Planetary and Space Science 103 (2014) 153–166

Contents lists available at ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

Possibility of H_2O_2 decomposition in thin liquid films on Mars

Akos Kereszturi [a,b,c,*], Sandor Gobi [a]

[a] Konkoly Thege Miklos Astronomical Institute, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, H-1121 Budapest, Konkoly Thege M. 15-17, Hungary
[b] New Europe School for Theoretical Biology and Ecology, Hungary
[c] NASA Astrobiology Institute, TDE Focus Group

ARTICLE INFO

Article history:
Received 4 August 2013
Received in revised form
25 July 2014
Accepted 26 July 2014
Available online 11 August 2014

Keywords:
Mars
Water
Oxidant
Regolith

ABSTRACT

In this work the pathways and possibilities of H_2O_2 decomposition on Mars in microscopic liquid interfacial water were analyzed by kinetic calculations. Thermal and photochemical driven decomposition, just like processes catalyzed by various metal oxides, is too slow compared to the annual duration while such microscopic liquid layers exist on Mars today, to produce substantial decomposition. The most effective analyzed process is catalyzed by Fe ions, which could decompose H_2O_2 under $\text{pH} < 4.5$ with a half life of 1–2 days. This process might be important during volcanically influenced periods when sulfur release produces acidic pH, and rotational axis tilt change driven climatic changes also influence the volatile circulation and spatial occurrence just like the duration of thin liquid layer.

Under current conditions, using the value of 200 K as the temperature in interfacial water (at the southern hemisphere), and applying Phoenix lander's wet chemistry laboratory results, the pH is not favorable for Fe mobility and this kind of decomposition. Despite current conditions (especially pH) being unfavorable for H_2O_2 decomposition, microscopic scale interfacial liquid water still might support the process. By the reaction called heterogeneous catalysis, without acidic pH and mobile Fe, but with minerals surfaces containing Fe decomposition of H_2O_2 with half life of 20 days can happen. This duration is still longer but not several orders than the existence of springtime interfacial liquid water on Mars today. This estimation is relevant for activation energy controlled reaction rates. The other main parameter that may influence the reaction rate is the diffusion speed. Although the available tests and theoretical calculations do not provide firm values for the diffusion speed in such a “2-dimensional” environment, using relevant estimations this parameter in the interfacial liquid layer is smaller than in bulk water. But the 20 days' duration mentioned above is still relevant, as the activation energy driven reaction rate is the main limiting factor in the decomposition and not the diffusion speed.

The duration of dozen(s) days is still longer but not with orders of magnitude than the expected duration for the existence of springtime interfacial liquid water on Mars today. The results suggest such decomposition may happen today, however, because of our limited knowledge on chemical processes in thin interfacial liquid layers, this possibility waits for confirmation – and also points to the importance of conducting laboratory tests to validate the possible process. Although some tests were already realized for diffusion in an almost 2-dimensional liquid, the same is not true for activation energy, where only the value from the “normal” measurements was applied.

Even if H_2O_2 decomposition is too slow today, the analysis of such a process is important, as under volcanic influence more effective decomposition might take place in thin interfacial liquids close to the climate of today if released sulfur produces $\text{pH} < 4.5$. Large quantity and widespread occurrence of bulk liquid phase are not expected in the Amazonian period, but interfacial liquid water probably appeared regularly, and its locations, especially during volcanically active periods, might make certain sites than others more interesting for astrobiology with the lower concentration of oxidizing H_2O_2.

1. Introduction

The aim of this work is to provide an overview of some important potential chemical reactions in a microscopic medium called liquid interfacial water to observe the possibility of H_2O_2 decomposition there, and partly to support orienting simulations today, and the interpretation of spectral based surface

---

* Corresponding author.
E-mail address: kereszturi.akos@csfk.mta.hu (A. Kereszturi).

http://dx.doi.org/10.1016/j.pss.2014.07.017
0032-0633/

compositional measurements on Mars. The role of aggressive oxidants is important to understand Mars, especially to clarify astrobiology and chemistry related issues. The topic of chemical reactions in interfacial water is also at the frontline of research: the microscopic medium is probably present on Mars, because of climate changes it might dominate in certain periods and could be more widespread than it is today, but the possible changes inside them have been poorly explored. Below, first we outline the background knowledge that suggests what liquid interfacial water probably occurs on Mars today and also under different past climates. In the main part of this work we give an overview of the current knowledge of chemistry going on in such thin liquid layers, focusing on the possibility of hydrogen peroxide decomposition. Although the knowledge on the exact realization of chemical processes with oxidants on Mars requires much work and laboratory tests, theoretical argumentation could point to such important directions that are important for successful future research. Findings in this topic might also help in the planning of future observations, detectors for probes, analog laboratory tests, and also give useful inputs to understand astrobiology related issues on Mars in general.

1.1. *Overview of current knowledge*

Here we outline the basic conditions on Mars, and also extrapolate the possible chemical reactions in thin liquid layers under current and past climates. Because of the changes in the orbital tilt of Mars (Mellon, 1999; Rubincam, 1990), water ice might have in the past different spatial and temporal distribution than today (Kanner et al., 2004; Haberle et al., 2003), and the solar insulation could also be modified (Yokohata et al., 2002) during this period. Our basic assumption is the conditions that are present today are characteristic for a substantial part of the Amazonian period (Golombek et al., 2006; Fastook et al., 2011), but occasionally more favorable conditions for the existence of liquid interfacial water might appear (Boxe et al., 2012; Burr et al., 2012; Dickson and Head, 2009; Dickson et al., 2009). Beside theoretical argumentation (Zent, 2006) the observed soluble materials (Kounaves et al., 2010; Kounaves et al., 2006) and salt distribution (Cull et al., 2010) at the Phoenix landing site is also compatible with the appearance of occasionally thicker water layer that could trigger chemical reactions. Small quantity of sulfates and ferric oxides might have formed by the acid fog model (Tosca et al., 2004), also favoring the existence of occasionally more active, but still thin, surface liquid water layer (Chevrier and Mathé, 2007).

