SIMS bias on isotope ratios in dolomite-ankerite: δ^{13}C & δ^{18}O matrix effects

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Analytical Method

SIMS (secondary ion mass spectrometry)

- Focused beam of Cs+ ions bombards sample (sputtering)
- Ions of interest collected, counted and ratios of different isotopes calculated (e.g., 18O/16O, 13C/12C)

Process

δ^{18}O Calibration

10-µm-diameter spot-size

3-µm-diameter spot-size

δ^{13}C Calibration

6-µm-diameter spot-size

Results

- SIMS bias on isotope ratios in dolomite-ankerite:
- The compositional dependence of SIMS δ^{18}O bias (‰) is expressed using the Hill equation, which is commonly employed to describe empirical relationships of the 'component concentration' vs. 'measured effect'. The Hill equation, which has wide-ranging applicability in describing empirical relationships, is expressed using the Hill equation, although the modeled effect for carbon is the opposite of that observed for oxygen (Fig. 3a; left-hand axis).
- In contrast, the magnitude of SIMS δ^{18}O bias from the suite of calibration standards (13 each for C and O isotopes) spanning the chemical compositional range between Fe# = 0.004 and 0.789 decreases exponentially with increasing Fe# (by -4.5‰; i.e., values become more negative and hence move further away from true VPDB values; Fig. 3a, right-hand axis). That is, the bias is smallest for end-member dolomite (~1.0-1.5‰ (2SD)).

Towards understanding the landscape of SIMS matrix effects for Ca-Mg-Fe carbonates

Fig. 3b. δ^{13}C plot showing SIMS δ^{13}C bias (‰) to the calibration of the dolomite-ankerite solid solution series (Fig. 1a) as well as a typical calibration using a 10-µm-diameter spot. The sample matrix effect is expressed as the difference between the measured value of δ^{13}C and the value predicted by the unknown's composition (all other measurements are normalized to a running standard for drift-monitoring purposes (commonly end-member dolomite standard UW6220; normalized values are thus expressed as 'bias*(STD-UW6220)').

Fig. 2b. δ^{18}O plot showing SIMS δ^{18}O bias (‰) to the calibration of the dolomite-ankerite solid solution series (Fig. 1a) as well as a typical calibration using a 6-µm-diameter spot. The sample matrix effect is expressed as the difference between the measured value of δ^{18}O and the value predicted by the unknown's composition (all other measurements are normalized to a running standard for drift-monitoring purposes (commonly end-member dolomite standard UW6220; normalized values are thus expressed as 'bias*(STD-UW6220)').

Fig. 1a. Plot relating SIMS δ^{13}C bias (‰) to the calibration of the dolomite-ankerite solid solution series (Fig. 1a) as well as a typical calibration using a 10-µm-diameter spot. The sample matrix effect is expressed as the difference between the measured value of δ^{13}C and the value predicted by the unknown's composition (all other measurements are normalized to a running standard for drift-monitoring purposes (commonly end-member dolomite standard UW6220; normalized values are thus expressed as 'bias*(STD-UW6220)').

Fig. 1b. Plot relating SIMS δ^{18}O bias (‰) to the calibration of the dolomite-ankerite solid solution series (Fig. 1a) as well as a typical calibration using a 6-µm-diameter spot. The sample matrix effect is expressed as the difference between the measured value of δ^{18}O and the value predicted by the unknown's composition (all other measurements are normalized to a running standard for drift-monitoring purposes (commonly end-member dolomite standard UW6220; normalized values are thus expressed as 'bias*(STD-UW6220)').

Abstract

This work explores the effects of δ^{18}O substitution on δ^{13}C and δ^{18}O bias (in carbon and mass spectrometry) in the analysis of carbonates with composition in the full range of dolomite-ankerite solid solutions (Ca-Mg-Fe). SIMS 13C and 18O calibration standards (13 each for CO isotopes) spanning the chemical compositional range between Fe# = 0.004 and 0.789 were analyzed to identify the δ^{13}C and δ^{18}O calibration behavior (‰) for 10 and 3 µm spots. For a given configuration of the analyzer (WiscSIMS 8000, 124, 126), the influence of instrumental parameters on total bias (bias*) can be characterized by two empirical parameters: 'bias' and 'max'. The δ^{18}O calibration behavior of the suite of δ^{18}O calibration standards (13 each for CO isotopes) spanning the chemical compositional range between Fe# = 0.004 and 0.789 was also characterized by 'bias' and 'max'. However, for δ^{18}O analysis, the best-fit value of the 'max' parameter behaves as an analytical session-specific scaling factor. Thus, while the δ^{18}O bias is ± 0.3‰ relative to NBS-19 for most standards in the suite, the averaged measured value of δ^{18}O for 10-µm spots and ± 0.7‰ (2SD) for 3-µm spots, based on the spot-size in question. SIMS δ^{13}C bias on isotope ratios in dolomite-ankerite, Part I: δ^{13}C bias calibration

[Background and motivation] Geostandard. Geoanal. Res. 2016;70(2):221-229. The compositional dependence of SIMS δ^{13}C bias (‰) to the calibration of the Dolomite-Ankerite series [Fe# = Fe/(Mg+Fe)] for a typical calibration using a 6-µm-diameter spot. The sample matrix effect is expressed as the difference between the measured value of δ^{13}C and the value predicted by the unknown's composition (all other measurements are normalized to a running standard for drift-monitoring purposes (commonly end-member dolomite standard UW6220; normalized values are thus expressed as 'bias*(STD-UW6220)').


[1] Focused beam of Cs+ ions bombards sample (sputtering)
[2] Ions of interest collected, counted and ratios of different isotopes calculated (e.g., 18O/16O, 13C/12C)