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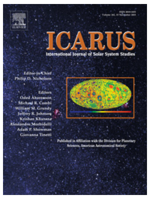

Mineralogical record of the redox conditions on early Mars

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ABSTRACT

Sulfates and Fe-oxides identified on the martian surface by orbital and in situ missions indicate that oxidizing conditions have existed on early Mars, at least locally and/or episodically. In the context of rock alteration and weathering, redox conditions are especially critical for the behavior of iron, which is soluble in its divalent state but insoluble in its trivalent state. Here, we combine results from a series of laboratory experiments conducted under Mars-like conditions to address the influence of highly-oxidizing compounds such as hydrogen peroxide (H_2O_2) on the alteration pathways of primary materials. We show that, if early Mars had a dense CO_2 atmosphere allowing for relatively “warm and wet” conditions and surface weathering, highly-oxidizing conditions would have strongly inhibited the formation of Fe/Mg-smectite clays from alteration of igneous ferromagnesian minerals, and possibly enhanced the formation of carbonates. But a decade of mineral mapping of the martian surface show abundant, widespread Fe/Mg-clays and rare carbonates, which we interpret here as a mineralogical record of poorly-oxidizing (or even reducing) conditions during most of the Noachian era. Oxidizing conditions would have occurred later in martian history as a consequence of a higher rate of H_2 escape or of a lower rate of volcanic outgassing, or both.

1. Introduction

The reddish coloration of Mars, easily discernible from Earth with the naked eye, is due to the widespread occurrence of oxidized, ferric iron (Fe^{3+}) in surface dust and soils. This long-recognized oxidation of the martian surface is thought to result mainly from geologically recent (i.e., Amazonian) processes that did not involve liquid water, but instead gas-solid reactions (e.g., Bibring et al., 2006; Gooding, 1978). However, the presence of oxidants or oxidation mechanisms does not have to be restricted to the most recent geological era. For example, the sedimentary record of Meridiani Planum – dated from the late Noachian or early Hesperian (Hynek et al., 2002) – requires oxidation to account for the mineralogical assemblage observed by the Opportunity rover (hematite and sulfates; e.g., McLennan et al., 2005). In addition, it has been proposed that the strongly acidic conditions implied by the presence of jarosite resulted either from the oxidation of Fe-sulfides (Chevrier et al., 2006; Dehouck et al., 2012) or of aqueous Fe^{2+} (Hurowitz et al., 2010). Therefore, the occurrence of oxidants or oxidation mechanisms may have played a key role in the surface processes all along the history of Mars.

In the past years, our group has conducted a series of laboratory experiments to study the alteration of primary materials (including silicates and sulfides) in conditions relevant for early Mars (Chevrier et al., 2004, 2006; Dehouck et al., 2012, 2014). Both poorly-oxidizing and highly-oxidizing conditions were tested through the use of hydrogen peroxide, H_2O_2. Accordingly, the goal of this paper is to synthesize and discuss the lessons learned from these various experiments about the effects of redox conditions on alteration pathways, and their implications for early Mars. Previously unpublished data are also presented to feed this synthesis and broaden the relevance of earlier results. In particular, our experimental results strongly suggest that poorly-oxidizing conditions were required to form the widespread Fe/Mg-smectites through weathering of the martian basaltic crust.

2. Oxidation on Mars

Redox conditions at the surface of a planet are primarily controlled by the composition of the atmosphere. On present-day Earth, the elevated concentration of O_2 resulting from active photosynthesis is largely responsible for the current highly-oxidizing

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conditions that prevail in most surficial environments, due to dissolution of O_2 in meteoric and marine waters. However, primitive atmospheres of terrestrial planets were devoid of O_2; instead, they were mainly composed of CO_2, N_2 and possibly reduced gases such as CH_4, NH_3 and H_2, thus creating poorly-oxidizing or even reducing conditions (e.g., Pollack and Yung, 1980). On Mars, the current concentration of O_2 in the atmosphere is low (~0.13%), and there is so far no compelling evidence for photosynthetic lifeforms that could have released abundant O_2 in the past. However, non-biological processes capable of creating oxidizing conditions may have occurred on early Mars, as detailed below.

Redox conditions are especially critical for the behavior of iron, which is soluble in its divalent state but insoluble (except under highly acidic conditions) in its trivalent state. Thus, in the context of basaltic rock alteration and weathering, differences in surficial redox conditions are expected to have a strong influence on the fate of iron and associated minerals (e.g., Gaudin et al., 2011; Greenberger et al., 2012). Because the martian crust is enriched in iron compared to the crust of the Earth (Taylor and McLennan, 2009), this influence is even more important for Mars.

Abiotic oxidation of ferrous iron can take place through different mechanisms: (1) alteration of Fe^{2+}-bearing minerals into Fe^{3+}-bearing products by reduction of H_2O during rock-water interactions (e.g., Oze and Sharma, 2007); (2) direct photo-oxidation of aqueous Fe^{2+} by ultraviolet irradiation (e.g., Braterman et al., 1983); or (3) chemical oxidation by reaction between Fe^{2+}-bearing minerals or aqueous Fe^{2+} and an oxidant produced by the UV photolysis of H_2O, such as O_2 or H_2O_2 (e.g., Hunten, 1979). All these mechanisms involve directly or indirectly the reduction of H_2O to H_2, and therefore require H_2 loss into space to prevent recombination reactions and obtain net oxidation at a global scale (e.g., Catling and Moore, 2003; Hurowitz et al., 2010; Kasting and Walker, 1981).

