

Exploring the relationship between molybdenum and organic matter through experimental approaches and XAS and NMR characterization

A. CHAPPAZ^{1*}, T.W. LYONS¹, J.P. FITTS²
AND S.C.B. MYNENI³

¹Dept. of Earth Sciences, Univ. of California, Riverside, CA 92521, USA (*correspondence: achappaz@ucr.edu)

²Brookhaven Natl. Lab, Upton, NY 11973 USA

³Princeton University, NJ 08544 USA

Although used widely in studies investigating the evolution of biospheric oxygenation, mechanisms of secondary molybdenum (Mo) fixation in settings rich in organic matter and hydrogen sulfide remain unclear. A key micronutrient playing a particularly important role in nitrogenase metalloenzyme systems, Mo is the most abundant transition metal in the modern ocean and is conservative with a residence time of ca. 700,000 years. Mo is soluble under oxic conditions as the molybdate ion (MoO_4^{2-}) but becomes insoluble in anoxic settings. Based on these redox properties, many studies have used Mo to trace the extent of euxinia in the ancient ocean. When $[\text{H}_2\text{S}]$ approaches a threshold value of ca. 10 μM , the molybdate ion is converted to particle reactive tetrathiomolybdate (MoS_4^{2-}) through a series of oxythiomolybdate ($\text{MoO}_x\text{S}_{(4-x)}^{2-}$) steps [1]. Surprisingly, we know little about the direct role of organic matter in sequestering Mo, although many studies suggest a dominant linkage to organic delivery and burial [2]. This gap limits the utility of the Mo paleoproxy.

Here, we present preliminary results that speak to the binding relationship between highly reactive MoS_4^{2-} and different varieties of bulk organic matter. Specifically, we emphasize two types of allochthonous natural organic material isolated via reverse osmosis and three forms of pure autochthonous organic matter produced from pure bacterial cultures (cyanobacteria, green algae, and heterotrophic bacteria). The nature of the Mo – organic matter relationship was analyzed via EXAFS and XANES techniques to identify Mo oxidation state, chemical structure, coordination environment and nearest neighboring atoms. To refine our investigations, experimental products were also analyzed with ^1H , ^{13}C and ^{95}Mo NMR and ESI-MS. Collectively, these data should illuminate the long-elusive details regarding organic-Mo coupling, including the dominant types of organic matter, the critical functional groups and the possible role of organic sulfurization.

[1] Helz *et al.* (1996) *GCA* **60**, 3631-3642. [2] Algeo & Lyons (2006) *Paleoceanogr.* **21**, PA 1016.

Mineral trapping in Deccan Basalt Province India: Implications for geological sequestration of CO_2

S.N. CHARAN, P.S.R. PRASAD AND D.S. SARMA

National Geophysical Research Institute (CSIR), Hyderabad 500606, India (nirmalcharan@gmail.com)

Atmospheric accumulation of CO_2 has drastically increased due to excess usage of fossil fuels in order to meet the ever increasing energy demands the world over. An option to mitigate the hazardous consequences of the above is the deep underground sequestration of CO_2 in suitable geological formations. Laboratory simulation experiments and field studies carried out here towards geological CO_2 sequestration are aimed at the feasibility of underground retention of CO_2 as a trapped solid phase stable over geological time scales. This study has shown that the injected CO_2 has reacted with the host rocks leading to the formation of secondary carbonate minerals due to mineral trapping. This study on the mafic-ultramafic rocks constituting the Deccan Continental Flood Basalt Province (DCFBP), India has shown appreciable concentration of iron, magnesium, calcium and suitable mineralogy, which make the DCFBP a potential reservoir system for underground geological sequestration of CO_2 . Most of the lava flows in the DCFBP have amygdular flow tops and bottom as well as interflow features, imparting the required porosity and permeability for CO_2 diffusion and storage. Under suitable conditions of temperature and pressure and local formation water's pH, the dissolved CO_2 interacts with iron, magnesium and calcium released due to reaction with primary pyroxene, olivine, plagioclase and glass especially at low pH, to form geologically stable ferrous, calcium and magnesium carbonates, as confirmed by laboratory experiments. The causative exothermic reactions are: (a) $2\text{Mg}_2\text{SiO}_4$ (Olivine) + CO_2 + $2\text{H}_2\text{O}$ = $\text{Mg}_3\text{SiO}_5(\text{OH})_4$ (Serpentine) + FeCO_3 (Ankerite) + MgCO_3 (Magnesite) and (b) $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Plagioclase) = $2\text{H}_2\text{O}$ + CO_2 = CaCO_3 (Calcite) + $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})$ (Clay). Laboratory experiments over 5 months duration at a temperature and pressure of 100° C and 60 bars of CO_2 , have shown growth of secondary Fe-, Ca- and Mg-bearing carbonates over the surface and in fractures of picritic basalts reacted with water and carbon dioxide in its supercritical condition. These secondary carbonates characterized by Infrared Spectroscopy and SEM techniques show (a) signatures which match well with ankerite (Iron carbonate), calcite (Calcium carbonate), magnesite (Magnesium carbonate) and (b) that they are made up of porous ankerite cores covered by fibrous calcite rich crusts with minor magnesite, serpentine and released silica.