Reconciling the sulfur atmospheric cycle of early Earth with the geological record

PASCAL PHILIPPOT AND MARK VAN ZUILEN

Geobiosphere, Institut de Physique du Globe, Sorbonne Paris Cité, Université Paris Diderot, CNRS, 1 rue Jussieu, 75238 Paris, France

The reports of mass-independent sulfur isotope anomalies (MIF-S) in sediments older than 2.45 Ga have been attributed to photolytic reactions involving volcanic SO_2 in an oxygen-poor atmosphere. Photolysis experiments of SO_2 coupled with various UV shielding scenarios provided additional links to the early atmosphere. However, no simple model can reproduce the mismatch in the $\Delta^{33}S$-$\delta^{34}S$ relationship between the reference Archaean sulfide array (positive $\Delta^{33}S$-$\delta^{34}S$ correlation) and product sulfate (negative $\Delta^{33}S$ but positive $\delta^{34}S$). The discrepancy in the temporal and spatial record of sulfur isotope anomalies, with three main sulfate horizons deposited within less than 300 Ma compare to a global distribution of sulfide over more than 1, 500 Ma, is also unexplained. Here we report a new $\Delta^{33}S$-$\delta^{34}S$ linear trends recovered in two felsic volcanic ash layers of the 3.2 Ga Mapepe Formation in South Africa. This « felsic volcanic array » forms a tight $\Delta^{33}S$-$\delta^{34}S$ linear correlation that is best approximated by SO_2 photolysis experiments at deep UV wavelength. The perfect match to the $\Delta^{33}S$-$\delta^{34}S$ values of associated sulfate and equivalent felsic volcanoclastic and sulfate horizons of the 3.5 Ga old Dresser Formation, Western Australia, indicates that the exogenic sulfur cycle that produced this array was linked to felsic volcanism and sulfate precipitation. An emerging scenario for the early Earth atmosphere is a continuous photochemical haze that is perturbed between 3.5 and 3.2 Gyr by massive and optically thick volcanic plumes. This volcanic activity coincides in time with a period of rapid crust formation (Valbaara supercontinent).

Microbial iron reduction under deep subsurface pressure conditions

AUDE PICARD[1,2,3]*, DENIS TESTEMALE[4], JEAN-LOUIS HAZEMANN[4] AND ISABELLE DANIEL[3]

[1]Max Planck Institute for Marine Microbiology, Biogeochemistry Department, Celsiusstraße 1, 28359 Bremen, Germany (*correspondence: apicard@mpi-bremen.de)
[2]MARUM, Center for Marine Environmental Sciences, Bremen, Germany
[3]Université de Lyon, F-69622, Lyon, France, Université Lyon 1, ENS Lyon, CNRS, UMR 5570, Laboratoire de Géologie de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France
[4]Institut Néel, CNRS, Université Joseph Fourier, BP166, F-38042 Grenoble Cedex 9, France

Pressure is a key parameter in the deep subsurface which has been estimated to contain a large microbial population [1]. However the effects of pressure on microbial processes involved in important biogeochemical cycles are not constrained yet. At present, iron oxides are recognized as the most abundant terminal acceptors for the oxidation of organic matter in anoxic environments imposing dissimilatory iron reduction (DIR) as a biogeochemically important process in aquatic sediments, soils and aquifers [2]. Many factors are known to influence iron reduction rate and extent, however to our knowledge pressure effects on microbial iron reduction have not been investigated. We investigated the pressure dependence on Fe (III) reduction by the bacterium *Shewanella oneidensis* MR-1 up to 100 MPa using *in situ* X-ray Absorption Spectroscopy (XAS). At pressures up to 70 MPa, MR-1 was able to reduce all 5 mM Fe (III) citrate provided. Above 70 MPa, the final amount of Fe (III) that MR-1 could reduce decreased linearly and DIR was estimated to stop at 109 ±7 MPa. The initial reduction rate was enhanced by pressure up to 40 MPa then decreased to reach 0 at ca 110 MPa. MR-1 is a piezosensitive bacterium with growth rate maximum at atmospheric pressure. However, it can still grow at relatively high rates up to 40 MPa. MR-1 could thus be a potential significant player of the iron cycle in most of the metal-rich freshwater and marine sediments where moderate pressures occur.

[1] Whitman W.B. Coleman D.C. Wiebe W.J. (1998) *Proc. Natl. Acad. Sci. USA* **95**, 6578-6583. [2] Nealson K.H. & Saffarini D. (1994) *Annu. Rev. Microbiol.* **48**, 311–343.