Calibration of matrix-dependent biases in isotope and trace element analyses of carbonate minerals

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I. INTRODUCTION

The development of a chronology of key events in the chemical and mineralogical evolution of planetary materials is critical to developing a detailed understanding of processes associated with the formation of the solar system. Such significant events include the accretion times of asteroids and the timing of important thermal processing events (e.g., circulation of hydrothermal fluids). Early solar system materials are found in primitive meteorites (“chondrites”) and specific mineral phases can be dated with high precision using a variety of short-lived radiometric systems. One such system is based on the radioactive decay of $^{53}$Mn to $^{53}$Cr. Carbonate minerals found in meteorite samples can be dated using this system provided that an accurate and precise value for the Mn/Cr ratio can be established. However, the ion yields of Mn and Cr vary substantially based upon the elemental composition of the matrix and require calibration using standards of known Mn and Cr concentrations to relate the measured Mn/Cr ratio to the true ratio with a “relative sensitivity factor.” The authors implant $^{52}$Cr into a suite of terrestrial calcite and dolomite samples of varied elemental compositions to produce matrix-matched standards for $^{53}$Mn-$^{53}$Cr analysis. Depth profiling of the implanted carbonates reveals variation in the relative sensitivity factors between carbonates low in Fe and Mn and dolomite rich in Fe and Mn. For carbonates with FeCO$_3$ > 8 mol. %, the relative sensitivity factor is constant at 0.88 ± 0.08 (2SD). For carbonates with FeCO$_3$ < 2 mol. %, the relative sensitivity factor is approximately 1.1. The authors also show that the use of an inappropriate relative sensitivity factor can lead to systematic errors in the age determined for meteoritic carbonate.

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may be calculated based on the inferred isotopic composition of Mn incorporated into the carbonate mineral \[(^{53}\text{Mn}/^{55}\text{Mn})_{\text{carbonate}}\].

\[
T_{\text{carbonate}} = 4563.4 + \frac{t_{1/2}}{\ln(2)} \times \ln \left( \frac{^{53}\text{Mn}/^{55}\text{Mn}}{3.24 \times 10^{-6}} \right),
\]

(1)

Because \(^{57}\text{Mn}\) has undergone one thousand half-lives since the formation of the carbonates, it can be considered to have decayed completely and the present day \(^{53}\text{Mn}/^{55}\text{Mn}\) ratio cannot be directly measured in meteoritic carbonate. However, Cr was strongly excluded from the mineral during its formation, and so \(^{53}\text{Cr}\) detected in meteoritic carbonates can be attributed to the decay of \(^{53}\text{Mn}\). Therefore, it is possible to infer the initial \(^{53}\text{Mn}/^{55}\text{Mn}\) ratio in a carbonate by determining the amount of radiogenic \(^{53}\text{Cr}\) present. This is done by observing the correlation of \(^{53}\text{Cr}/^{52}\text{Cr}\) with the parent-element/daughter-element ratio, \(^{53}\text{Mn}/^{52}\text{Cr}\). Previous analyses of meteoritic carbonate using this system suggest that most carbonates formed 3–7 Myr after the birth of the solar system.4-8

Meteoritic carbonates are small, difficult to separate from the host meteorite, and texturally complex. Therefore, most meteoritic carbonate is dated \textit{in situ} using secondary ion mass spectrometry (SIMS or ion probe), allowing both Mn and Cr species to be sampled from identical volumes in individual grains. To infer the correct formation age of a carbonate requires that the Mn/Cr ratio be determined accurately and precisely, but elemental ratios are difficult to measure by ion probes, as the ion yields of different elements often vary substantially based upon the elemental composition of the matrix, a phenomenon known as the "matrix effect." The magnitude of this effect is difficult to model and must be corrected empirically by measuring standards of similar chemical composition and known Mn/Cr ratio (i.e., "matrix-matched"). Carbonates, in particular, exhibit strong matrix effects related to the abundance of Fe in the target carbonate.8

