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Oxygenic photosynthesis and the oxidation state of Mars

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Abstract. The oxidation state of the Earth's surface is one of the most obvious indications of the effect of life on this planet. The surface of Mars is highly oxidized, as evidenced by its red color, but the connection to life is less apparent. Two possibilities can be considered. First, the oxidant may be photochemically produced in the atmosphere. In this case the fundamental source of O₂ is the loss of H₂ to space and the oxidant produced is H₂O₂. This oxidant would accumulate on the surface and thereby destroy any organic material and other reductants to some depth. Recent models suggest that diffusion limits this depth to a few meters. An alternative source of oxygen is biological oxygen production followed by sequestration of organic material in sediments—as on the Earth. In this case, the net oxidation of the surface was determined billions of years ago when Mars was a more habitable planet and oxidative conditions could persist to great depths, over 100 m. Below this must be a compensating layer of biogenic organic material. Insight into the nature of past sources of oxidation on Mars will require searching for organics in the Martian subsurface and sediments.

Introduction

The Biology Experiments on the *Viking* missions to Mars detected an unexpected reactivity in the Martian soil. This reactivity manifested itself in the release of O₂ from the soil upon humidification (Oyama and Berdahl, 1977). The release was at levels of 70–770 nmol cm⁻³, much larger than expected from adsorption theory (Ballou *et al.*, 1978). In addition, when a radiocarbon labeled nutrient solution was added to the Martian soil radioactive CO₂ was released (Levin and Straat, 1977). These reactions are thought to arise from distinct mechanisms since the O₂ release was not altered by heating while the CO₂ release was destroyed by prolonged exposure to temperatures

near 100°C. Further indication of the reactive nature of the Martian soil is the absence of organic materials at the ppb level (Biemann *et al.*, 1977). Unfortunately, the *Viking* landers could not sample soils below about 10 cm and so the depth of these organic-free, apparently oxidizing, soils is unknown. Gooding (1992) has pointed out that the class of meteorites known as the SNC—of putative Martian origin—are also oxidizing with the dominant forms of C and S being carbonate and sulfate and iron being ferric. These meteorites date back from 200 to 1300 million years suggesting oxidizing conditions on the near surface of Mars at least that long ago (Gooding, 1992).

Mars should not be red, it should be grey. The infall of meteoritic material should be a net source of organics at the present time and throughout Martian history (Biemann *et al.*, 1977). In fact, models for the late accretion of volatiles and organics to the Earth and Mars suggest that the surface of Mars should have been rich in organic material due to infalling comets (Chyba *et al.*, 1994). Organic material destroyed by the shock of entry would produce a gas of reducing nature because the (H₂+C)/O ratio is greater than unity.

In this paper we consider two possible sources of oxidation on Mars: photochemical and biological. Photochemical production of oxidants occurs due to the photolysis of H₂O and the loss of H₂ to space. This process is known to be occurring in the present atmospheres of Mars and Earth. Biological production of oxidants results when photosynthesis utilizes H₂O as the terminal electron donor in the production of organic material from CO₂. Net accumulation of O₂ results if this organic material is buried in sediments. Clearly photochemical oxidant production is occurring on Mars, the question of interest here is whether oxygenic photosynthesis ever occurred there, and the record, if any, it has left in the sediments.

Photochemical oxidant production

It has been suggested that atmospheric photochemistry is producing H₂O₂ in the Martian atmosphere and that the

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deposition of these molecules onto the soil is a source of oxidizing power (Hunten, 1979; Bullock *et al.*, 1994). The standard model used to explain the *Viking* Biology Experiment results invokes the existence of at least two oxidants in the Martian soil, a thermally stable oxidant such as KO_2 or CaO_2 as well as a thermally labile oxidant such as H_2O_2 (Klein, 1978; Zent and McKay, 1994), presumably both are derived from atmospheric H_2O_2 .

It is important to note here that the production of net oxidation on Mars at the present time is zero because for every H_2 molecule that escapes one O atom escapes as well (McElroy *et al.*, 1977; Liu and Donahue, 1976) thus effectively resulting in the escape of H_2O . Only if the H_2 escapes and the O is left behind is there a net source of oxidant. Presumably if there were a sink for O on the surface—as would have occurred early in Martian history—there would be a net production of oxidant. In a recent theoretical paper Fox (1993) has suggested that the escape flux of O may not balance the H_2 loss. If these calculations are correct, this could imply that there remains a surface sink of O or, alternatively that the present atmosphere is not in steady state.

Despite uncertainties in our understanding of the redox balance of the present Mars atmosphere the photodissociation rate of H_2O is an upper limit to the photochemical production of oxidant on Mars. The present rate of oxidant production due to photolysis of water, about $6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ (Liu and Donahue, 1976; McElroy *et al.*, 1977), would produce a layer of iron oxide about 10 m thick over 3 billion years if there were no escape of O_2 .

