage some of the volcanic SO_2 stored at earlier times, released back to the atmosphere. In this time range (2 to 1 bar p_{CO2} range), the surface temperature has been buffered, during and after episodes of sulfur release, at a temperature from 230 K (p_{CO2}=2 bar) to 210 K (p_{CO2}=1 bar). For p_{CO2}<1 bar, all the released SO_2 remains in the atmosphere, with no more trapping in clathrates.

Accordingly, we have proposed the hypothesis that the formation of sulfate minerals could have been triggered by a fall of early Mars atmosphere pressure below ~2 bar and that this change occurred close to the late Noachian/Hesperian transition.

Major geomorphological processes compatible with this scenario: Two major geomorphological units are compatible with our scenario:

1) The presence of a thick Mars-wide sedimentary formation of sulfate, including in very uncommon places at high topography, such the Interior Layer Deposit (ILD) at the top of Valles Marineris. Eolian deposition was proposed from geomorphological arguments. For ILD in Valles Marineris, the formation as thick as 5 km must be done in 400 Myrs, after the tectonic opening at 3.9 Ga and the formation of the floor 3.5 Ga. In our scenario, 20 m to 50 m Global Equivalent Layer (GEL) sulfur particles could have precipitated directly from atmosphere in 40 to 1000 Myrs, in agreement with the observation.

2) The chaotic terrains, at equatorial region, could have been formed by disruption of the CO_2 clathrate in the past at the late Hesperian/Amazonian period. This interpretation is compatible with our scenario since the formation of clathrate must have been global during the Noachian, it should also affect equatorial region. The reason for such a disruption has been debated, including climatic change, internal heat flux, fracture propagation, and seismic activity. We propose here that the disruption may be due to the pressure decrease below 2 bar. In our scenario, a GEL of CO_2-SO_2 clathrate ranging from 290 m to 720 m depth has been destabilized. Scaling this volume to the province of the chaos (1/10 surface of Mars) is compatible with the typical height loss in chaos ~3000 m (Fig. 2).

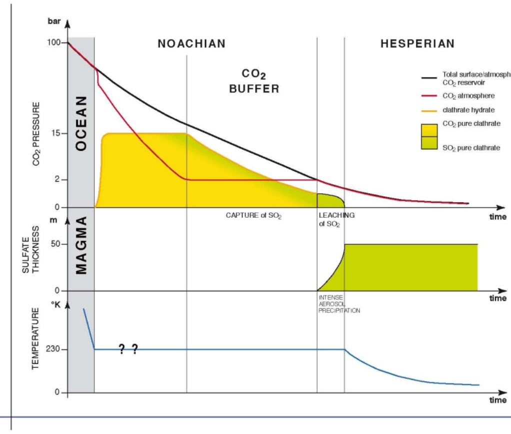

Fig. 2. Schematic representation of sulfur and CO_2 reservoir during the Noachian and Hesperian period. The total volatile surface/atmosphere CO_2 reservoir is decreasing due to thermal escape and possible formation of carbonates in the subsurface, from an initial budget ~100 bar. After magma ocean crystallization, CO_2 and water condense in form of clathrate (15 bar of CO_2 at maximum can be stored in form of clathrate when reacting with the total Martian water content of 1000 m GEL). After volcanic release of S, atmospheric SO_2 is systematically enriched in the condensating clathrate, triggered either by climatic changes or by global cooling due to aerosol formation. The CO_2 clathrate acts as an atmospheric buffer when the atmospheric pressure reaches 2 bar. After the complete consumption of CO_2 clathrate, the atmospheric pressure can drop below 2 bar and massive release of SO_2 from the clathrate induces the condensation of aerosols and precipitation as a Mars-wide sulfate layer (50 m represent the total SO_2 outgassed from Tharsis formation). This scenario represents the equilibrium state of surface/atmosphere but significant departure may have happened due to large impacts.

Ongoing work: In the frame of a French-Chinese cooperative program, we are now working on the implementation of a more complete photochemical-radiative-hydrological model to study the possible occurrence of warm episodes triggered by the release of large amounts of SO_2, and investigate whether such episodes would have been able to explain the formation of valley networks.

References:

[1] J.-P. Bibring et al. (2006) *Science, 90,* 5772, 400-404. [2] F. Tian et al. (2010) *Planet. Sci. Lett., 295,* 412-418. [3] E. Chassefière et al. (2013), Icarus, 223, 878-891. [4] J.-H. Van der Waals and J.-C. Platteeuw (1959) *Adv. Chem. Phys., vol. 2, Interscience, New-York*, 1-57.