In order to obtain accurate elemental ratios, it is necessary to relate the true concentrations of each element \((C_a)\) and \((C_b)\) to the intensities \((I_a)\) and \((I_b)\) measured by the ion probe via a relative sensitivity factor, or "RSF,” shown in Eq. (2),

\[
\text{RSF} = \frac{C_a}{C_b} = \frac{I_a/I_b}.
\]

(2)

Reference materials (or "standards") can be analyzed to determine an RSF provided that the concentrations of the target elements are known and homogeneously distributed. In the case of carbonate minerals, however, such reference materials for the Mn/Cr ratio cannot be found in nature due to the strong exclusion of 3+ ions such as Cr from the carbonate crystal structure, and synthetic materials face challenges associated with growing homogeneous Cr-doped calcite7,9 and synthesizing dolomite10. Because matrix-matched reference materials of the known Mn/Cr ratio are not easily acquired or made, previous studies of meteoritic carbonate were restricted to using RSF values determined on materials of known Mn/Cr ratios which did not closely match the chemistry of the target carbonate minerals (and thus could be subject to matrix effects).

As an alternative to unaltered naturally occurring or synthetic RSF reference materials, ion accelerators can be used to implant \(^{53}\text{Cr}\) into natural minerals with excellent lateral homogeneity.11 This technique allows any implanted material to become a standard of known Cr concentration so long as the total amount of implanted ions, or fluence, can be determined following correction for any initial Cr present. In a study where a variety of carbonate minerals were implanted with \(^{53}\text{Cr}\), the RSF between Mn and Cr was shown to vary significantly as a function of the Fe and Mn contents of the mineral.9

Previously implanted materials have been used to constrain the RSF for a large chemical range of carbonates. However, most carbonates appropriate for Mn-Cr dating in meteorites are dolomites containing up to ~20 mol.% Fe. Only two carbonates implanted previously are within this range of natural meteoritic carbonate, dolomites with 25 and 9 mol.% Fe (replacing Mg). The variation of the RSF in carbonate minerals relevant to studies of meteorite ages, i.e., the full range of matrix effects, is not yet determined. In this work, we measured the RSF of calcite and dolomite minerals with Fe contents ranging over 0–20 mol.% in order to improve the accuracy of radiometric dating of carbonate in meteorites.

II. EXPERIMENT

A. Sample selection and preparation

Natural carbonate minerals were selected from the UCLA mineral collection, including calcite \((\text{CaCO}_3)\), Fe-poor dolomite \([\text{CaMg(CO}_3\text{)}_2]\), and Fe-rich ferroan dolomite \([\text{Ca(Mg,Fe)(CO}_3\text{)}_2]\). The minerals span the range of Fe contents observed in meteoritic carbonate, between 0 and 20 mol.% \(\text{FeCO}_3\). A comparison of carbonate minerals in our study, meteoritic carbonate, and previously implanted carbonates can be found in the supplementary material.20 A large crystal fragment of each mineral was embedded in Field’s Metal and/or indium in the center of an aluminum disk, and polished to better than 0.25 \(\mu\text{m}\) using a Beuhler MetaDi Supreme polycrystalline diamond compound. Samples of NIST 612 and NIST 614 soda lime glasses, which are certified concentration reference materials containing 36 ppm and 1 ppm Cr and 39 ppm and 1.3 ppm Mn, respectively,12 were also mounted to be used to calibrate the implant fluence.

B. Electron probe microanalysis

The chemical composition and homogeneity of each mineral was determined using the JEOL Superprobe electron microprobe analyzer (EPMA) at UCLA using an accelerating voltage of 15 kV with a beam defocused to 10 \(\mu\text{m}\) to avoid damage to the carbonate minerals. Full details of the EPMA analytical conditions can be found in the section "Supplementary Methods" of the supplementary material.20 In all cases, Cr concentrations in these natural carbonates were below the detection limit of the EPMA (~120 ppm). Carbonate minerals with homogeneous Fe content—that is, minerals for which repeated analyses remained within 2SD (internal error) of one another—were selected for depth profiling. The mounted fragment of the ferroan dolomite MS1312 was found to have two domains with distinct Fe and Mn concentrations, and
these domains were treated separately. The composition of each selected carbonate mineral is summarized in Table I, with the two domains of MS 1312 reported as MS 1312_D1 and MS1312_D2 referring to the high and low Mn domains, respectively.

