

## EXPRESS LETTER

# Mn/Cr relative sensitivity factors for synthetic calcium carbonate measured with a NanoSIMS ion microprobe

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Mn/Cr relative sensitivities for a synthetic calcite and a terrestrial olivine (San Carlos olivine) were measured using spot and rasterized modes with a NanoSIMS ion probe. Counting rates of  $^{43}\text{Ca}^+$ ,  $^{52}\text{Cr}^+$ ,  $^{53}\text{Cr}^+$  and  $^{55}\text{Mn}^+$  from the synthetic calcite by spot analysis mode decreased with time (and depth of crater). This may be interpreted as due to charge-up of the deep crater formed by primary ion bombardment because of poor conductivity of carbonate. The relative Mn/Cr sensitivity of carbonate measured by spot analysis mode decreased with time. It may be necessary to use a time-dependent relative sensitivity factor for chronological studies of meteoritic carbonates. The time-averaged RSF for the calcite spot analysis is significantly lower than that for San Carlos olivine. The instrumental isotopic fractionation of the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio measured with the NanoSIMS 50 seems to be different between the calcite and San Carlos olivine.

Keywords: secondary ion mass spectrometry, Mn–Cr chronology, relative sensitivity, carbonate, isotope

## INTRODUCTION

$^{53}\text{Mn}$  which decays to  $^{53}\text{Cr}$  with a half life of 3.7 Ma was present in the early solar system (Birck and Allegre, 1985). The  $^{53}\text{Mn}$ – $^{53}\text{Cr}$  system is useful for measuring time spans of various events such as solidification of achondrites (Lugmair and Shukolyukov, 1998) and aqueous activities on carbonaceous chondrite parent bodies (Endress *et al.*, 1996; Hutcheon *et al.*, 1998).  $^{53}\text{Mn}$ – $^{53}\text{Cr}$  ages of Mn-bearing carbonates measured by secondary ion mass spectrometry (SIMS) have been reported for many CI and CM chondrites (e.g., de Leuw *et al.*, 2009). However, the  $^{55}\text{Mn}^+ / ^{52}\text{Cr}^+$  relative sensitivity factor (RSF: defined by  $(^{55}\text{Mn}^+ / ^{52}\text{Cr}^+)_{\text{SIMS}} / (^{55}\text{Mn} / ^{52}\text{Cr})_{\text{TRUE}}$ ) which is necessary for calculating Mn/Cr ratios on isochron diagrams has not been reported for carbonates. In many previous studies, RSFs of silicates were used as a proxy. This is due to difficulties in determining RSFs for carbonates because natural terrestrial carbonates usually do not contain significant amounts of chromium. Therefore, the accuracy of previously reported Mn–Cr ages of carbonates is questionable. Here we report a RSF for a synthetic calcite measured by SIMS.

## EXPERIMENTAL

Mn-, Cr-bearing Ca-carbonate (calcite) crystals were grown by a method similar to that described by Gruzinsky (1967). Many meteoritic carbonates used for Mn–Cr chronology are dolomite rather than calcite. But synthesizing dolomite is difficult and we have not yet succeeded in synthesizing Cr-bearing dolomite.  $\text{NH}_4\text{Cl}$  (5.5 g; >98.5% purity),  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  (4.9 g; 75.5–77.5% as  $\text{CaCl}_2$ ),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.014 g; >99% purity),  $\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot (\text{H}_2\text{O})_2$  (>0.5 g: this is dump and cannot be weighed accurately),  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  (1 g; >98% purity) and  $\text{CH}_3\text{COONa}$  (7.65 g; >98.5% purity) were dissolved in distilled water (~300 ml) in a conical flask. A glass tube containing  $(\text{NH}_4)_2\text{CO}_3$  powder was placed on top of this flask. The assembly was kept at ~32°C for 14 days in a closed system under  $\text{N}_2$  atmosphere.  $\text{CO}_2$  and  $\text{NH}_3$  gases generated by decomposition of  $(\text{NH}_4)_2\text{CO}_3$  diffused into the solution, producing spherical Mn-, Cr-bearing Ca carbonate grains. The reaction is, in essence,  $\text{CaCl}_2 + (\text{NH}_4)_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NH}_4\text{Cl}$ . Mn and Cr substitute Ca in the carbonate. These grains were set in an epoxy resin and polished for scanning electron microscopic (SEM) observation and SIMS measurements. Crystal structure of the Ca-carbonate was examined by electron backscatter diffraction (EBSD). A ThermoNoran PhaseID system attached to a SEM (Hitachi, S-4500) was used for the EBSD acquisition. The accelerating voltage was 20 kV.

