How the sedimentary Re/Mo ratio and Tl enrichments trace past and present opaline productivity

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Here, we critically examine how the trace metals Mo, Re and (the rather enigmatic) Tl may serve as indicators of productivity events, as shown for Late Quaternary organic/opal-rich, fast accumulating sediments in upwelling areas off Peru and Namibia.

In all Peruvian samples, Mo and Re are highly enriched. The ultimate trapping mechanism for Mo in the sediments is H_2S availability, i.e., the intensity of sulfate reduction. Rhenium, by contrast, seems to accumulate via diffusion across the sediment-water interface according to the extent of reducing conditions (Böning et al., 2004; 2009).

Opal was determined in Peruvian surface samples (0-1 cm, 16 stations, 85 to 1400 m water depth) and in a long Pleistocene core by Wolf (2002). Interestingly, low Re/Mo ratios (close to and below the sea water value, i. e. $\leq 2 * 10^{-4}$) as well as Tl are significantly correlated with opal contents in samples from the surface and the long core ($r^2 > 0.8$). Our data clearly show that such low Re/Mo ratios are typical of fine-grained sediments rich in fresh organic matter (no coarse material, no phosphorites). Off Namibia opal-rich sediments show high contents in Re and Mo and very low Re/Mo ratios, averaging $0.5 * 10^{-4}$. In short and long cores off Namibia and Peru, where Re/Mo is $\leq 1 * 10^{-4}$, Tl seems exclusively associated with opal (as seen in a significant correlation of Tl/Al with Si/Al; $r^2 > 0.8$).

How do we explain such low Re/Mo ratios? Even if the trapping mechanisms are different for Mo and Re, Crusius et al's. (1996) Re-Mo relationship is quite useful. These authors proposed that a Re/Mo ratio close to the seawater ratio ($0.8 * 10^{-4}$) reflect the quantitative removal of both Re and Mo from solution. But the Re/Mo ratio below the seawater ratio cannot be explained by diffusion of both elements and quantitative enrichment in the sediments. Indeed, the diffusion of Re and Mo is limited off Namibia and Peru given the enormous biogenic particle rain. Hence, we propose an additional preconcentration step for Mo on particles to explain the very low Re/Mo ratios, while Re only seems to accumulate via diffusion. However, our data suggest that the carrier phases are not Mn-oxides but fresh biogenic detritus. Further, since Mo and Cd are well correlated (Böning et al., 2004) our findings suggest a similar, biodetrital source for both elements. This would imply a non-conservative behaviour of Mo, which corroborates findings where dissolved Mo becomes depleted in coastal and open-ocean waters and consequently enriched on biogenic particles after algal blooms (Tuit and Ravizza, 2003; Dellwig et al. 2007). Concerning Tl, it is yet to be determined wether this element is directly associated with the opaline hard parts or the related fresh organic matter. However, the implied particle reactivity of Tl suggests a non-conservative behaviour of this element. Further, our data do not support an involvement of Tl with Mn but rather an association with biological cycling.

References: Böning, P. et al. (2009) Mar. Geol. 259, 112-121; Böning, P. et al. (2004) Geochim. Cosmochim. Acta 68, 4429–4451; Crusius, J. et al. (1996) Earth Plan. Sci. Lett. 145, 65-78; Dellwig, O. et al. (2007) Geochim. Cosmochim. Acta 71, 2745-2761; Tuit, C. and Ravizza, G. (2003) Geochim. Cosmochim. Acta 67, A495, Suppl. 1; Wolf, A. (2002) Dissertation, University of Kiel, Germany, pp. 88.