Clumped isotopes applied to Silurian brachiopod shells, Gotland/Sweden

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Several O and C isotope records from the Silurian sequence of Gotland/Sweden are published, which are based on brachiopod shell calcite [1,2], micritic limestones [3] and biogenic phosphates [4]. All recorded isotope curves show similar trends with pronounced shifts in $\delta^{18}O$ and $\delta^{13}C$. Besides, three C isotope excursions are measured globally. Correlation between the C and O isotope signals supports the assumption that the values are of primary origin.

We are applying the carbonate clumped isotope thermometer to brachiopod shells from Gotland to decipher both, temperature and $\delta^{18}O$ of Silurian ocean water. Based on the ordering of isotopes, i.e. on the clumping of ^{13}C-^{18}O within carbonate groups of minerals, precipitation temperatures can be estimated independently of the isotopic composition of the water from which the crystals grew. The measure of temperature is Δ_{47}, which describes the deviation of the 47/44 abundance ratios in CO_2 derived from H_3PO_4 digestions of carbonates from the corresponding stochastic 47/44 ratios.

Due to different pre-analyses of brachiopod shells from Gotland various researchers interpret most of these fossils not to be influenced by diagenesis [1,2], and stable isotope ratios are assumed to be preserved. However, temperatures between 40 and 60°C are estimated from first Δ_{47} measurements, which indicate a diagenetic overprint that affected at least ^{13}C-^{18}O clumping in carbonate groups. It needs to be proven, whether the $\delta^{18}O$ values reflect a pristine signal or had been reset at least in parts, and whether geochemical signatures of these fossils can be used for paleoreconstructions. This will be tested by a comparison of Δ_{47} and $\delta^{18}O$ values of pristin and altered shell sections which were already identified using CL and SEM. Additionally, trace element concentrations were measured.

High resolution sampling along ontogenetic transects of four brachiopods indicate variations in $\delta^{18}O$ of about 1.5‰ within the single shells expressed by a constant trend to lower values with increasing distance to the hinge, but a shift to higher values in the most anterior part. Δ_{47} analyses along growth directions of these brachiopods might provide additional information whether the O isotopic pattern reflects primary fluctuations of temperature or $\delta^{18}O$ during growth of the organisms.

[1] Samtleben et al. (1996) *IJES* **85(2)**, 278-292. [2] Wenzel and Joachimski (1996) *PPP* **122(1-4)**, 143-166. [3] Munnecke et al. (2003) *PPP* **195(1-2)**, 99-124. [4] Wenzel et al. (2000) *GCA* **64(11)**, 1859-1872.

Phosphate reaction with PbS stimulates microbial S oxidation

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Introduction

The reaction of lead (Pb) and phosphorus-containing compounds causes the formation of pyromorphite-type mineral phases [1]. These mineral phases have a low solubility and bioaccessibility, making their formation a viable option for stabilizing Pb contamination in soil and waste rock [1]. In cases where an insoluble mineral such as galena (PbS) is the primary form of Pb the effect of phosphorus amendment on the sulfur speciation and the microbial interactions are still poorly understood.

Methods

Pure culture experiments were set up with *Bosea* sp. str. WAO, an autotroph which is capable of growth on several reduced sulfur sources [2]. Replicate flasks containing 40 mM phosphate buffered growth medium and 2 mM PbS were amended with either live cells (active), killed cells (sterile control), or no cells (background control). Flasks were maintained aerobic by shaking and incubated at 30°C. Periodic samples were taken to measure sulfate, total dissolved sulfur, and Pb in the bulk medium and solid phase.

Results and Conclusions

The addition of phosphate to the growth medium containing powdered PbS caused the abiotic exchange of sulfide for phosphate, producing lead phosphate $Pb_9(PO_4)_6$, and was confirmed by powder XRD. The released sulfide was then available for strain WAO to use as an energy source for growth.

The microbial oxidation of the released sulfide to sulfate was compared to background and sterile controls. Active cultures containing 2 mM PbS produced ~1.7 mM sulfate as measured by IC within 9 days of incubation. No production of sulfate was measured in the background and sterile controls during the incubation period. Metal analysis by ICP-OES measured less than 0.2 mM of Pb in the bulk medium after incubation for active or control, while 2 mM was recovered after acid extraction of the precipitate.

WAO preferentially colonized the PbS mineral surface to gain access to the released sulfide as shown with epifluorescence microscopy on slide cultures of mineral powder. The biomass of strain WAO increased on the mineral surface over time and was also shown to be closely associated using confocal microscopy.

Although the phosphate amendment makes the Pb less bioavailable, it is increasing the availablity of sulfide which can stimulate the growth of sulfide oxidizing organisms and the production of sulfate. In situations where there are high concentrations of these sulfidic minerals the addition of phosphate may increase the microbial S oxidation, an important contributor to acid mine drainage.

[1] Kumpiene *et al.* (2008) *Waste Management* **28**, 215-225. [2] Rhine *et al.* (2008) *Environmental Sci. Technol* **42**, 1423-1439.