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SIMS- and IRMS-based study of apatite reference materials reveals new analytical challenges for oxygen isotope analysis

Alicja Wudarska[1,2], Michael Wiedenbeck[2], Ewa Słaby[1], Chris Harris[3], Michael M. Joachimski[4], Christophe Lécuyer[5], Kenneth G. MacLeod[6], Andreas Pack[7], Torsten Vennemann[8], Frédéric Couffignal[2], Johannes Glodny[2], Christof Kusebauch[2], Małgorzata Lempart[1], Yadong Sun[4], and Franziska Wilke[2]

[1]Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, Poland (ndgiera@cyf-kr.edu.pl)
[2]GFZ German Research Centre for Geosciences, Potsdam, Germany
[3]Department of Geological Sciences, University of Cape Town, Cape Town, South Africa
[4]GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Erlangen, Germany
[5]Laboratoire de Géologie de Lyon, UMR CNRS 5276, Université Claude Bernard Lyon 1, Lyon, France
[6]Department of Geological Sciences, University of Missouri, Columbia, USA
[7]Georg-August Universität, Geowissenschaftliches Zentrum, Göttingen, Germany
[8]Institute of Earth Surface Dynamics, University of Lausanne, Lausanne, Switzerland

Minerals of the apatite group, especially hydroxylapatite $Ca_5(PO_4)_3OH$, are valuable archives for reconstructing environmental conditions occurring throughout the Earth's history (e.g., Joachimski *et al.* 2009). Apatite oxygen isotope compositions have proved useful in studies of conodonts as well as fish and mammalian teeth and bones. Secondary ion mass spectrometry (SIMS) is a rapid and precise technique that enables the investigation of small and heterogeneous samples. However, this method is constrained by the availability of matrix-matched reference materials (RMs). The most commonly used RM for calibrating $\delta^{18}O$ phosphate SIMS measurements – Durango apatite – has been found to be heterogeneous (Sun *et al.* 2016); therefore, we have undertaken this study, in which we have characterized a new suite of RMs for oxygen isotope analyses of apatite. Four potential apatite RMs obtained from various sources were assessed for $^{18}O/^{16}O$ homogeneity using SIMS. The major and trace element compositions were determined by electron probe microanalyses (FE-EPMA), while the contents of OH^- and CO_3^{2-} were assessed using thermogravimetric analysis (TG) and infrared spectroscopy (IR). The $\delta^{18}O$ reference values have now been determined in six independent laboratories using isotope ratio mass spectrometry (IRMS) and applying different analytical protocols, which fall into two groups: laser fluorination and high-temperature reduction of Ag_3PO_4. The first method provides the information on "bulk" oxygen compositions, while the second determines the composition of phosphate-bound oxygen. The repeatability of SIMS measurements on random crystal fragments was better than 0.25‰ (1 standard deviation, 1s) for the different RMs, confirming good homogeneity at the nanogram scale. The IRMS-determined $\delta^{18}O_{SMOW}$ values, which fall between ~5 and ~22‰ for the different samples, cover almost the full range of compositions found in igneous, metamorphic and biogenic apatite samples. However, the IRMS data collected using different techniques show offsets of

~1-2‰. The $\delta^{18}O$ values obtained using laser fluorination are, in most cases, lower than those acquired by high-temperature reduction. Furthermore, the data collected within each group of IRMS methods reveal differences between laboratories, which do not correlate with the chemical composition of the apatite crystals. This suggests a more complex behavior of apatite during sample processing for conventional $\delta^{18}O$ analyses as compared to other minerals such as tourmaline, and highlights the importance of the characterization of RMs with the support of multiple laboratories applying different protocols.

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References

Joachimski *et al.* 2009. Earth and Planetary Science Letters, 284, 599-609. doi: 10.1016/j.epsl.2009.05.028

Sun *et al.* 2016. Chemical Geology, 440, 164-178. doi: 10.1016/j.chemgeo.2016.07.013