During the more favorable periods the duration of water ice cover might be longer at certain locations and by greater mobility of H_2O salts could become solved, increasing the thickness of the liquid layer. In the following the possible presence and characteristics of thin liquid water layers on Mars today are outlined first, the Martian surface conditions are summarized regarding the parameters that might influence the reactions in this liquid (pH, composition) are discussed second, and the specific issues regarding the chemical properties at microscopic scale in thin interfacial water layer are presented third. The estimation of various chemical reactions and chemical pathways are described in Sections 4 and 5, focusing on identifying which reactions might have been the most probable in thin liquid layers and how could their realization be tested or analyzed by future experiments.

The existence of a thin interfacial liquid water layer on Mars was suggested by the following observations. At the southern hemisphere on Mars, at the area of seasonal cap water ice without carbon dioxide ice cover can be observed in small patches (Schmidt et al., 2009) during springtime, when the seasonal cap is receding. These water ice patches occur above all at the outer ring-like area of the so-called Dark Dune Spots (Kereszturi and Rivera-Valentin, 2012). Such water ice covered small areas were identified in Richardson crater (72S 179E) between Ls=200 and 220 when the daily maximal temperature was between 190 and 220 K (Figs. 1 and 2). At the northern hemisphere the water ice forms a wide annulus at the outer edge of the receding polar cap. The higher latitude part of the water ice might be of a refrozen (cold trapped) H_2O layer along the edge of the receding carbon-dioxide seasonal cap on the top of the carbon-dioxide ice, but large area of this annulus is composed of only water ice on the surface (Appere et al., 2011; Pommerol et al., 2011) without CO_2 ice below it. In the later area at the 300–330 geographical longitude zone between Ls=290 and 330 the daily maximal temperature is around 180 K using TES-based temperature data (Kereszturi and Appere, 2014), which also suggest the possible appearance of liquid interfacial liquid water. Besides these observational data, theoretical argumentation and laboratory analysis also suggest

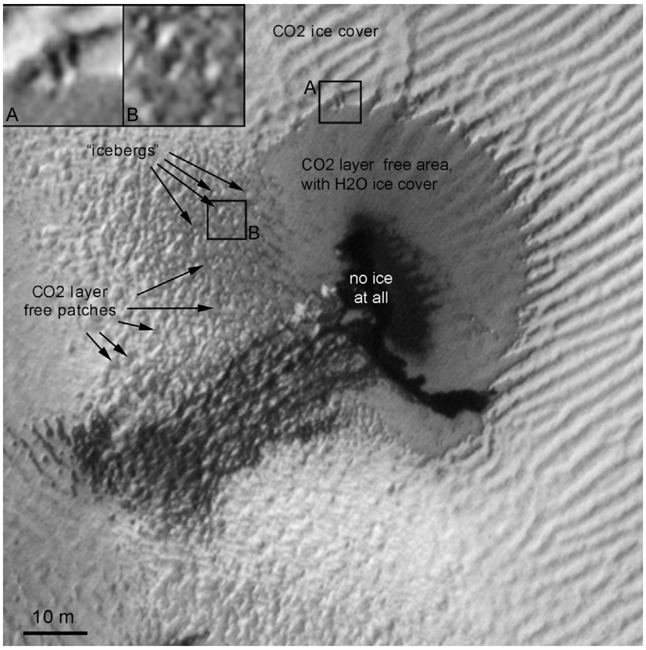

Fig. 1. Example of a 100 × 100 m^2 sized area with a spot, where water ice covers the surface (gray area) without CO_2 ice (bright surroundings) in Richardson crater (HiRISE image PSP_003386_1080). At the large, ring-shaped area the temperature of the water ice produces thin liquid layer along the contact surface with mineral grains, where chemical reactions might take place.

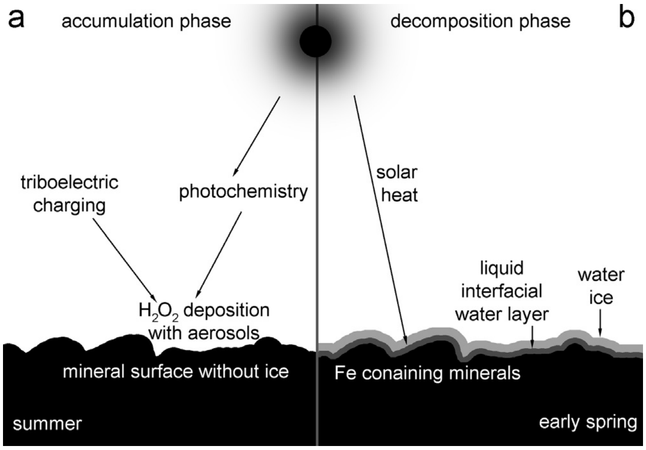

Fig. 2. Schematic figure of factors that influence H_2O_2 accumulation (a) and decomposition (b).