

## Triple oxygen isotope composition of bioapatite

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The reconstruction of paleo-atmospheric CO<sub>2</sub> levels by proxies is still on debate. The  $\Delta^{17}\text{O}$  of air O<sub>2</sub> varies with atmospheric CO<sub>2</sub> concentrations. Higher CO<sub>2</sub> concentrations result in lower  $\Delta^{17}\text{O}$  values of O<sub>2</sub>, whereas lower CO<sub>2</sub> lead to a smaller  $^{17}\text{O}$  anomaly of air O<sub>2</sub>. Pack et al. [1] proposed that bioapatite of terrestrial mammals can be used as proxy for the  $\Delta^{17}\text{O}$  of ambient air and hence atmospheric CO<sub>2</sub> levels. Mammals breathe in O<sub>2</sub> to metabolize carbohydrate, fat, and protein. The  $\Delta^{17}\text{O}$  anomaly of air O<sub>2</sub> is transferred to the reaction products CO<sub>2</sub> and H<sub>2</sub>O. Both, CO<sub>2</sub> and H<sub>2</sub>O equilibrate with body water, so that the anomaly is transferred from inhaled O<sub>2</sub> to body water of mammals. Bioapatite crystallizes in isotopic equilibrium from body water. Because body water contains a fraction of anomalous O<sub>2</sub> from respiration of air O<sub>2</sub>, bioapatite should carry information on the isotope composition of air O<sub>2</sub>. The amount of oxygen from respired air O<sub>2</sub> can be estimated using a mass balance model [1].

We collected modern samples of bioapatite of marine vertebrates that crystallized at temperatures between 0°C and 37°C. For the sample preparation, the modern samples were treated with 2 ml H<sub>2</sub>O<sub>2</sub> (30%) for more than 12 hours to remove the organic matter. Afterwards pretreated samples were heated to 1000°C to remove the carbonate fraction of the bioapatite [2]. The triple oxygen isotope measurements of the phosphate fraction of the bioapatite were conducted by laser fluorination using BrF<sub>5</sub>.

We will present new data on the temperature dependence of the equilibration  $\theta$  value between water and bioapatite.

[1] Pack et al. (2013) *Geochimica et Cosmochimica Acta*. **102**, 306-317. [2] Lindars et al. (2001) *Geochim Cosmochim Acta* **65**, 2535-2548.