C. Ion implantation

The mount was coated with a 30 nm layer of gold to ensure conductivity and prevent charging during ion implantation and ion probe analysis. The mount was implanted with a 185 keV $^{52}$Cr$^+$ ion beam at a nominal fluence of $4 \times 10^{13}$ ions/cm$^2$, rastered over the entire surface. A mass filter was used to separate $^{52}$Cr$^+$ and $^{53}$Cr$^+$ after Cr ionization, ensuring that only $^{52}$Cr$^+$ was implanted. If some amount of $^{52}$Cr$^+$ was included during implantation, the $^{52}$Cr$^+$ abundance observed during depth profiling would increase and then decay similarly (though at lower abundance) to $^{53}$Cr$^+$, which was not observed in any of our implanted materials. The implantation was carried out by Leonard Kroko, Inc.

1. Modeling of backscatter effects during implantation

Variation in the chemistry of implanted targets can impact the total quantity and distribution of implanted ions within the target material. In particular, a target containing a higher proportion of high-Z elements such as Fe will backscatter the incident ion beam more efficiently than a target with fewer high-Z elements. If backscatter effects are sufficiently strong, dolomite samples with higher Fe contents could receive a lower dose of $^{52}$Cr$^+$ ions than targets with low Fe.

To constrain the magnitude of the backscatter effect in our implanted minerals, we used the SRIM (Stopping Range of Ions in Matter) program to simulate a dose of $2000^{52}$Cr$^+$ ions with an energy of 185 keV into soda lime glass, pure CaCO$_3$, CaMgCO$_3$, and then decay similarly (though at lower abundance) to $^{53}$Cr$^+$, $^{52}$Cr$^+$, and $^{53}$Mn$^+$ was counted using an electron multiplier. The profile MS1317 No. 2 was acquired by sputtering for over twice as long to test whether the signal varied with increasing depth. For the ferroan dolomite MS1312, the two depth profiles were placed in the two different compositional regions: the profile “MS1312 No. 1” was collected from the higher-Mn domain (MS1312_D1), and the profile “MS1312 No. 2” from the lower-Mn domain (MS1312_D2).

Each material was sputtered until the $^{52}$Cr$^+$ and $^{53}$Cr$^+$ signals decayed to a stable background, which occurred in approximately 30 min. Representative profiles of the intensities as collected from NIST glass NBS 614 and the natural carbonate MS1317 are shown in Figs. 1 and 2, respectively. The maximum implanted $^{52}$Cr$^+$ concentration depth is deeper in the NIST 614 glass, and the implant profile decays to background more slowly than in the MS1317 dolomite, which we attribute to the effect of mineral density identified during our SRIM modeling. Additional profiles for all sputtered materials are included in the supplementary material.

To get the implantation profile of $^{52}$Cr, the measured $^{52}$Cr$^+$ signal was corrected for the natural abundance of $^{52}$Cr in the mineral, which is calculated by multiplying the $^{52}$Cr$^+$ signal by the terrestrial $^{52}$Cr/$^{53}$Cr ratio of 8.8190. The corrected $^{52}$Cr$^+$ signal was calculated at every block using the $^{53}$Cr$^+$ intensity recorded in the same block. This dynamic correction was necessary as the abundance of both Cr isotopes varied with depth over the time of the profile. Besides the variation in $^{52}$Cr abundance attributed to the effect of mineral density identified during our SRIM modeling, additional profiles for all sputtered materials are included in the supplementary material.

Table I. Summary of elemental composition of carbonate minerals determined by electron probe microanalysis. Concentrations are reported in molar percent except when concentrations of Mn are reported in ppm as $\mu$g Mn/g. Errors are reported as 2SD mol. % and incorporate the internal variation during analysis and the SD of repeated analyses. The detection limit of Fe and Mn is approximately 120 ppm, and elements below the detection limit are marked “b.d.”. Compositions marked with an asterisk denote material compositions determined by a higher current beam following depth profiling analysis [see supplementary material (Ref. 20)].

