

## Distribution and redox status of Arsenic in framboidal pyrite from estuarine sediments

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Synchrotron  $\mu$ XRF measurements of 106  $\mu$ m-sized pyrite framboids from anoxic sediments of the Achterwasser lagoon, a part of the estuarine system of the river Oder, SW Baltic Sea, show highly variable As concentrations ranging from 6 to 1140  $\mu$ g/g within the uppermost 50 cm of the sediment column. Even within a single depth layer, the As concentration of different framboids vary greatly with no clear depth trend visible. Median values calculated from  $\mu$ XRF data for each depth layer are similar to the chemical extraction data (28 to 143  $\mu$ g As per g pyrite), suggesting that the applied extraction procedure yields realistic average As concentrations in pyrite from bulk sediment. Pyrite can account for 9 to 55% (average 22%) of the total As budget of the sediments indicating that authigenic pyrite plays an important role in the geochemical cycling of As in coastal sediments.

High-resolution  $\mu$ XRF mapping of single pyrite grains shows that As is distributed inhomogeneously within larger framboids, and more regularly in the smaller pyrite grains. This may be due to changing pore water composition during pyrite growth, with larger and older framboids being subjected to more frequent changes in the pore water composition as compared to the smaller and younger framboids from the same depth layer.

XANES spectra indicate that a considerably part of As is present in higher valence state (+III/+V) in samples from near the sediment/water interface. This can be explained by frequently occurring resuspension of the surficial sediments to the oxic water column due to wave action and subsequent re-deposition. This process might be responsible for adsorption of As(V) oxyanions onto pyrite. Reduced As(-I) species become more important in the deeper samples, reflecting decreasing redox potential and increased time since deposition. This suggests that adsorbed As(V) and As(III) species will be reduced by the sulfidic pore waters prior incorporation during pyrite growth.

## Degassing of oceanic H<sub>2</sub>S and its delivery to terrestrial ecosystems during the Permo-Triassic extinction

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Evidence is growing that drastic changes in the oceanic sulfur cycle were intimately linked with the greatest extinction of the Phanerozoic at the Permo-Triassic boundary. Isotopic changes in proxies for seawater-sulfate suggest the transformation of a significant portion of the marine sulfate reservoir to dissolved sulfide by bacterial sulfate reduction during the late Permian (Newton *et al.*, 2004). Rapid return to <sup>34</sup>S depleted sulfate at the extinction level can be explained by ocean overturn and re-oxidation of this sulfide, providing a kill mechanism in the form of H<sub>2</sub>S poisoning. Modelling using end-Permian boundary conditions permits the escape of this sulfide from the surface of the ocean (Kump *et al.*, 2005), so ocean overturn and sulfide release could therefore link the marine and terrestrial extinctions which are closely spaced in time. Here we present new results from lacustrine sediments from north-west China, and re-interpret existing results from South Africa (Maruoka *et al.*, 2003). Sulfate concentrations in freshwater lake systems are low when compared to supplies of reactive Fe and organic matter. Hence, sulfate is often quantitatively reduced and preserved as pyrite in lake sediments, recording the isotope composition of the original sulfate.

Isotope data from both localities record relatively stable backgrounds ( $\delta^{34}\text{S}$  between -4 to +5‰, China, and 0 to +5‰, South Africa), within the normal range for weathered sulfate from large geologically diverse catchments. Close to the P-Tr boundary these stable records are interrupted by rapid negative shifts to around -12‰  $\delta^{34}\text{S}_{\text{VCDT}}$  (both locations).

These excursions could not be caused by inputs of volcanogenic sulfur ( $\delta^{34}\text{S}$  -5 to +5‰), and provide the first direct evidence of transfers of oceanic derived H<sub>2</sub>S to terrestrial ecosystems. The exact role of H<sub>2</sub>S in the terrestrial extinction is unclear. Possible mechanisms include direct poisoning, acidification, or as part of an ozone depletion scenario, leading to radiation exposure (Lamarque *et al.*, 2007).

## References

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