Oxidation of Fe^{2+}-bearing minerals by reduction of H_2O occurs in environments devoid of O_2 and UV irradiation. The most common example of this kind of reactions on Earth is the production of magnetite and/or Fe^{3+}-serpentine (along with gaseous H_2 and CH_4) from Mg-rich igneous minerals. Even though this “serpentinization” reaction is generally considered to be restricted to hydrothermal conditions, it has been shown to occur at low temperature as well (down to 30°C), although at modest rates (Bristow et al., 2015; Neubeck et al., 2011; Oze and Sharma, 2007). In such low temperature conditions, smectite becomes the dominant secondary product in lieu of serpentine (Bristow et al., 2015; Dehouck et al., 2014).

Following Cairns-Smith (1978), Braterman et al. (1983) proposed that UV photo-oxidation has been partly, if not entirely, responsible for the deposition of the Precambrian banded iron formations (BIFs) in Earth oceans. Based on their experimental results, these authors estimated that a top 100 m of sea water could be depleted in Fe^{2+} by one to six months of sunshine (or even less in the absence of an ozone screen), even under an O_2-free atmosphere. Although this hypothesis may be superfluous for the Earth due to the appearance of photosynthetic lifeforms, it may be applicable to Mars (e.g., Catling and Moore, 2003; Hurowitz et al., 2010). Nonetheless, photo-oxidation has some limitations. The most obvious one is that it requires exposure of Fe^{2+}-bearing fluids to UV light; thus, oxidation of iron through this process is excluded in groundwater and strongly reduced in ice/snow-covered water (compared to open water, UV irradiance through ice and snow is reduced by up to several orders of magnitude; e.g., Perovich, 2002). In addition, photo-oxidation is slow compared to precipitation of Fe^{2+}-bearing gels or minerals in silica- and/or CO_2-rich waters (Konhauser et al., 2007), thus precluding the effective transformation of Fe^{2+} into Fe^{3+} by this mechanism.

UV photolysis of H_2O molecules in planetary atmospheres produces a variety of hydrogen and/or oxygen-bearing compounds (e.g., Hunten, 1979; Kasting and Walker, 1981), some of which – including O_2 and H_2O_2 – are strong oxidants. These oxidizing compounds are then transported toward the surface, where they can precipitate or dissolve into liquid H_2O and react with aqueous Fe^{2+} or directly with Fe^{2+}-bearing minerals. Like photo-oxidation, this process has been proposed as an alternative to biological oxidation for the formation of terrestrial BIFs, but it is generally believed that the rate of oxidant production by photolysis was too slow compared to the release of reduced gases (mainly H_2) by volcanoes to provide net oxidation (e.g., Kasting and Walker, 1981). Nonetheless, Liang et al. (2006) argued that photochemically-produced H_2O_2, accumulated during “Snowball Earth” episodes, may have been directly responsible for some “great oxidation events” recorded in iron and manganese-bearing Precambrian deposits. Today, H_2O_2 is found in virtually all water reservoirs, including air, clouds, rain, snow (up to $\sim 10^{-5}$ mol/L; e.g., Bales et al., 1995) and surface waters (up to $\sim 10^{-7}$ mol/L; e.g., Gerringa et al., 2004). Its role in alteration processes is generally negligible due to the high availability of atmospheric O_2, as well as the high amounts of liquid H_2O in which it is mixed; however, it has been proposed that H_2O_2 could be the dominant oxidizing species in low O_2 conditions and could thus explain higher-than-expected oxidation rates (Kanzaki and Murakami, 2013).

Production of oxidants by UV photolysis in the atmosphere – or, alternatively, directly at the surface (Yen et al., 2000) – has also been invoked to explain the oxidizing nature of the present-day martian regolith, thought to be responsible for the non-detection of organics by the Viking landers (e.g., Hunten, 1979). Hydrogen peroxide, in particular, has received a lot of attention, because it is considered as one of the best candidates to explain the Viking results (Bullock et al., 1994; Keresztúri and Góbi, 2014; McDonald et al., 1998; Zent, 1998). Reaction between H_2O_2 and Fe^{2+}, known as the Fenton reaction, is known to readily degrade organic compounds. Moreover, H_2O_2 has been detected in the atmosphere (Clancy et al., 2004; Encrenaz et al., 2004) and is suspected to diffuse up to several meters into the regolith (Bullock et al., 1994; Zent, 1998).

Among the three mechanisms described above, oxidation by photolysis-derived oxidants is likely to be the most efficient in surficial/shallow conditions, because: (1) contrary to “serpentinization” (e.g., Oze and Sharma, 2007), Fe^{2+} oxidation by O_2 or H_2O_2 primarily depends on the abundance of oxidant in the system (Kanzaki and Murakami, 2013) and can therefore proceed at high rate even at low temperature (half times are of the order of minutes in seawater; e.g., Millero et al., 1987); and (2) contrary to photo-oxidation, it has the potential to create oxidizing conditions in environments protected from direct UV exposure, through diffusion or percolation (if mixed with liquid H_2O) into the ground. Accordingly, we review below the influence of hydrogen peroxide on alteration pathways as observed in a series of laboratory experiments that we conducted under simulated early Mars conditions.

3. Effects of redox conditions on alteration pathways

In the past years, we have reported in several publications the results of laboratory experiments studying the alteration of various primary materials in conditions relevant for early Mars (see Table 1 for an overview). Here, we combine some of these earlier results with previously unpublished data in order to specifically address the question of how redox conditions may have influenced the secondary mineralogy of early Mars. One major assumption of these experiments is that the atmosphere of early Mars was dominated by CO_2 as it is today, but denser (climate modeling studies typically explore atmospheric pressures up to a few bars; e.g. Forget et al., 2012), as suggested by various geological evidence for