<table>
<thead>
<tr>
<th>Name</th>
<th>Ca ±</th>
<th>Mg ±</th>
<th>Fe ±</th>
<th>Mn ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>99.4</td>
<td>0.8</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>MS1317*</td>
<td>50.1</td>
<td>4.0</td>
<td>49.0</td>
<td>0.4</td>
</tr>
<tr>
<td>MS1317*</td>
<td>50.2</td>
<td>0.3</td>
<td>48.2</td>
<td>0.3</td>
</tr>
<tr>
<td>MS1318</td>
<td>48.0</td>
<td>0.2</td>
<td>42.7</td>
<td>0.3</td>
</tr>
<tr>
<td>MS1305*</td>
<td>49.5</td>
<td>0.3</td>
<td>49.4</td>
<td>0.4</td>
</tr>
<tr>
<td>MS1312_D1*</td>
<td>50.1</td>
<td>0.3</td>
<td>18.8</td>
<td>0.7</td>
</tr>
<tr>
<td>MS1312_D2*</td>
<td>49.6</td>
<td>0.4</td>
<td>21.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>

D. Depth profiling

The implanted carbonate standards and NIST standard materials were analyzed on the Cameca ims-1290 ion microprobe at UCLA equipped with an Oregon Physics Hyperion oxygen plasma source. Two separate areas of each target material were analyzed by sputtering with a 2 nA O$^{+}$ primary ion beam focused into a $\sim 3\mu$m spot rastered over $\sim 50\mu$m by $\sim 50\mu$m areas in each implanted material. A field aperture was inserted into an ion image plane to restrict the collected ions to the central 20 $\mu$m area of each raster square. A 75 $\mu$m entrance slit was used. Secondary ions of $^{44}$Ca$^+$, $^{52}$Cr$^+$, $^{53}$Cr$^+$, and $^{53}$Mn$^+$ were counted using an electron multiplier. The profile MS1317 No. 2 was acquired by sputtering for over twice as long to test whether the signal varied with increasing depth. For the ferroan dolomite MS1312, the two depth profiles were placed in the two different compositional regions: the profile “MS1312 No. 1” was collected from the higher-Mn domain (MS1312_D1), and the profile “MS1312 No. 2” from the lower-Mn domain (MS1312_D2).

E. Surface profilometry

The depth of each ion beam raster square was measured using the Dektak XT stylus profilometer at the Molecular...
Materials Research Center at the California Institute of Technology. Profiles were collected using a stylus tip diameter of 2 μm, a vertical range of 6 μm, and a vertical resolution of 0.1 nm. Each raster was profiled two times along perpendicular axes. The depth of each profile was determined using the Bruker Vision64 software, which determines the vertical distance between the flat region surrounding the rastered area and the flat bottom of the profile, which trims the edges of the rastered area from the depth. The rastered areas were flat and did not show significant curvature at their bottoms. The average value of the depth of the two profiles was taken as the depth of the rastered area. The depth of each profile is summarized in Table II, and additional information including SEM imagery of the rastered areas can be found in the supplementary material.

III. RESULTS AND DISCUSSION

A. Calibration of implant fluence

While ion implantation guarantees a laterally homogeneous concentration of the implanted species, the accuracy of the fluence delivered can only be guaranteed to 10%–20% of the nominal requested fluence. It is therefore necessary to independently calibrate the 52Cr⁺ fluence received using materials with known (and homogeneous) Cr concentration. In this case, the two co-implanted NIST glasses described above were used to calibrate the implant fluence as previously described by Steele et al. in Eq. (3), where

\[ F_{52\text{Cr}} = \frac{C_{52\text{Cr}}}{{A_{52\text{Cr}}}D t} \, , \]

where \( F_{52\text{Cr}} \) refers to the actual fluence of the implanted 52Cr, \( C_{52\text{Cr}} \) refers to the true concentration of 52Cr as certified by NIST, \( A_{52\text{Cr}} \) refers to the depth of the analysis crater, \( D \) refers to the depth of the analysis crater, \( A_{52\text{Cr}} \) refers to the sum of all 52Cr⁺ counts attributed to the implant, corrected for the background concentration of 52Cr as described above, and can be represented as the area beneath the thin black line in Fig. 1. \( I_{52\text{Cr}} \) refers to the intensity (cps) measured by the electron multiplier of the background 52Cr⁺, as calculated from the intensity of 53Cr⁺, the non-implanted Cr species of known concentration; and \( t \) is the total time of the profile in seconds.

