Gem-quality apatite as reference material for oxygen isotope analysis of biogenic apatite by the secondary ion mass spectrometry

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Oxygen isotope ratios ($\delta^{18}O$) of biogenic apatite have been widely used to reconstruct palaeotemperatures in the distant past. The development of secondary ion mass spectrometry (SIMS) enables in situ $\delta^{18}O$ analyses on single microfossil elements, but requires a calibration employing reference materials (RMs) with a matrix that is "similar" to the samples. We investigated several gem-quality apatites to evaluate their potential as RMs by using both gas source isotope ratio mass spectrometry and SIMS. Compared to the oxygen isotope composition of bio-apatite ranging from 9-25‰ VSMOW, all gem-like apatites investigated here have lower $\delta^{18}O$ values of between 6-11‰ VSMOW due to their magmatic origin. We have found large variations in $\delta^{18}O$ for gem-like apatites both between crystals from a single deposit as well as within individual crystals. Durango apatite has an inter-crystal $\delta^{18}O$ range of 4.9‰ (N=9). Madagascar 1st Mine apatite and Ipria apatite have inter-crystal $\delta^{18}O$ ranges of 3.5‰ (N=9) and 2.9‰ (N=8), respectively. Madagascar Green apatite and South Africa Blue apatite have the smaller inter-crystal $\delta^{18}O$ ranges of 1‰ (N=8) and 0.9 (N=6). Durango apatite, which has been previously used as a RM for SIMS analyses, is the most heterogeneous in $\delta^{18}O$ with an intra-crystal variation in $\delta^{18}O$ up to 2‰. Due to the large intra-crystal variation observed in $\delta^{18}O$, Durango apatite cannot be considered as a suitable reference material, and data calibrated to Durango apatite should be treated with caution.