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Chemical compositions of the carbonate grains were measured with a wavelength-dispersive spectrometer (JEOL, JXA-8900R). The measurements were made at 15 kV and a sample current of 12 nA. Measurement times for Cr and Mn were 1 minute. To minimize damage to the carbonate, the electron beam was defocused to  $\sim 20 \mu\text{m}$  in diameter. Even then, some  $\text{CO}_2$  was lost from the carbonate. Therefore, cation abundances were calculated assuming that the sum of cations is 20 atomic %, as expected for stoichiometric carbonate.

SIMS measurements were made using NanoSIMS 50 at the Ocean Research Institute, the University of Tokyo. A focused primary  $\text{O}^-$  beam  $\sim 1 \text{ nA}$  in intensity and  $\sim 5 \mu\text{m}$  in diameter was used.  $^{43}\text{Ca}^+$ ,  $^{52}\text{Cr}^+$ ,  $^{53}\text{Cr}^+$  and  $^{55}\text{Mn}^+$  secondary ions were analyzed in a combined peak jumping/multi detection mode. Typical count rates of these ions are  $5 \times 10^4$ ,  $4 \times 10^4$ ,  $4 \times 10^3$  and  $3 \times 10^4$ , respectively. The mass resolving power ( $M/\Delta M$ ) was  $\sim 3500$ , sufficient for resolving all relevant interferences.  $^{43}\text{Ca}^+$ ,  $^{52}\text{Cr}^+$  and  $^{55}\text{Mn}^+$  ions were measured with 3 electron multipliers (EM) at one magnetic field setting.  $^{53}\text{Cr}^+$  was measured at another magnetic field setting with the EM used for the  $^{52}\text{Cr}^+$  measurement so that  $^{53}\text{Cr}/^{52}\text{Cr}$  isotopic ratios can be measured accurately. The counting times at the first and second magnetic fields were 2 and 5 seconds, respectively. The waiting time before start of counting at these fields was 2 seconds. One analysis consisted of 100 to 150 cycles of magnetic field jumping and took  $\sim 1500$  seconds.

The relative sensitivities between the electron multipliers used for the Mn and Cr measurements were checked intermittently during the measurement session. A dead time ( $\sim 44 \text{ ns}$ ) of the counting system was corrected. EM background that was much less than 1 cps was not corrected because it was negligible compared with the count rates of  $^{55}\text{Mn}$  and  $^{52}\text{Cr}$ .

At an early stage of this study, it was noticed that the Mn/Cr relative sensitivity was dependent on the depth of the crater produced by the primary ion bombardment. To investigate this depth dependence, both spot analyses that produced deep craters and rasterised analyses that produced shallow craters were made. In the latter analyses, the primary beam was rasterised over a  $20 \mu\text{m} \times 20 \mu\text{m}$  area. Presputtering times were 5 minutes and 15 minutes for the spot analyses and rasterised analyses, respectively. Crater depths produced by SIMS were measured using a confocal laser scanning microscope (Model 1LM21, Lasertec Inc.).

We did not measure the primary ion beam intensity accurately because it is a cumbersome process for the NanoSIMS 50. Hence, the secondary ion yields (ion counts/primary ion beam intensity) were not determined accurately and we report depth profiles of  $^{43}\text{Ca}^+$ ,  $^{52}\text{Cr}^+$ ,  $^{53}\text{Cr}^+$  and  $^{55}\text{Mn}^+$  that were normalized to the initial  $^{55}\text{Mn}^+$

