

## Seasonal variation of oxygen and organic carbon isotopes and skeletal aragonite from *Unionidae* in the Rhine river

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Seasonal variations in the oxygen and carbon isotopic composition of Rhine River water were compared with the isotopic record from recent and historical specimens of freshwater bivalves (*Unionidae*). The purpose of this study was to investigate these aragonitic bivalves as proxies for climate change. Seasonal variations in the river water  $\delta^{18}\text{O}$  are on the order of 1 to 2 ‰. During the summer, the run-off is dominated by Alpine melt-water, resulting in average values of -10 to -10.5 ‰, whereas the non-Alpine contribution is higher during winter, as indicated by mean  $\delta^{18}\text{O}$  values of -8.5 to -9 ‰. The  $\delta^{18}\text{O}$  of growth increments in the prismatic shell layer of *Unio crassus nanus* corresponds perfectly to what is predicted by known fractionation of  $^{18}\text{O}$  between water and aragonite. Variations in  $\delta^{18}\text{O}$  and the river water temperature are faithfully recorded by relatively large growth increments during summer. The isotopic signatures of individual flood events are also recorded in the shells. In summer, snowmelt-related Alpine waters with low DIC contents and heavy  $\delta^{13}\text{C}$  lake productivity signals (-9 ‰) were observed at Cologne. In winter, however, the components of the non-Alpine Rhine dominate the discharge at Cologne. Waters had light  $\delta^{13}\text{C}_{\text{DIC}}$  signals of -11‰ soil respiration in the non-Alpine zone. Sampling of Lake Constance waters showed the effect of bioproductivity in the summer surface water. Bioproductivity is related to the withdrawal of light organic carbon and has a positive  $\delta^{13}\text{C}_{\text{DIC}}$  increase of 2 ‰ in the surface waters.

## Speciation of Cu and Zn in natural hydrothermal boiling systems: Evidence from fluid inclusion studies by X-ray absorption techniques

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Metal speciations in fluids are responsible for the partitioning of metals into the liquid and vapour phase during fluid phase separation and can lead to major changes in fluid compositions of hydrothermal systems. Here we present data for the partitioning behaviour of Cu and Zn in coexisting liquid and vapour phase fluid inclusions formed by sub-critical phase separation. Synchrotron-radiation induced micro X-ray fluorescence analysis (SR-XRF) and temperature-dependant X-ray absorption near edge structure (XANES) experiments were performed on individual inclusions. The studied fluid inclusion boiling assemblages are hosted in quartz from miarolitic cavities of the Torres del Paine granite complex (Chile). The formation temperatures of hydrothermal quartz in vugs range between 280°C and 340°C.

SR-XRF element maps revealed that Cu and Zn show a contrasting partitioning behaviour: while Cu is dominantly detected in vapour-rich inclusions, zinc is more abundant in brine-type inclusions.

XANES experiments were performed at temperatures up to 460°C using a Linkam THMSG-600 heating-stage. Measurements were carried out at ID22 and FAME, ESRF with spot sizes of 4 and 15  $\mu\text{m}$ , respectively. In vapour-rich inclusions, most of the Cu is concentrated in daughter crystals. During heating runs, the daughter crystals dissolve and Cu oxidation state changes between 190°C and 280°C from  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$ . While  $\text{Cu}^{2+}$  seems to be coordinated with water ligands forming the complex  $\text{Cu}[\text{H}_2\text{O}]_6^{2+}$ ,  $\text{Cu}^{1+}$  is coordinated by two chlorine ions forming  $\text{Cu}[\text{Cl}_2]$ . In brine-type inclusions, Cu is contained in the liquid phase. XANES-spectra show that Cu dissolved in brines has an oxidation state of 2<sup>+</sup> between 25°C and 460°C. These findings are in accordance with the interpretation that at temperatures of phase separation  $\text{Cu}^{1+}$  species is more stable and responsible for the concentration of Cu in the vapour phase.

XANES spectra indicate that Zn is most probably complexed as  $\text{ZnCl}_4^{2-}$  in the temperature range 25–370° for both, liquid and vapour rich inclusions. This shows that in contrast to Cu, changes in speciation are not responsible for the partitioning of Zn into the liquid and the vapour phase.