

## Precise Re-Os age with exceptionally high $^{187}\text{Re}/^{188}\text{Os}$ for black shales heralds Permo-Triassic extinction, Norwegian shelf and East Greenland

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The Permian-Triassic transition coincides with the largest mass extinction in Earth history. Understanding the causes that led to this biotic catastrophe requires detailed examination of bio/chemo stratigraphic changes pinned in absolute time. Here we report Re-Os data for well-defined black shale horizons in Upper Permian successions from the Mid-Norwegian shelf and East Greenland. These data provide (1) high-precision depositional ages; (2) constraints on the initial Os isotope ratio for Late Permian seawater; and (3) geochemical evidence for extraordinary paleoenvironmental conditions at the onset of the Permo-Triassic extinction.

A drill core penetrating a turbidite succession offshore mid-Norway provides three intervals of organic-rich shale. These intervals yield precise and indiscernible Re-Os isochrons at 252 Ma with MSWDs  $\sim 1$ . Accompanying well-determined initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios of  $\sim 0.6$  are distinctly less than Middle Triassic seawater [1]. Re concentrations increase dramatically upsection, whereas common Os concentrations vary little, resulting in a systematic increase of  $^{187}\text{Re}/^{188}\text{Os}$  approaching the Permian-Triassic boundary. Most of the shales have extraordinarily high  $^{187}\text{Re}/^{188}\text{Os}$  (ca. 2000 to 6000), compared to  $^{187}\text{Re}/^{188}\text{Os}$  ratios typical of black shales (ca. 1 to 600, and rarely  $>1300$ ).

The second studied section from the Ravnefjeld black shales in East Greenland (drill core 303102) yields an identical age of  $\sim 252$  Ma and also has exceptionally high  $^{187}\text{Re}/^{188}\text{Os}$ , affirming the proposed correlation between the shale intervals, now on both sides of the Norwegian Sea.

These new data place a precise time pin in both sections and record catastrophic changes approaching the Permian-Triassic boundary. Experimental work suggests that high  $^{187}\text{Re}/^{188}\text{Os}$  in shales is achieved only under highly reducing conditions [2]. Thus, the remarkably high  $^{187}\text{Re}/^{188}\text{Os}$  ratios may indicate an unprecedented degree of basin anoxia.

Support: Petromaks (NFR 180015/S30), Statoil, Eni-Norge.

[1] Xu *et al.* (2009) *EPSL*, **288**, 581–587. [2] Yamashita *et al.* (2007) *GCA*, **71**, 3458–3475.

## Identification of metacinnabar in mixed mercury, sulfide, and dissolved organic matter solutions through chromatographic concentration and EXAFS

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Mercury speciation in environmental systems that contain mixtures of mercury, sulfide, and dissolved organic matter (DOM) has important ecological and human health ramifications. We have identified evidence of colloidal metacinnabar using synthetic systems with 10 or 50 mg L<sup>-1</sup> DOM, 100  $\mu\text{M}$  total sulfide, and a range of mercury concentrations (350 pM to 1.4  $\mu\text{M}$ ). Solutions were run through a column of C<sub>18</sub> resin to concentrate hydrophobic mercury species in preparation for X-ray spectroscopy. Extended X-ray absorption fine structure (EXAFS) spectroscopy of the mercury on the resin indicates a mercury-sulfur bond distance of 2.52 Å, with approximately three sulfur atoms coordinating the mercury atom. The coordination number is lower than expected, but the Hg-S bond distance is consistent with metacinnabar. The bond distance does not match the sulfide-free mercury-DOM model that was also determined. These results are the first direct evidence of the presence of metacinnabar in systems that contain dissolved organic matter, sulfide, and relatively low mercury concentrations.