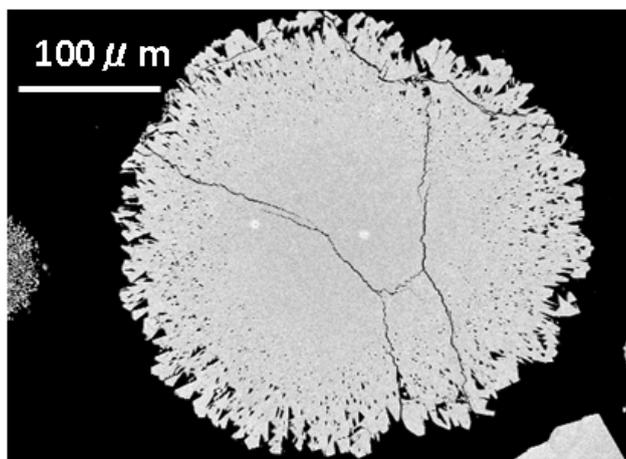


Fig. 1. Backscattered electron microscope image of a synthetic Mn-, Cr-bearing calcite.

count rate, instead of the absolute secondary ion yields. In addition to the synthetic carbonate, San Carlos olivine grains were measured under the same condition, to see if olivine was a good proxy for calcite.

## RESULTS

The typical size of the synthetic carbonate grains is  $\sim 300 \mu\text{m}$  (Fig. 1). According to the EBSD, the crystals are calcite. Mn and Cr concentrations are high at the grain center and decrease toward the rim. SIMS measurements were made near the center of a grain where both Mn and Cr concentrations are nearly constant. The Cr and Mn concentrations around the SIMS spots ranged from 0.15 to 0.22 atomic % and from 0.17 to 0.22 atomic %, respectively. The crater depths are  $10\text{--}17 \mu\text{m}$  and  $\sim 1 \mu\text{m}$  for spot and rasterised analyses, respectively.

Typical depth profiles of a rasterised analysis of olivine, a spot analysis of olivine, a rasterised analysis of calcite, and a spot analysis of calcite are shown in Fig. 2.  $^{43}\text{Ca}^+$ ,  $^{52}\text{Cr}^+$ ,  $^{53}\text{Cr}^+$  and  $^{55}\text{Mn}^+$  profiles are nearly flat for the rasterised analyses for both calcite and olivine (Figs. 2a and 2c). For the spot analyses of olivine, ion count rates initially increased and started to decrease around 500 seconds (Fig. 2b). For the spot analysis of calcite, ion count rates decreased almost from the start of the measurement (Fig. 2d). Such a steep depth profile is rather unusual.

$\text{Mn}^+/\text{Cr}^+$  RSFs are shown as a function of time in Fig. 3. The RSF for the spot analysis of calcite (Fig. 3d) clearly shows time dependence, whereas rasterised analysis of calcite (Fig. 3c) does not for a similar duration of measurement. The RSFs of olivine are nearly constant for both spot and rasterised analyses (Figs. 3a and 3b).

