

Calcium and magnesium isotopes reveal Earth system response in the aftermath of a Cryogenian glaciation

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Neoproterozoic response to, and recovery from, a postulated greenhouse state following global glaciation represents an acute test of feedbacks within the Earth system to maintain an equable environment. One explanation for the severe environmental change predicts progressive build-up of $p\text{CO}_2$ during extreme glaciation, and rapid melt back and influx of atmospheric CO_2 into the ocean [1]. A boron isotope study of post-glacial carbonates from Namibia identified a temporary ocean acidification (pH \sim 7), potentially linked to oceanic uptake of carbon dioxide [2]. $\delta^{44}\text{Ca}$ (0.4 to 1.3‰) and $\delta^{26}\text{Mg}$ (-2.1 to -1.4‰) excursions in Neoproterozoic carbonate profiles elucidate the recovery of the Earth System from such an ocean acidification event and elevated greenhouse gas concentrations in the glacial aftermath. Both isotope patterns indicate an enhanced weathering influx following the glaciation demise, and increase in global temperature and precipitation in the greenhouse aftermath. This enabled the ocean to return to normal pH after climatic amelioration. Differences in time-development of the Ca and Mg isotope patterns reflect a change from carbonate- to silicate-dominated weathering flux and suggest primary dolomite formation during “cap dolostone” sedimentation. Differences in the magnitude of both isotope patterns across the palaeocontinental margin of the Congo Craton suggest a local influence potentially overprinting and amplifying the global pattern. Thus, extreme regional signals can lead to an overestimate of the global chemical weathering flux.

[1] Hoffman *et al.* (1998) *Science* **281**, 1342–1346. [2] Kasemann *et al.* (2010) *Geology* **38**, 775–778.

Tungsten species in natural ferromanganese oxides related to its different behavior from molybdenum in oxic ocean

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Different concentrations of Mo and W in oxic ocean attribute to their different distributions at the seawater/ferromanganese oxide interface. Recent studies also revealed large isotopic fractionation of Mo on ferromanganese oxides, which leads to the utility of Mo isotope systems as a paleoredox proxy. In contrast to extensive attentions on Mo, chemistry of W at the solid/water interface is poorly understood. The aim of this study is to reveal the W species in natural ferromanganese oxide, which affects its different behaviors from Mo in modern oxic ocean.

Conventionally, it has been difficult to obtain high quality fluorescence XAFS spectra of trace amount of W because of interferences of intense scattering and/or fluorescence from other predominant elements, such as Fe, Mn, Ni, Cu, and Zn. Here, we applied wavelength dispersive XAFS method, where Bent Crystal Laue Analyzer was used in front of detector to selectively extract fluorescence X-rays of W [1].

We revealed that the W species are in distorted *Oh* symmetry in natural ferromanganese oxides. The host phase of W is suggested to be Mn oxides. We also found that the W forms inner-sphere complexes in hexavalent state and distorted *Oh* symmetry on both synthetic ferrihydrite and $\delta\text{-MnO}_2$. It is known that Mo forms a distorted *Oh* inner-sphere complex on Mn oxides and a *Td* outer-sphere complex on ferrihydrite, and the host phase of Mo in natural ferromanganese oxides is $\delta\text{-MnO}_2$ [2]. Therefore, the different behaviors of W and Mo at the seawater/ferromanganese oxide interface can be caused by (i) the stability of inner-sphere complexes on the Mn oxides and (ii) mode of attachment (inner- or outer-sphere) on Fe oxyhydroxides. In addition, preferential adsorption of lighter W isotopes is expected based on the molecular symmetry of the adsorbed species, implying the potential significance of the W isotope systems as paleoredox proxy similar to Mo [3].

[1] Kashiwabara *et al.* (2011) *Geochim. Cosmochim. Acta.* **75**, 5762–5784. [2] Kashiwabara *et al.* (2010) *Chem. Lett.* **39**, 870–871. [3] Kashiwabara *et al.* (2013) *Geochim. Cosmochim. Acta.* **106**, 364–378.