Recent modeling studies suggest that the depth of the penetration of H_2O_2 —the likely photochemical oxidant and at least the most mobile—is small. Bullock *et al.* (1994) developed a coupled soil/atmosphere transport model for H_2O_2 on Mars. Their results suggest that the concentration of H_2O_2 in the soil goes to zero at a finite depth, a consequence of nonlinear diffusion in the soil. A significant result of their model is that for a wide range of H_2O_2 lifetimes (up to 10^5 years), the extinction depth was found to be less than 3 m. Thus only a fraction of the potential total photochemical oxidation is realized with the rest escaping to space as O_2 . The depth of the oxidizing layer in this case (10 m) is shown in Fig. 1.

It is possible that the escape rate was much higher in the past. The D/H ratio on Mars is six times the terrestrial value (Owen *et al.*, 1988) which may support this suggestion. Alternatively, the D/H value may simply reflect equilibration over geologically recent times of only that water in the exchangeable atmosphere-surface reservoirs (Carr, 1990). However, the depth of oxidation is fundamentally limited by the ability of oxidants to diffuse into the soil. This may be enhanced due to gardening of the soil layers by meteors and wind action but these effects have only mixed the top few meters of the Martian surface in the last few billion years (Flynn and McKay, 1990; Arvidson, 1986).

On a warm early Mars, in the presence of liquid water, transport of oxidants to depths may not have been limited by diffusion. However, it is unknown if in a thicker, warmer, atmosphere photochemistry would be still able to produce oxidants and at what level. Nonetheless, while

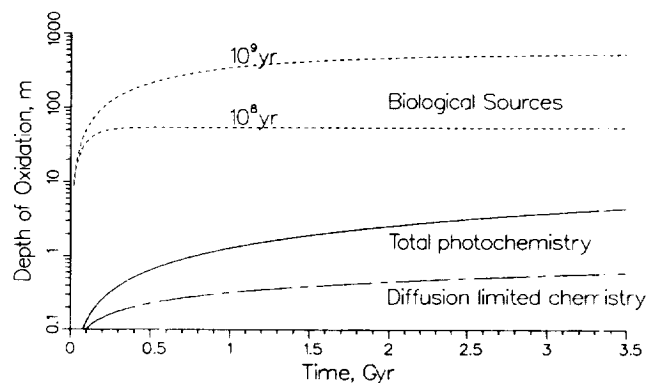


Fig. 1. Depth of oxidation over time for several cases. The solid line refers to the present photochemical production of oxidant assuming an initial reducing state of the Martian surface and ignoring diffusion limitations. The long-dash line refines this model by using the diffusion model of Bullock *et al.* (1994). The upper dashed lines show the results for a presumed biological source of O_2 . Here the net accumulation of oxygen is determined by the rate of sediment burial for the early Earth (DesMarais *et al.*, 1992). The two cases correspond to exponential decline after 3.8 Gyr ago with timescales of 10^6 and 10^9 years

oxidation to depths greater than tens of meters might indicate that there was an alternative source of oxidant on Mars it might also be explained by invoking alternative abiotic processes.

Biological source

Life is a plausible source because there is considerable evidence that the early environment on Mars, 3.5 Gyr ago, was characterized by liquid water on the surface and possibly a dense atmosphere of CO_2 and N_2 (Pollack *et al.*, 1987; Kasting, 1991). From studies of the Earth's earliest biosphere we know that by this time life had originated on the Earth (Awramik *et al.*, 1983; Schopf, 1983). The types of cells detected suggest the presence of cyanobacteria, and therefore O_2 producing photosynthesis, at that time (Schopf and Packer, 1987; Schopf, 1993; Awramik, 1992).

The development of oxygenic photosynthesis is problematical in that it appears to require prior aerobic conditions to promote tolerance of oxidative products and dependence on the more energetically costly mode of splitting water in photosynthesis (Towe, 1978; Fridovich, 1978). Atmospheric models of the early Earth show that photolysis of water is simply not able to alter the redox balance of the global environment (Kasting and Walker, 1981; Levine *et al.*, 1982). To resolve this paradox we have proposed a scenario involving the photochemical production of H_2O_2 in the atmosphere acting to remove the reductants from local lakes or basins (McKay and Hartman, 1991). Without reductants photosynthetic organisms would have had no choice but to use water as the terminal electron donor. In addition, the presence of H_2O_2 would have promoted the development of enzymes such as catalase that protect against reactive oxidants. With no reductants available and with the biochemical machinery necessary to protect against oxidic byproducts



