Early and Middle Jurassic $\delta^{13}C$ and $\delta^{18}O$ trends: A high resolution dataset from the UK

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Low-Mg-calcite fossils have been extensively utilized to obtain past seawater chemistry and to reveal major environmental changes in Earth history [1, 2]. The resolution of these first generation long-term studies is often at biozone levels only. Recent work on major Phanerozoic events showed that distinctly higher resolutions are possible, revealing short-term stable isotope fluctuations and helping to discover its causes. Here we present new carbon and oxygen isotope data from mollusks and brachiopods collected from marine Early to Middle Jurassic successions of the UK representing a new generation of data in terms of temporal resolution. Together with literature data for the T–J boundary [3] and the Toarcian OAE [4] a nearly complete high-resolution record is now available. The fossils have been screened by various techniques, such as scanning electron microscopy and chemical analysis, to check for post-depositional alteration. The carbon isotope fluctuations obtained from the analyzed samples are the following: (1) a positive excursion in the earliest Sinemurian *Conybeari* zone, (2) a negative shift in the Sinemurian *Bucklandi* zone, (3) a negative excursion at the Sinemurian–Pliensbachian boundary (upper *raricostatum* and lower *jamesoni* zones), and (4) a positive excursion in the Late Pliensbachian *margaritatus* zone. The new oxygen isotope fluctuations in general correspond to those of the carbon isotopes, but with the exception for the Sinemurian–Pliensbachian boundary event, which is characterized by a positive $\delta^{18}O$ trend during the negative $\delta^{13}C$ excursion. This positive trend represents most likely bottom water cooling as a result of the Early Pliensbachian transgression. In addition, an Aalenian–Bajocian positive $\delta^{18}O$ excursion is identified. The new high resolution dataset shows partly a strong similarity between the positions of the global warming and cooling events within transgressive and regressive phases of second-order depositional sequences though the Early Jurassic supporting the idea that second-order depositional sequences are a result of eustatic sea-level changes at that time.

[1] Veizer *et al.* (1999) *Chem. Geol.* **161**, 59–88. [2] Jenkyns *et al.* (2002) *J. Geol. Soc. London* **159**, 351–378. [3] Korte *et al.* (2009) *J. Geol. Soc. London* **166**, 431–445. [4] Bailey *et al.* (2003) *Earth Planet. Sci. Lett.* **212**, 307–320.

Geo-bio interactions in hydrothermal fluids and their potential role for hydrothermal metal fluxes

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Hydrothermal vents emit fluids with high concentrations of many metals at the seafloor. Until recently it was assumed that the precipitation of most metals (e.g. Cu and Fe) during mixing with seawater reduces their net fluxes from the hydrothermal systems into the open ocean to negligible values. However, the recent discovery of significant organic complexation of Cu and Fe in the hydrothermal fluids and rising plumes, has urged a revision of trace metal fluxes from deep-sea hydrothermal vents. We demonstrated using field data and geochemical modeling [1] that the presence of organic ligands stabilizing dissolved trace metals strongly competes with metal precipitation and significantly increases the dissolved metal concentrations in hydrothermal fluids and plumes. According to our calculations, hydrothermal metal fluxes may be significantly larger than previously assumed, i.e. up to 20% of the deep-ocean dissolved Fe and Cu budget can be assigned to hydrothermal sources.

While the importance of organic ligands for hydrothermal metal fluxes seems to be acknowledged by now, the nature and origin of these organic molecules is still unclear. Amino acids, probably of biogenic origin, which have been found in significant concentrations in hydrothermal fluids [2], and other organic molecules containing thiol groups would be potential candidates for stable metal complexation. In lab experiments with hydrothermal microbial cultures along Cu concentration gradients the production of organic Cu-binding ligands by the microbial communities due to increasing Cu stress was studied. Ligand production increased significantly with increasing Cu concentrations, implying microbial influence on dissolved metal concentrations, speciation and mineral precipitation in the hydrothermal vent environment. Our work suggests a significant modification of hydrothermal fluid chemistry and hydrothermal metal fluxes by biological processes.

[1] Sander & Koschinsky (2011) *Nature Geosc* **4**, 145–150. [2] Klevenz *et al.* (2010) *Geochem J* **44**, 387–397.