

High-precision $^{34}\text{S}/^{32}\text{S}$ measurements from vertebrate bioapatites using purge-and- trap EA-IRMS technology

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In ecological studies, sulfur isotope compositions ($\delta^{34}\text{S}$) of soft tissues (e.g. hair, skin, nail, collagen...) allow the determination of both past and present-day living environments of organisms. However, technical limitations have prevented so far reliable sulfur isotope analyses of minerals with a low sulfur content, such as bioapatite, which is the crystalline component of skeletal tissues. The development of “purge and trap” technology in elemental analysers recently demonstrated new possibilities to solve those technical difficulties^[1]. Using a VarioPYROcube Elemental Analyser (EA) interfaced in continuous flow mode to an Isoprime 100 Isotope Ratio Mass Spectrometer (IRMS), we have first measured the low-S bearing phosphorite BCR32 against the two $\delta^{34}\text{S}$ Reference Calibrated Material (RCM) NBS127 and IAEA-SO5. We measured a $\delta^{34}\text{S}_{\text{V.CDT}}$ of 18.3‰ ($1sd = 0.4$; $n = 20$) in agreement with that published by Fourel et al. (2014)^[2]. Using BCR32 as a compositional and isotopic reference material, we have then measured the $\delta^{34}\text{S}$ of various bioapatite tissues (bone, dentin and enamel) from both modern and fossil vertebrates living in different environments (marine, freshwater and terrestrial). Our results demonstrate the capacity of this analytical setup to measure the $\delta^{34}\text{S}$ of low-S bioapatite samples (0.14 to 1.19% wt%) with excellent analytical precision ($1sd = 0.3$; $n = 23$). Our results also show that $\delta^{34}\text{S}$ values of bioapatite allow the discrimination between modern and fossil vertebrates living in marine environments from those living in freshwater and terrestrial ones. Sulphur isotope analysis of bioapatite has therefore a great potential to track the living environment of extinct vertebrates for which only fossilized bones or teeth have been preserved.

[1] Fourel *et al.* (2014) Rapid Commun. Mass Spectrom. **28**, 2587-2594

[2] Fourel *et al.* (2014) Geostandards and Geoanalytical research. **39**, 47-53