Each NIST glass was profiled twice, and the fluence was calculated from each of the four profiles. There was no difference observed in the fluence calculated within a single NIST glass material or between the NIST 614 and 612 glasses. The implant fluence was determined to be 2.76 ± 0.22 × 10¹³ ions/cm², a significant deviation from the nominal fluence of 4 × 10¹³ ions/cm². Quoted uncertainties are 2SD in the calculated fluence and incorporate uncertainties in the Cr concentrations of the NIST glass reference materials and the variability of the calculated fluence between the rastered areas; other sources of error (e.g., of crater depth determinations) contribute negligibly to the overall uncertainty.
B. Calculation of relative sensitivity factors

The relative sensitivity factor of an implanted natural material can be calculated according to Eq. (4), where \(C_{55\text{Mn}}\) represents the concentration of \(55\text{Mn}\) as determined by EPMA, \(D\) represents the depth of the rastered area, \(A_{52\text{Cr}^+}\) represents the total number of counts of implanted \(52\text{Cr}^+\) (as defined above), \(I_{55\text{Mn}}\) represents the measured signal intensity of \(55\text{Mn}^+\) during the depth profile, \(F\) represents the fluence of \(52\text{Cr}\) implanted as calculated above, and \(t\) represents the total duration of the profile.

\[
\text{RSF} = \frac{C_{55\text{Mn}}DA_{52\text{Cr}^+}}{I_{55\text{Mn}}Ft}. \quad (4)
\]

The RSF values for each implanted carbonate, along with the parameters from Eq. (3) used to calculate the RSF, are summarized in Table II. The relationship between the RSF value and the Fe content of the carbonate is shown in Fig. 3. Uncertainties in the derived RSF value incorporate errors in the Mn concentration and the fluence. As the relative uncertainty for the fluence determination is 8% (= 2SD) (quantified empirically from depth profiling of the implanted NIST glasses; see above), the error for the RSF for most carbonates is dominated by the error in the Mn concentration as determined by the EPMA. All repeated measurements of the RSF of carbonate materials are within error of one another. Because the calcite Mn concentration was below the detection limit of the EPMA (120 ppm), a Mn concentration of 100 ppm was used in order to perform the calculation. Therefore, the calcite RSF of 1.63 represents an upper bound and is associated with an error of 100%.

C. Nonlinear variation of relative sensitivity factors

For dolomite samples with \(\text{FeCO}_3 > 8\%\), the RSF remains constant at 0.88 ± 0.08 (2SD). At lower Fe content, the RSF value is higher, rising to around ~1.1 when \(\text{FeCO}_3\) approaches zero. This trend is consistent with previous studies of matrix effects in instrumental fractionation for carbonate minerals, which also show that isotope fractionation effects change substantially as small amounts of Fe are added to the carbonate but then become nearly constant once some threshold Fe concentration is reached.\(^{15,16}\)

D. Discussion

1. Comparison of RSFs with previous work

A previously quantified implanted ankerite (24 and 1.4 mol. % Fe and Mn, respectively) is similar to our MS1312 material, though MS1312 contains significantly more Mn.\(^3\) Despite substantial

### Table II. Results of RSF values derived from the depth profiling of natural carbonate minerals. The error on the RSF value is 2SD. Refer to Table I for additional information about error in Fe and Mn concentrations. Fe and Mn concentrations are reported in mol.% or ppm as μg Mn/g.

