

## Arsenic in surface sediments of a harbor sludge dumping site and a natural deposition site in the Helgoland Mud Area, North Sea

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In order to analyse differences in concentration, speciation and total mobility of arsenic two different locations were studied near the Helgoland Mud Area, North Sea.

The first location is characterised by natural sedimentation, the second by deposited sediments dredged from the port of Hamburg. Porewater as well as sediment profiles were analysed with respect to arsenic compounds (As (III) and total As) and major redox species as total and reactive manganese and iron. The sediment samples were handled under inert atmosphere before and during extraction by water, phosphate, hydrochloric acid and aqua regia. Total element contents in porewater and leachable extracts of sediment fractions were analysed.

The results show a strong redox coupling of arsenic with manganese and iron. Oxidized arsenic seems to adsorb to manganese- and iron-oxyhydroxides in surface sediments. In contrast to the solid samples, the pore water data shows a release of As (III) into porewater when manganese- and iron-oxyhydroxides are reduced in the upper part of the cores. Also a remobilisation of As (V) occurs. Downward diffusing arsenic can be fixed by carbonate below the zone of manganese and iron reduction. In the anoxic parts of the sediments As (III) and As (V) are released and could be fixed at authigenic iron sulphide or arsenic sulphides formation. A sulfidic precipitation of arsenic in iron-dominated systems is limited by the occurrence of HS<sup>-</sup>.

Total solid-phase contents in leachable extracts of sediment fractions of the natural area show significant higher arsenic concentrations than the core of the anthropogenic dumping area. This is due to the higher fines content of the Helgoland mud area.

Higher total porewater contents of iron and arsenic in the core of the anthropogenic dumping area thus due to higher turnover rates of organic matter by iron reduction. Higher concentrations of arsenic may be due to a higher availability of iron in the dumped sediments.

## Sub-arc $\delta^{11}\text{B}$ : The introduction of boron isotope heterogeneity into the convecting mantle

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The Cerro del Almirez Massif in Spain preserves field evidence for the prograde transition from antigorite-serpentinite (ant-serp) to chlorite-harzburgerite (chl-harz) in a paleo-subducting slab. This study investigates B isotope fractionation in the sub-arc region, where fluid loss accompanies prograde metamorphism under well constrained pressure and temperature conditions (650 °C, 1.7 GPa [1]). Boron isotopes are strongly fractionated during the dehydration of ant-serp, with a sharp decrease of  $\delta^{11}\text{B}$  across the ant-serp to chl-harz isograd. Ant-serp has a  $\delta^{11}\text{B}$  of +22.6 ‰ ( $\pm 1.6$ ), similar to the heaviest  $\delta^{11}\text{B}$  in serpentinites recovered from the forearc region of the Mariana subduction zone [2, 3], whereas prograde lithologies preserve  $\delta^{11}\text{B}$  of +3.3 ‰ ( $\pm 0.3$ ) to  $\delta^{11}\text{B}$  of -3.5 ‰ ( $\pm 0.3$ ).

Although the rapid drop in  $\delta^{11}\text{B}$  demonstrates that massive B isotope fractionation occurs at sub-arc depths, the absolute amount of boron lost during dehydration is negligible compared to B lost from the downgoing slab in the forearc at the onset of subduction (c. 85%)[4]. Lithologies on either side of the isograd contain 7-12 ppm B with only minimal loss of B accompanying dehydration. This means that any B that survives ant-serp dehydration has the potential to be transported past the sub-arc region and into the deep, convecting mantle. Prograde chlorite is not the major host of this boron - it is mostly contained in prograde olivine-hosted inclusions[5], unlikely to suffer any subsequent dehydration reactions. The delivery of B with  $\delta^{11}\text{B}$  of +3.3 ‰ to  $\delta^{11}\text{B}$  of -3.5 ‰ into the asthenosphere therefore provides a possible source for OIB (e.g.[6]) whose  $\delta^{11}\text{B}$  is significantly lighter than primitive mantle.

- [1] Padrón-Navarta *et al* (2011) *J. Petrol.* **52**, 2047-2078.  
[2] Savov *et al* (2007), *J. Geophys. Res.*, doi:10.1029/2006JB004749 [3] Pabst *et al* (2012) *Lithos* **133**, 162-179. [4] Kodolanyi and Pettke (2011) *Chem. Geol.* **284**, 351-362. [5] Scambelluri *et al* (2004) *Earth Planet. Sci. Lett.* **222**, 217-234. [6] Turner *et al* (2007) *Nature* **447**, 702-705.