

## Water, minerals, and the fate of organic matter on Mars

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The Martian surface is characterized by an oxidizing regolith [1], high levels of ultraviolet radiation [2], and temperature ranges that limit the stability of liquid water [3]. The surface of Mars has yet to yield a single detectable organic molecule despite input from exogenous sources [4], implying some active and geologically rapid mechanism for oxidation. Substantial work has gone into identifying this process in near-surface Martian environments [5-7] with a general consensus that photolytic oxidation is limited to the immediate surface of UV-exposed regolith, while secondary oxidation mechanisms control organic matter oxidation with depth.

To elucidate the mechanisms and extent of oxidation in the near surface conditions of Mars, we studied the rate of amino acid oxidation in mineralized iron sulfate brines as inferred for hypothetical sulfate ground water systems or liquid condensates at mineral grain boundaries. The presence of metal-rich, saline brine systems increased the rate of amino acid oxidation and racemization by several orders of magnitude relative to pure aqueous systems [8]. Further studies utilizing regolith analogs support the notion of water as the driving force behind oxidation mechanisms; results indicate that amino acids show a depth-dependent oxidation rate that is explained by the active diffusion and condensation of water vapor at mineral grain boundaries. This implies that interaction of even minute amounts of liquid water with organic-bearing mineral deposits will cause the rapid oxidation of mineral-embedded organics; biomarker detection strategies must focus on sampling materials and sites with minimal diagenetic alteration since deposition.

[1] Zent & McKay (1994) *Icarus* **108**, 146–157 [2] Cockell *et al.* (2000) *Icarus* **146**, 343–359 [3] Kuznetz & Gan, D.C. (2002) *Astrobiology* **2**, 183–195 [4] Chun, S.F.S. *et al.* (1978) *Nature* **274**, 875–876 [5] Garry *et al.* (2006) *Meteoritics & Planetary Science* **41**, 391–405 [6] Stoker & Bullock (1997) *Journal of Geophysical Research-Planets* **102**, 10881–10888 [7] ten Kate *et al.* (2005) *Meteoritics & Planetary Science* **40**, 1185–1193 [8] Johnson & Pratt (2010) *Icarus*, in press

## Isotopic compositions of Archean and Proterozoic rocks: Paleo-ocean proxies or microbial cycling?

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A fundamental component to the debate on the origin of the large C, S, and Fe isotope excursions in Archean and Proterozoic marine sedimentary rocks is whether the compositions reflect those of seawater, providing a paleo-ocean proxy, or if they record microbial authigenic and diagenetic processes, or both. The large Fe isotope excursion that is seen in Neoproterozoic and Paleoproterozoic marine sedimentary rocks occurs several hundred m. y. before the rise in atmospheric O<sub>2</sub> and an increase in the range of  $\delta^{34}\text{S}$  values in sedimentary sulfides, and is coincident with a major excursion in kerogen C isotope compositions. Oxidation of hydrothermally sourced aqueous Fe (II) has been proposed to explain the excursion to negative  $\delta^{56}\text{Fe}$  values via a reservoir effect for Fe (II) in the oceans, where Fe isotopes would be a direct proxy for the isotopic composition of the oceans [1]; this proposal negates a direct role for biology in producing the isotopic variations. This model is plausible for low-Fe samples such as Ca-Mg carbonates, but it is a difficult mechanism to explain negative  $\delta^{56}\text{Fe}$  values in Fe-rich rocks, and it does not explain the correlations between  $\delta^{56}\text{Fe}$ ,  $\delta^{13}\text{C}_{\text{kerogen}}$ , and  $\delta^{34}\text{S}$  in rocks of this age; the alternative interpretation is that the isotopic compositions of Fe, C, and S reflect microbial cycling [2], in which case the isotopic compositions are not a direct proxy for the oceans.

Fe and S isotope excursions in the Cretaceous may provide insight into isotopic variations in the Neoproterozoic and Paleoproterozoic, because free O<sub>2</sub> clearly existed in the atmosphere in the Cretaceous, and seawater Fe (II) was low. The coincidence of very low seawater sulfate contents in the Cretaceous with a negative  $\delta^{56}\text{Fe}$  excursion before OAE-2 provides strong support for microbial Fe cycling as the mechanism for producing the isotopic variations, because a reservoir effect produced by extensive oxide precipitation, as proposed for the Precambrian [1], is not plausible. Low sulfate contents in the Cretaceous, as well as the Neoproterozoic and Paleoproterozoic, would have favored dissimilatory iron reduction (DIR) over bacterial sulfate reduction (BSR), and such a model well explains the similar changes in  $\delta^{34}\text{S}$  and  $\delta^{56}\text{Fe}$  values observed for these time periods.

[1] Rouxel *et al.* (2005) *Science* **307**, 1088–1091. [2] Johnson *et al.* (2008) *Ann. Rev. Earth Plan. Sci.* **36**, 457–493.