Plenary Session
Room Great Lakes B - Session PS1-MoM

Plenary Session I

Moderator: Jerry Hunter, University of Wisconsin

8:40am **PS1-MoM-2 Plenary Lecture: Oxygen Isotope Analysis in Carbonates: Accuracy vs. Precision***, **John Valley**, N. Kita, K. Kitajima,* University of Wisconsin-Madison **INVITED**

Carbonate minerals form at a wide range of temperature and pressure, are common on Earth, and found elsewhere in the Solar System. Oxygen isotope ratios ($\delta^{18}O$) in carbonates are a powerful tool to understand the thermal and fluid history of igneous and metamorphic rocks [7], and sedimentary processes including the formation of diagenetic cements ([1] Fig. 1b-d), speleothems, mollusks, foraminifera ([4] Fig. 2b-e), fish otoliths ([2] Fig. 3) and pearls. Most of these samples are zoned at µm-scale and conventional analysis by acid dissolution and gas-source mass spectrometry (GSMS) results in averaged compositions and lost information. Applications such as paleoclimatology, reservoir studies of sedimentary basins and diffusion/kinetics of mineral reaction require SIMS.

SIMS analysis (1-10 µm beam) can be correlated with microscopy (Fig. 1b, 2b-d) and other in situ techniques in images or by QGIS to reveal otherwise unknown correlations and detail. Small pits (<2 µm) are visible with UV optics on IMS-1280. Spot-to-spot precision is improved to 0.2‰ (2SD) in 10 µm spots by appropriate sample preparation, attention to "down-hole" sputtering effects, and frequent standardization, and in smaller spots with a FC amplifier and 10^{12} ohm resistor. However, chemically matched carbonate reference materials (RMs) are necessary for accurate calibration to the international VSMOW or VPDB scales. A suite of 30 inorganic Ca-Mg-Fe carbonate mineral RMs demonstrates that IMF (bias) for $\delta^{18}O$ varies predictably by up to 19‰ at WiscSIMS (IMS-1280) (Fig. 1a); correlated analysis of cations by EPMA allows accurate calibration ±~0.5‰.

In contrast to inorganic carbonates, biocarbonates can have complex textures and contain additional components not amenable to EPMA including water and organics, making calibration by inorganic RMs questionable. SIMS analyses are often offset to lower values than GSMS data. Values of $\Delta^{18}O$(GSMS-SIMS) correlate with $^{16}O^{1}H/^{16}O$ (SIMS) in young biocarbonates ([5] Fig. 2a). Many biocarbonates have relatively constant OH/O and can be corrected with a constant offset [8], but samples with variable OH/O ([2] Fig. 3) should be interpreted with caution.

[1] Denny AC et al. (2020) Chem Geol, 531: 1-20

[2] Helser T et al. (2018) Rapid Comm Mass Spectrometry. 32: 1781-1790

[3] Kita NT, et al. (2011) SIMS XVII Proceedings, 43: 427-431

[4] Kozdon R et al. (2013 Paleoceanography 28:1-12

[5] Orland IJ et al. (2015) AGU Fall Meeting, Abstr. # PP52B-03

[6] Śliwiński MG et al. (2018) Geostand Geoanal Res, 42: 49-76

[7] Valley JW and Kita NT (2009) MAC Short Course. 41: 19-63

[8] Wycech J et al. (2018) Chem. Geol. 483:119-130

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