Fig. 2. *Viking* orbiter image of Hebes Chasma (0 S, 75 W). This canyon is a box canyon about 280 km long. The mesa in the center of the canyon shows layered deposits that are believed to have been deposited in standing bodies of water (Nedell *et al.*, 1987). If all the deposits mapped by Nedell *et al.* are organic then 30 hPa of O₂ would have been released

in place, the stage would be set for the development of oxygenic photosynthesis. Evidence for the antiquity of oxygenic photosynthesis in oxic lakes as discovered by Buick (1992) from the Archean period (2.7×10^9 years ago) is consistent with our hypothesis. Given the similarity of the environments on the early Mars and early Earth it is plausible that life originated on Mars and oxygenic photosynthesis also began there at a very early stage through the action of photochemically produced oxidants.

Given biological production of O_2 , net oxidation is produced when the reduced organic material is sequestered into non-exchangeable sedimentary reservoirs. This does not necessarily result in the buildup of oxygen in the atmosphere. On Earth, several geological processes acted to nullify the biological production of O_2 . Recycling of sediments on the Earth by plate tectonics and the associated thermal processing of subducted sedimentary material exhumes and oxidizes the reduced organic material consuming any oxygen that was produced by their initial burial. Furthermore volcanic sources of reduced gases (especially H_2) also consume O_2 . Together these effects limited the buildup of O_2 on the Earth until about 2.5 Gyr ago. Thus, Earth may have spent over 1 Gyr producing O_2 before the titration of the sources of reductants was complete.

Mars, however, lacks plate tectonics and thus deep sedimentary layers on that planet would be more stable than on the Earth. Furthermore, volcanic activity on Mars appears significantly diminished compared to the Earth both in magnitude and duration (e.g. Greeley and Spudis, 1981). An implication of this is that while the transition to an oxidizing atmosphere on Earth required a billion years, the transition may have been much more rapid on Mars. Mars may have experienced an oxygen rich atmosphere long before the Earth and oxidizing conditions could have predated many of the surfaces on Mars. Thus, both organic and oxidized materials may be buried deep in the stratigraphic column.

We have considered a biological source by computing the oxidation produced by the net burial rate of sedimentary organic material for the Proterozoic Earth, between 2.5 and 0.8 Gyr ago, as determined by DesMarais *et al.* (1992) of $\approx 10^{12}$ mol yr⁻¹. In Fig. 1 we show the results for two cases; one in which this production rate continues for 10^9 yr and one in which this continues for only 10^8 yr.

If the biological production of O_2 played a role in the redox state of the present Mars there must be an associated store of organic material at depth in these stable sedimentary layers. There are several sites where deep stable sedimentary layers of organic material might be found on Mars. Hebes Chasma, shown in Fig. 2, provides one such example. Nedell *et al.* (1987) have determined that the layered sediments in this canyon and associated canyons were probably deposited in standing bodies of water. They estimated that the total volume of sediments was 1.3×10^5 km³. We consider the limiting case; if this volume of material was entirely composed of organic material of equivalent stoichiometry (CH_2O) this would have released sufficient oxygen to produce 30 hPa of O_2 —comparable to the amount produced by photochemistry. Scott *et al.* (1991) have identified other basins on Mars

which potentially contain orders of magnitude more sedimentary material. Interestingly, Wright *et al.* (1989) have reported trace organics in one of the SNC meteorites (EETA 79001), more than 400 ppm degradable organic material. The isotropic ratio of carbon 13 to carbon 12 in the organic material is suggestive of a biological origin, although terrestrial contamination in these measurements cannot be ruled out (Jakosky, 1991). The implications of these low levels of organics are not fully understood. If a layer of organic rich sediments was found on Mars it is likely that the isotopic composition of these organics could be used to determine if they were of biological origin (Schidlowski, 1992).

Conclusion

If the oxidation seen on Mars is a photochemical product, the fundamental source of oxidation is the escape of H_2 to space and the active oxidant produced is H_2O_2 . The resulting oxidation is limited in total amount and ability to diffuse to depth. If the oxidant is a product of biological photosynthesis, then the oxidant produced is O_2 . This oxidant would accumulate if the reduced carbon was buried in sedimentary basins. It is important to note that while we know that photochemical production of oxidants is occurring on Mars, any past biological source is speculative at this time. The key signature of possible sources of oxidation on Mars is the fate of the reductant produced. For photochemical processes the reductant is lost to space and only the oxidant remains. If oxidation is biological then the reduced carbon must also be found in the subsurface—as occurs on Earth. If the oxidized surface layer is underlaid by a layer of organic material this could be consistent with oxygenic photosynthesis. Isotopic analysis may provide further evidence of biological origin of the organic material. Thus, the key to understanding the past oxidation history of Mars is to search for organics, be they shallow or deep.

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