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New insights for studying phosphate stable oxygen isotopes in bioapatites interpreted from their geochemistry

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Fossil bioapatite is widely used as a proxy to estimate paleoclimatic and/or – environmental conditions. However, the scarcity of well–preserved specimens in some samples mingled with their small sizes frequently compromise the application of notable geochemical techniques (e. g., laser fluorination). While some *in–situ* and non–destructive methods allow studies of single specimens, it is important to understand the specimens' microstructure and the elemental– and isotopic variations between structurally different parts. These parameters may vary as a function of the environmental conditions during the formation of biogenic tissue. To better understand the nature of bioapatites, different geochemical techniques were applied to apparently well–preserved samples of distinct age: conodonts (Early Triassic, CAI 1 to 2), fossil (Paleogene) and modern shark teeth. The microstructure and element distribution of the samples were investigated using scanning electron microscopy (SEM) and an electron microprobe (EMPA), respectively. Paleoenvironmental conditions and relative sea water temperatures in which bioapatites were formed is grounded in stable oxygen isotope analyses ($\delta^{18}O_{PO4}$). Two methods were used for measurements of the $\delta^{18}O_{PO4}$ values: a classical method using bulk sampling and high temperature reduction (HTR) analysis, and *in–situ* measurements by secondary ion mass spectrometry (SIMS). Quantitative analyses and chemical maps of segminiplanate conodont P_1–elements are often found to be heterogeneous in terms of their element concentrations. The reason for this heterogeneous element distribution may be related to conodonts retracting their teeth during growth, suggested notably by variations in Mg, S and Na concentrations. Stable oxygen isotope measurements by HTR reproduced better than ±0.3 ‰ of standard deviations for most bioapatites. Conodonts from Timor analyzed by SIMS could be separated into three distinct groups (TM_{base}, TM_{post}, TM_{inner}), based on differences in their $\delta^{18}O_{PO4}$ values. In the analyzed samples where the hyaline crown is mixed with the albid crown, variations in $\delta^{18}O_{PO4}$ values are larger (TM_{post}: 16±1 ‰, n = 13; TM_{inner}: 15.7±1.9 ‰, n = 11) than samples where only the hyaline crown was analyzed (TM_{base}: 17.1±0.2 ‰, n = 12). Moreover, the $\delta^{18}O_{PO4}$ values from the latter dataset overlap with those from Timor samples analyzed by HTR (17.3±0.4 ‰, n = 7). Shark teeth had a larger variation in their $\delta^{18}O_{PO4}$ values as well when analyzed by the *in–situ* technique. The inter–tissue $\delta^{18}O_{PO4}$ variation between enameloid zones in the same tooth is up to 5.5 ‰. The heterogeneity in the elemental concentrations of the studied bioapatites apparently do not result in significantly machine fractionation for the *in–situ* (SIMS) stable oxygen isotopic measurements.

Instead, variation of $\delta^{18}O_{PO4}$ values appears to be sensitive to remains of organic matter/carbonate in phosphate, analytical artefacts related to sample topography (for sharks) or vital effects. Based on these results, the conodont sample set from Timor (*Scythogondolella* ex. gr. *milleri*) was chosen as an internal standard for stable isotope analyses in bioapatite of the SwissSIMS laboratory. This new in–house standard could be used to normalize the oxygen isotope values and consequently help interpret variations in paleoclimate and/or – environmental conditions for bioapatite.