The Mo isotopic composition of rivers suggests complete euxinia in the Proterozoic ocean

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Quantifying the extent of past marine anoxia has become a key research goal in recent years [e.g. 1, 2]. Placing firm constraints on the oxygenation history of the ocean is essential for our understanding of the interaction between ocean and atmospheric chemistry, biological evolution, and nutrient controls on primary productivity. Recently, the isotopic record of the marine geochemistry of molybdenum has shown promise as such a palaeoredox indicator [1]. However the use of Mo isotopes in this way has been hampered by the fact that the isotopic composition of rivers, the dominant input of Mo to the oceans, is unknown and has been assumed to be that of average continental Mo isotopic composition.

We report here the isotopic composition of the dissolved Mo content from a selection of global rivers. In contrast to the expected value of 0‰ for the continental source to the oceans, the rivers sampled exhibit a range of Mo isotope compositions with $\delta^{97/95}$Mo always positive and ranging from 0.1 to 1.5‰. Further, there is a general relationship between $\delta^{97/95}$Mo and the reciprocal dissolved Mo concentration, defining an average $\delta^{97/95}$Mo input to the oceans of +0.7±0.2 ‰. Anciliary data, as well as published constraints on riverine Mo geochemistry, demonstrate that the mechanism for the observed isotopic fractionation is adsorption onto Fe-Mn oxides.

This process must occur wherever Mo exists as an oxidised aqueous species, therefore providing a mechanism for Mo isotopic fractionation in rivers since the onset of oxidative weathering on the continents ca. 2.2 billion years ago [3]. The estimated value for the $\delta^{97/95}$Mo input of Mo from rivers has profound implications for recent Mo isotope data from Mid-Proterozoic [1] and Mesozoic OAE [4] black shales [4]. Reported oceanic $\delta^{97/95}$Mo from these periods approach of the value we find in modern rivers suggesting perhaps a lower limit of riverine and oceanic $\delta^{97/95}$Mo after the onset of oxidative continental weathering and further implies near complete euxinia in the global ocean during these periods.

References

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Long-term geochemical evolution of the near field repository: Insights from reactive transport modelling and experimental evidences

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The hydrogeochemical role played by clay-based barriers in a high-level nuclear waste (HLNW) repository is twofold: (1) the retardation of the groundwater inflow to the waste canisters, and (2) the retention of radionuclides in case of canister failure. The latter is especially relevant taking into account that parameters such as pH and redox state will control the solubility and sorption of radionuclides. The long-term evolution of the porewater chemistry of the barrier system depends mainly on the nature of the inflow groundwater and on the composition of clay material. On one hand, groundwater chemistry may undergo sharp changes due to the climatic evolution, mainly linked to glaciation / deglaciation cycles. On the other hand, the buffering response of barrier to these changes will intimately be associated with the composition and content of some accessory minerals in the clay (dissolution/precipitation of carbonate, sulphate and iron-bearing minerals).

In this work, the long term response of bentonite barrier due to the interaction with groundwater is evaluated by using reactive transport calculations. We considered a granitic groundwater and two commercial bentonites, MX-80 Wyoming-type and Deponit CA-N Milos-type. Moreover, a temperature gradient has also been considered.

The results indicate that the interaction of a granitic groundwater with the bentonite buffer has minor effects on the pH evolution of the system, buffered by carbonate minerals. The redox state seems to be controlled by the regional groundwater, in equilibrium with pyrite and siderite. Composition of the surface sites in montmorillonite in bentonite significantly change since an increase of calcium occupancy is predicted by the model, related to calcium sulphate dissolution.

Finally, temperature gradient caused by heat generation in the canister leads to a general decrease of pH. In addition, it affects the content and distribution of some accessory minerals such as gypsum or silica.

Recent experiments with high-density unsaturated bentonite performed in the frame of NF-PRO European project give support to the results obtained with the model.