Standardization of SIMS Analysis Of O and C isotope ratios In Carbonates From ALH84001   J. M. Eiler[1], J.W. Valley[2] and C.M. Graham[3], [1]Geological and Planetary Science, Caltech, Pasadena, CA 91125, [2]Geology and Geophysics, University of Wisconsin, Madison, WI 53706, [3]Geology and Geophysics, University of Edinburgh, Edinburgh, Scotland

Previous bulk analyses of carbonate in the SNC meteorite ALH84001 have demonstrated ranges of 10's of permil in both carbon and oxygen isotope ratios [1-4]. We have attempted to constrain the source of these variations by ion microprobe analysis of the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in ~20-30 µm diameter spots of the carbonate and coexisting silicate phases. In this paper we describe the methods and standardization of the analysis of carbonates. The results from the ALH84001 meteorite are described in an accompanying paper [5].   Twelve carbonate minerals were characterized by electron microprobe analysis and conventional C and O isotope ratio measurements and were found to be sufficiently homogeneous for use as ion microprobe standards. These 12 included: two calcites, two aragonites, Fe-dolomite, three magnesio-siderites (Mg-Sid-1,-2 and-3, X_{Fe} = 0.96, 0.86, 0.71), magnesite, rhodochrosite, strontianite, and witherite. O and C isotope ratios were measured in these materials using the Cameca ims 4f at the University of Edinburgh. A primary beam of Cs^+ ions was used together with an electron flood gun for charge neutralization. Analyses were made at high energy offset (350±25 eV for O; 250±25 eV for C). Other analytical details are reviewed elsewhere [6,7]. Analyses on these standards had average internal and point-to-point precisions of ±1 ‰ (1) for $^{18}O/^{16}O$ and ±1.5‰ for $^{13}C/^{12}C$.

Results: 400 analyses of $^{18}O/^{16}O$ and 100 of $^{13}C/^{12}C$ were made of these 12 standards to assess standard homogeneity and instrument stability. Of these, 216 analyses of $^{18}O/^{16}O$ (in 10 analytical sessions) and 23 of $^{13}C/^{12}C$ (in 1 analytical session) permit comparison of instrumental fractionations (e.g., α_{SIMS} for oxygen = $^{18}O/^{16}O_{measured}$ / $^{18}O/^{16}O_{real}$) among standard materials. These comparisons have been grouped into averages for each material in each session, and all sessions were mutually normalized to a constant value of α_{SIMS} for a mineral analyzed in other sessions. The relative differences in α_{SIMS} between any two materials in different analytical sessions had an average reproducibility of ±0.0008 (12 comparisons). Several correlatives with α_{SIMS} were found:

Oxygen • Positive correlations were observed among: α_{SIMS}, mean atomic weight, and relative differences in the useful ion yield (i.e. counts per second per nA of primary beam current) An example of one of these 3 correlations is shown in Fig. 1. A similar correlation exists between α_{SIMS} and the ratio: $(Yield_{rel})$ / (sputtering rate). These correlations likely reflect coupling of α_{SIMS} with the probability of O ionization, although further work is needed to constrain the underlying cause.

• α_{SIMS} is positively correlated with the atomic fraction of Fe among divalent cations in the subset: calcite, aragonite, Fe-dolomite, Mg-Sid-1, -2 and -3 (Fig. 2). This result is similar to that previously observed in silicates [6], where such a correlation is robust and shared among several mineral groups.

• Magnesite (α_{SIMS} = 0.905, X_{Fe}=0) violates the relationship in Fig. 2, showing that α_{SIMS} is highly non-linear along some solid solutions. If variations in a_{SIMS} among solid solutions were linear, the data for magnesite and Mg-Sid-1 predict that Mg-Sid-2 and Mg-Sid-3 should have α_{SIMS} values of 0.956 and 0.948, respectively. Their actual values are much higher (0.963 and 0.958). Similarly, α_{SIMS} in calcite and magnesite are 0.905 and 0.925, but that of Fe-dolomite is 0.932; higher than both and far from the value of 0.920 expected from linear mixing among Fe-Mg-Ca end members. Both of these relationships indicate that linear mixing among solid solution end members is not an appropriate general means of standardizing the analysis of carbonate solid solutions, and may introduce systematic errors of 10‰ in some cases.

• Values of α_{SIMS} in all four calcites and aragonites are within error of each other, suggesting that structure has little or no influence on a_{SIMS} among carbonates.

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Carbon • SIMS for C is well correlated with the fraction of Fe among divalent cations for calcite, Fe-dolomite, Mg-Sid-1 and Mg-Sid-3, but magnesite violates this relationship, as was observed for oxygen.

• SIMS for two different orientations of calcite (parallel and normal to the C axis) are within error of each other, further suggesting that structure exhibits little or no control on SIMS among carbonates.

Conclusions: The relationships among relative secondary ion yield, SIMS, and mean atomic mass are the most fundamental result of this study and are most likely to ultimately yield a rigorous correction scheme. However, the trend in Fig. 1 is sensitive to uncertainties in the independent variable over the range of interest for carbonates from ALH84001 ($Yield_{rel}$~0.3), such that it is not a precise calibration method for this case using existing data. The empirical relationship between SIMS and X_{Fe} (Fig. 2) is less sensitive to typical uncertainties in the independent variable (X_{Fe}), and based upon similar relationships in silicate minerals it is like to be robust for Fe-rich (X_{Fe}>0.1) compositions. We have therefore used the line in Fig. 2 as the basis for calibrating the analyses, and a similar relationship to calibrate analyses of $^{13}C/^{12}C$. This calibration yields an SIMS for $^{18}O/^{16}O$ of ~0.939 for most carbonate analyzed[5] in ALH84001.   Calibration with the trend in Fig. 1 and similar correlations using ($Yield_{rel}$/sputter rate) or mean atomic mass in the X axis yield similar SIMS values of 0.931-0.939, but with greater uncertainty for any given point due to the precision of determinations of sputter rate and $Yield_{rel}$.

References: [1] Romanek et al. (1994) Nature, 372; [2] Grady et al. (1994) Meteoritics 29; [3] Jull et al. (1995) Meteoritics 30; [4] Leshin et al. (1996) GCA 60; [5] Valley et al. (1997), LPSC abstract; [6] Eiler et al. (1997) Chemical Geology, in press; [7] Valley et al. (1997) in McKibben et al. (eds.) Soc. Econ. Geol. Reviews v. 7.

Figure 1) Plot of SIMS for O vs. the relative useful ion yield ($Yield_{rel}$ = counts per second per nA of the primary beam, normalized to a value of 1 for the maximum observed). $Yield_{rel}$ was determined under constant conditions and is therefore interpreted to be proportional to differences in sputtering yields and/or ionization efficiencies rather than transmission or detection efficiency.

Figure 2) Plot of SIMS for O as a function of X_{Fe} (= Fe/(Fe+Mg+Ca+Mn). Fe content is a good predictor of SIMS among Fe-rich carbonates, as it is among silicates (ref. 3). Magnesite violates this trend, and thus this line is likely inappropriate for calibrating analyses of carbonates with X_{Fe}<0.1.