SIMS bias on isotope ratios in siderite-magnesite: $\delta^{18}O$ & $\delta^{13}C$ matrix effects

Maciej G. ŚLIWIŃSKI[1*], Kouki KITAJIMA[1,2], Michael J. SPICUZZA[1], Ian J. ORLAND[1], Akizumi ISHIDA[1,2,4], John H. FOURNELLE[3] and John W. VALLEY[1,2]

[1] WiscSIMS, Dept. of Geoscience, University of Wisconsin-Madison, Madison, WI, 53706 (msliwinski@wisc.edu; +1 (425)-681-4288)   [2] NASA Astrobiology Institute, Dept. of Geoscience, University of Wisconsin-Madison, Madison, WI, 53706   [3] Dept. of Earth Science, Tohoku University, Sendai, Japan, 9808578

OBJECTIVE

This work explores the effects of Fe^{2+} substitution on SIMS $\delta^{13}C$ and $\delta^{18}O$ bias in the analysis of carbonate minerals with compositions that fall along the siderite-magnesite solid-solution series [$FeCO_3$-$MgCO_3$]. Bias is the per mil (‰) difference between measured 'raw' and 'true' (i.e., VPDB or VSMOW) values of $\delta^{13}C$ or $\delta^{18}O$ (also referred to as 'instrumental mass fractionation'). The component of total bias related specifically to variations in sample chemistry along a solid-solution can be referred to as the sample 'matrix effect'.

BACKGROUND & MOTIVATION

Carbonates of the siderite-magnesite series are encountered in many different geological environments on Earth [1] as well as in Martian meteorites [2,3]. Some examples of siderite (+/- Mg) occurrences include concretions/cements in marine and fresh-water sediments, banded-iron formations (BIFs) and carbonatite deposits. Magnesites (+/-) occur, for example, in association with evaporitic sediments and as a product of weathering / hydrothermal alteration of igneous and metamorphic rock bodies rich in Ca-Mg-Fe silicate minerals.

The isotopic composition of the carbon and oxygen atoms they contain are widely used in the geosciences as proxies for inferring the conditions of carbonate formation. Of interest most commonly is the temperature of precipitation, the source(s) of carbon, and the nature/source of the fluids involved (e.g., marine, meteoric, mixed or hydrothermal waters). Variations in the $\delta^{13}C$ and $\delta^{18}O$ signatures of pedogenic (soil) carbonates, for example, are frequently used as indicators of past ecologic and climatic change on the continents [4-6].

The motivation for this research grew out of a need for standards in the wake of recent technical advances in carbonate $\delta^{13}C$ and $\delta^{18}O$ microanalysis by SIMS, and the potential applicability of this technique in a wide variety of paleoenvironmental and paleoclimatic studies, as well as in the intensifying research efforts concerned with geologic carbon-sequestration [7,8].

FROM THE LITERATURE -

PEDOGENIC SIDERITE NODULES (SPHEROSIDERITES)

FROM [13]: (Top) Sphaerosiderite nodules (mm-scale) weathering out of a paleosol (Cretaceous Dakota Formation). (Bottom) Sphaerosiderite nodules in thin section (plane-polarized light). (Cretaceous Caballos Formation of Colombia).

FERROAN-MAGNESITES (AMONG OTHER CARBONATES) IN MARTIAN METEORITE ALH84001

FROM [14]: Thin-section view of carbonate globules in Martian meteorite ALH84001 (plane-polarized light). The amberish-colored cores consist of ankerite and siderite, whereas the clear rims are composed of magnesite (host-rock = pyroxenite).

FROM [3]: Ca-Mg-Fe carbonate ternary diagram showing the range of compositions encountered in Martian meteorites and surface rocks (Spirit Lander mission). Shaded regions: calculated carbonate stability fields at 700°C.

FERROAN-MAGNESITES (AMONG OTHER CARBONATES) IN POSSIBLE TERRESTRIAL ANALOGUES

FROM [14]: (Left) Thin-section view of carbonate globules in hydrothermally-altered basalts from Spitsbergen (plane-polarized light). The amberish-colored cores consist of ankerite and siderite, whereas the clear rims are composed of magnesite. (Right) Ca-Mg-Fe carbonate ternary diagram showing the compositions encountered in this proposed terrestrial analogue environment in relation to the carbonate compositions in Martian meteorite ALH84001 (shaded gray field).

PROCESS

Isotope ratios in carbonates can now be routinely measured in-situ from micrometer-scale sample domains with sub-per mil (‰) precision [9]. The accuracy of measurement, however, depends in large-part on the availability and overall quality of matrix-matched standards, as the bias imparted to isotope ratios during sputtering from the sample surface and the subsequent passage of ions through the mass spectrometer cannot be accurately predicted from first principles for naturally-occurring minerals and glasses.