<table>
<thead>
<tr>
<th>Name</th>
<th>RSF</th>
<th>±</th>
<th>Depth (nm)</th>
<th>SD (%)</th>
<th>(55\text{Mn}) (cps)</th>
<th>(A_{52\text{Cr}^+}) (counts)</th>
<th>Time (s)</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite No. 1</td>
<td>1.66</td>
<td>1.5</td>
<td>301</td>
<td>1.0</td>
<td>138</td>
<td>115 472</td>
<td>1637</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>Calcite No. 2</td>
<td>1.60</td>
<td>1.5</td>
<td>297</td>
<td>1.7</td>
<td>163</td>
<td>131 794</td>
<td>1612</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>MS1317 No. 1</td>
<td>1.03</td>
<td>0.67</td>
<td>302</td>
<td>2.0</td>
<td>462</td>
<td>118 566</td>
<td>1767</td>
<td>b.d.</td>
<td>(317)</td>
</tr>
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<td>MS1317 No. 2</td>
<td>1.32</td>
<td>0.86</td>
<td>285</td>
<td>4.0</td>
<td>915</td>
<td>158 026</td>
<td>1761</td>
<td>b.d.</td>
<td>(317)</td>
</tr>
<tr>
<td>MS1317 No. 1</td>
<td>1.16</td>
<td>0.25</td>
<td>327</td>
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<td>3326</td>
<td>151 971</td>
<td>1470</td>
<td>1.4</td>
<td>0.2</td>
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<tr>
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<td>1.23</td>
<td>0.27</td>
<td>651</td>
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<td>2506</td>
<td>143 986</td>
<td>3470</td>
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<td>0.2</td>
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<td>MS1318 No. 1</td>
<td>0.867</td>
<td>0.16</td>
<td>293</td>
<td>0.6</td>
<td>28 369</td>
<td>214 744</td>
<td>1842</td>
<td>8.2</td>
<td>1.1</td>
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<tr>
<td>MS1305 No. 1</td>
<td>0.865</td>
<td>0.3</td>
<td>332</td>
<td>0.7</td>
<td>1976</td>
<td>152 105</td>
<td>1859</td>
<td>0.9</td>
<td>(558)</td>
</tr>
<tr>
<td>MS1305 No. 2</td>
<td>0.825</td>
<td>0.29</td>
<td>329</td>
<td>0.8</td>
<td>1965</td>
<td>145 875</td>
<td>1861</td>
<td>0.9</td>
<td>(558)</td>
</tr>
<tr>
<td>MS1312 No. 1</td>
<td>0.848</td>
<td>0.07</td>
<td>275</td>
<td>2.6</td>
<td>157 260</td>
<td>181 010</td>
<td>1915</td>
<td>22.8</td>
<td>8.2</td>
</tr>
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<td>MS1312 No. 2</td>
<td>0.927</td>
<td>0.08</td>
<td>315</td>
<td>5.7</td>
<td>105 714</td>
<td>177 507</td>
<td>2387</td>
<td>21.9</td>
<td>6.6</td>
</tr>
</tbody>
</table>
differences in the analytical conditions between this work and the previous study, the RSF value of 0.888 obtained for MS 1312 is higher than, though similar to, the value determined in the previous work for this similar mineral and is consistent with the overall trend of lower RSF with higher Fe content. Comparison of our MS1318 material (8.2 and 1.1 mol. % Fe and Mn) with a similar ferroan dolomite (8.5 and 0.5 mol. % Fe and Mn) show that the RSF value of 0.867 for MS 1318 is higher than that determined for the previously quantified dolomite, though we note that Steele et al. report only the standard error for their study. For comparison with other determinations of the calcite RSF, a nearly pure CaCO3 calcite was also implanted. However, only an upper limit of 120 ppm could be established for the Mn abundance for this material by EPMA. The calcite RSF we calculate assuming a Mn concentration of 100 ppm, though consistent within error with previous calcite RSF determinations of 1.16–1.41, is associated with large errors related to poor constraints on the Mn concentration.

