

## What is the real correction factor for $\delta^{18}\text{O}$ measurements of apatite carbonates?

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Isotopic determinations from carbonates have been performed since the early days of geochemistry. They have undergone substantial evolution with the development of more automated systems. This has especially benefited to the analyses of carbonate radicals present in the crystal lattice of biogenic apatite minerals. This is of significant importance for the analyses of tooth enamel or bone from modern samples as well as archaeological or fossil samples. Oxygen isotope compositions of bioapatite carbonate are commonly used to reconstruct paleoclimates, dietary habits and migration pathways in combination with carbon and strontium isotope compositions. Passey et al. in 2007 had already demonstrated that the  $^{18}\text{O}/^{16}\text{O}$  ratios of the  $\text{CO}_2$  gas resulting from the reaction of phosphoric acid with fossil tooth enamel or bone carbonates followed fractionation patterns depending on both reaction temperature and sample ultrastructure and chemistry. One difficulty was to reliably measure the fractionation factors at  $25^\circ\text{C}$  which could only be realized offline.

We have reconsidered Passey et al. experiments using a new fully automated system isoFLOW-precisION. This system allows us to prepare and measure automatically  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of carbonates with high sensitivity (0.03‰; 0.05‰ respectively for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  down to 100ug). We have adapted the system to perform phosphoric acid reactions and isotopic measurements at temperatures of  $25^\circ\text{C}$ ,  $50^\circ\text{C}$ ,  $70^\circ\text{C}$  and  $90^\circ\text{C}$ . We applied this technique to a large collection of bone and tooth enamel from actual, archaeological and fossil samples. Our results are first in good agreement for samples that had already been published in Passey et al. 2007. Secondly, we propose new fractionation factors to correct  $\delta^{18}\text{O}$  from apatite carbonates as a function of the chemistry and mineralogy of bioapatites in the temperature range mentioned above. We demonstrate that for some samples, using the wrong fractionation factors, the final error associated with the  $\delta^{18}\text{O}$  measurements can reach 1%. To further investigate the causes of those sample-related variations we have performed major and trace elements analyses which give us clues to understand this phenomenon.

Référence : B.H. Passey, T.E. Cerling and N.E. Levin (2007) Rapid Comm. In Mass Spectrom., 21, 2853-2859.