For many mineral families wherein the compositional end-members form extensive or complete solid-solutions with one-another – such as the carbonates – proper standardization remains a work in-progress for the community of SIMS laboratories around the world.

Samples of naturally-occurring magnesites and siderites were acquired for testing.

Subsampling.

Sub-sample preparation (e.g., removal of weathered/altered rinds).

Preparation of clean grain split (425-710 μm size-fraction)

Grain-mount - Each potential standard material was evaluated for chemical and isotopic homogeneity (by EPMA & SIMS, respectively)

RESULTS

A suite of 13 calibration standards was developed for both isotope systems, spanning the compositional range between Fe# = 0.002 and 0.997 [Fe# = molar Fe/(Mg+Fe)].

The calibration curves of both isotope systems are non-linear (**Fig. 1**) and have, over a 2-year period, fallen into one of two distinct and largely self-consistent shape categories (data from 10 analytical sessions) despite adherence to well-established analytical protocols for carbonate $\delta^{13}C$ and $\delta^{18}O$ analyses at WiscSIMS (CAMECA IMS 1280). The cause of this is not well understood at present, and stresses the importance of having available a sufficient number of well-characterized standards so that potential complexities of curvature can be adequately delineated and accounted for on a session-by-session basis.

As with the dolomite-ankerite series [10,11], mass bias for the magnesite-siderite solid-solution is consistently most sensitive to changes in composition near the iron-free end-member. With increasing Fe-content up to ~20 mol% $FeCO_3$ (i.e., Fe# 0-0.2), $\delta^{13}C$ bias increases by 3-4.5‰, whereas $\delta^{18}O$ bias decreases by up to 13-15‰ (the magnitude of this bias can vary by 1-2‰ on a session-specific basis; refer to the right-hand y-axis of Fig. 1). Between the end-members of the series, the magnitude of $\delta^{13}C$ bias increases by a total of 10-11‰ (magnesite-siderite), whereas the magnitude of $\delta^{18}O$ bias decreases by 13-16‰ (refer to the right-hand y-axis of Fig. 1).

As an example, if uncorrected, the presence of 1-2 mol% $FeCO_3$ in a sample material of unknown isotopic composition would produce an accuracy error of ~1‰ for $\delta^{13}C$ and ~2-3‰ for $\delta^{18}O$ measurements.

$$bias^*(RM - UWMgs1) = C_1\left(\frac{nx^{n-1}}{k^{n} + x^{n}}\right) + C_2(x^d) + C_3 \quad (x = Fe\#)$$

EXAMPLES OF THE MORE COMMON BIAS BEHAVIOR OBSERVED TO DATE.

The left-hand y-axis pertains to the working calibration curves, where bias measurements are normalized (or "anchored") to a running standard used for drift-monitoring (in this case end-member magnesite "UWMgs1"). Normalized values are thus expressed as "$\delta^{13}C$ or $\delta^{18}O$ bias*(STD-UWMgs1)."

The right-hand axis pertains to bias values pre-normalization (in other words, simply the per mil difference between 'raw' and 'true' $\delta^{13}C$ or $\delta^{18}O$ value of each standard). Note that all bias values for this series are negative. Thus, when describing general trends, the bias is said to increase as value become more negative (and vice versa).

The compositional dependence of SIMS $\delta^{13}C$ and $\delta^{18}O$ bias*(RM-UWMgs1) (i.e. the sample matrix effect) was empirically regressed using a mathematical expression stemming from the family of Hill-type functions (here a modified form of eq. 27 of Goutelle et al., 2008; Fig. 1).

The resulting calibration residuals are ≤ 0.5‰ for $\delta^{18}O$ analyses performed using either a 3- or 10-μm diameter spot-size and for $\delta^{13}C$ analyses performed using a 6-μm spot. This is considered a measure of analytical accuracy relative to the certified reference material NIST-19 (calcite).

Based on the spot-to-spot reproducibility of running standard values (n = 8) that "bracket" each set of 10 sample measurements, the analytical precision associated with 10- and 3-μm $\delta^{18}O$ spots is ±0.3‰ and ±0.7‰ (2SD, standard deviations), respectively, and that associated with 6-μm $\delta^{13}C$ spots is ±0.6-1.2‰ (2SD).

THE BIGGER PICTURE:

CONTOURING THE MATRIX EFFECT LANDSCAPE FOR THE Ca-Mg-Fe CARBONATES

$\delta^{13}C$

$\delta^{18}O$