Mo isotope proxy for ancient anoxia: Insights from a modern anoxic basin

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Insights into biogeochemical cycling in ancient anoxic environments can be gleaned from studies of their modern day analogues. One such setting is the Golfo Dulce, a ~200 m deep semi-restricted basin on the Pacific coast of Costa Rica. As a result of limited exchange with the open ocean, the deeper parts of the basin experiences sub-oxic to anoxic conditions, but little or no sulphate-reduction, for the majority of the year. The Golfo Dulce thus provides a natural laboratory to study biogeochemical cycling of redox sensitive trace metals, such as molybdenum (Mo), under conditions that are perhaps analogous to those of Archaean/Proterozoic oceans. Mo, and its isotopes, have recently emerged as potentially powerful proxies for reconstruction of past oceanic and atmospheric redox state[1,2]. The palaeoproxy power of Mo rests on its redox-bimodal aqueous geochemistry and associated isotopic fractionation during removal to oxic or euxinic sedimentary environments.

Here we focus on Mo systematics in both pore waters and sediments, obtained from 50cm sediment cores across the basin. Mo cycling is investigated across pronounced down-core redox gradients and variable bottom water redox conditions, as suggested by corresponding Fe and Mn pore-water profiles. At the deeper anoxic site, δ^{98}Mo begins increasing, by 2‰ in total, at the sediment/water boundary. The same pattern is seen in the core retrieved from beneath oxic bottom water, but in this case further down-core. With the isotopic variation there is a corresponding decrease in Mo concentration. Such a correlation could be explained by removal of Mo from the pore waters as a thio-molybdate species, in the presence of low dissolved sulphide. This process is thought to preferentially remove light Mo isotopes[3]. These data will be interpreted in light of their accompanying solid phase systematics, along with emerging data on experimental controls on Mo isotope fractionation during early diagenesis.

[1] Scott *et al.* (2008) *Nature* **452**, 456-459. [2] Anbar *et al.* (2007) *Science* **317**, 1903-1906. [3] Poulson *et al*. (2006) *Geology* **34**, 617-620.

Reaction pathways for rising hyperalkaline groundwater in a bentonite mine in the Philippines

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The Zambales Ophiolite in the Philippines comprises a thick ultramafic sequence overlain by gabbro, diabase complex, a pillow basalt unit and overlain by tuffaceous siltstone and sandstones referred to as the Aksitero Formation. A hyperalkaline spring called the Manleluag Hyperalkaline Hot Spring (pH 10-11) found within the gabbro section of the ophiolite, is postulated to be associated with the hydrous reactions with gabbros at depth and interaction upon rising with a bentonite deposit formed from the tuffaceous sandstone and siltstone nearby (i.e. Akistero Formation). The reaction pathway for rising hyperalkaline groundwater that interacts with the overlying bentonite deposits is illustrated in a rock core taken from a continuous section from the bentonite connecting to the underlying basalt deposit. Stratigraphically-oriented geochemical and mineralogical analyses of the sliced cores indicate a mixture of smectite and zeolite formed from the progressive alteration of the basalt with hyperalkaline water. This study highlights a natural analogue site located in the Philippines.