2. Uncertainty in Mn concentration

Large errors in the RSF when FeCO3 < 2% are due to challenges in quantifying the Mn concentration by EPMA. In these low-Mn carbonates, Mn is heterogeneous on the order of a few 100 ppm at the spatial scale of our analyses. At low Mn concentration, this heterogeneity combined with a —120 ppm detection limit of EPMA leads to substantial uncertainty in the calculated RSF. Although this might appear to be a significant problem in quantifying systematics of the matrix effect, in practice it is not very important. Meteoritic dolomite typically incorporates MnCO3 > 2 mol. % and FeCO3 > 4 mol. %, Therefore, we do not expect large errors due to poor Mn (or Fe) quantification in natural meteoritic carbonate.

3. Change of RSF with depth

In a previous study by Doyle et al., the Mn/Cr RSF was shown to vary with depth during the analysis of olivine, a mineral that naturally incorporates trace amounts of Cr. These analyses were performed in the “spot mode,” as is typical for 53Mn/52Cr geochemical analyses. The craters produced by Doyle et al. were 3 and 5 μm in diameter with a significantly greater depth/diameter ratio than those produced in our study; where the primary beam was rastered over a 50 × 50 μm2 area resulting in shallow (<1 μm deep) craters. Doyle et al. further found that the magnitude of the RSF variation changed depending upon the Fe content of the olivine: for an olivine of low Fe content (Fa20), the value of the RSF increased by 10% over the course of the analysis, whereas for an olivine of higher Fe content (Fa40), it increased only by only 4%. Because we have implanted Cr into the target, we cannot characterize any possible depth-dependent RSF variations for carbonates using the same method as has been applied to olivine.

Matrix effects are challenging to predict and model. As an example, in stable isotope analyses of δ18O in carbonates of varying Fe content, increasing Fe content results in a bias toward higher values of δ18O. In contrast, δ18O in olivine would show the opposite relationship with the increasing Fe content. Therefore, we do not make a quantitative attempt to use the variation in RSF during the sputtering of olivine to predict the behavior of the carbonate RSF.

In this work, we show that the RSF decreases from ∼1.1 at 0 mol. % Fe to 0.88 at 8–20 mol. % Fe for an overall change of 19%. The magnitude of this effect is larger than the depth-induced RSF change observed in olivine, although we do not know how carbonate would compare with olivine in terms of the degree of RSF variation with depth. As we continue to develop this method, we plan to conduct test analyses on implanted standards using smaller raster sizes (different crater aspect ratios) to assess the variability of the RSF in these different materials.

4. Effect of incorrect RSF usage

To illustrate the importance of selecting the appropriate RSF value on the determination of initial 53Mn/55Mn in a carbonate, we consider a fictional dolomite with an inferred 53Mn/55Mn ratio of 4.00 × 10−6 before correction for matrix effects. Since the inferred 53Mn/55Mn ratio is inversely proportional to 55Mn/52Cr, a smaller RSF value would result in a smaller true 53Mn/52Cr [Eq. (2)] and thus a higher 53Mn/55Mn. If this hypothetical carbonate was corrected using an RSF value of 1.1 appropriate for a low-Fe dolomite, it would correspond to a 53Mn/55Mn ratio of 3.64 × 10−6 for an age, as calculated by Eq. (1), of 3.9 Myr after the birth of the solar system. On the other hand, if an RSF value of 0.88 is used as would be more appropriate for a high-Fe dolomite, the inferred 53Mn/55Mn ratio would be 4.55 × 10−6 corresponding to an age of 2.1 Myr after the birth of the solar system—a significant difference of 1.8 Myr. Because the 53Mn/55Cr chronometer is used only within the first 15 Myr of the solar system’s history, a systematic error of 1.8 Myr would represent a significant change to the interpretation of the chronology of hydrothermal alteration in the parent asteroid of a given meteorite.

IV. SUMMARY AND CONCLUSIONS

We used ion implantation of a suite of terrestrial dolomite reference materials to show that the relative sensitivity factor for dolomite with 8%–20% FeCO3 is 0.88 ± 0.04, consistent with previous estimates made for carbonates containing higher FeCO3. At low Fe and Mn content, the RSF is ∼1, although this value is associated with significant error due to uncertainties in the Mn concentration.

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