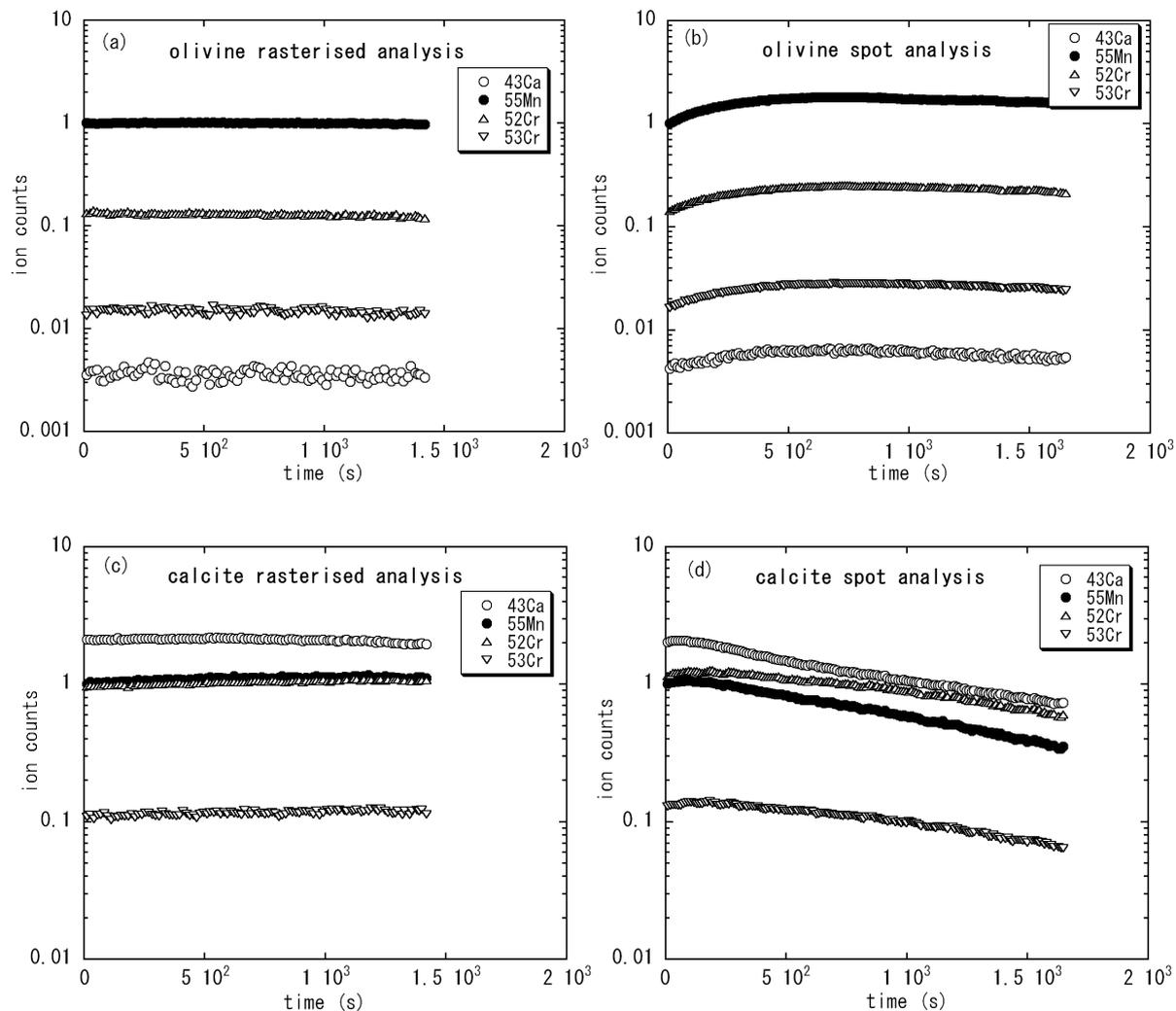


Fig. 2. Normalized depth profiles for olivine rasterised analysis (a), olivine spot analysis (b), calcite rasterised analysis (c) and calcite spot analysis (d). Count rates are normalized to the respective initial Mn count rate.

The time-averaged RSF for each measurement was calculated from the ratio of the total  $^{55}\text{Mn}^+$  counts to the total  $^{52}\text{Cr}^+$  counts over the entire measurement time ( $\sim 1500$  seconds), rather than the average of  $^{55}\text{Mn}^+ / ^{52}\text{Cr}^+$  ratios. This is because in measurements of meteoritic Cr-poor carbonates,  $^{52}\text{Cr}^+$  counts could be zero during the counting time of one cycle, causing difficulties in calculating the RSF. To avoid such a problem, an average Mn/Cr ratio for a meteoritic carbonate has to be calculated from the ratio of the total  $^{55}\text{Mn}^+$  counts to the total  $^{52}\text{Cr}^+$  counts. The same procedure was adopted for the synthetic calcite. The average RSFs and the  $2\sigma$  standard deviations for repeated measurements of olivine and calcite are shown in Table 1.

Average  $^{53}\text{Cr}/^{52}\text{Cr}$  isotopic ratios are also shown in Table 1. Although the attached errors are large, the aver-

age  $^{53}\text{Cr}/^{52}\text{Cr}$  for olivine obtained with NanoSIMS is similar to that ( $\sim 0.1125$ ) obtained with Cameca-6f (our unpublished data). The average  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios for calcite (for both rasterised and spot analyses) are lower than those for olivine. (For the spot analyses, time interpolation was made in calculating the ratios in order to account for the quick decreases in the count rates.) Although the exact Cr isotopic ratio of the synthetic calcite is not known, its Cr was derived from  $\text{CrCl}_3$  reagent and is not expected to have large isotopic anomalies (Schoenberg *et al.*, 2008). Therefore, the data in Table 1 suggests that there is a significantly large instrumental Cr isotopic fractionation between calcite and olivine measured by SIMS spot analyses. Hoppe *et al.* (2007) also reported Cr isotopic fractionation of  $9 \pm 7\%$  between carbonates and the San Carlos olivine. The fractionation observed in this study,

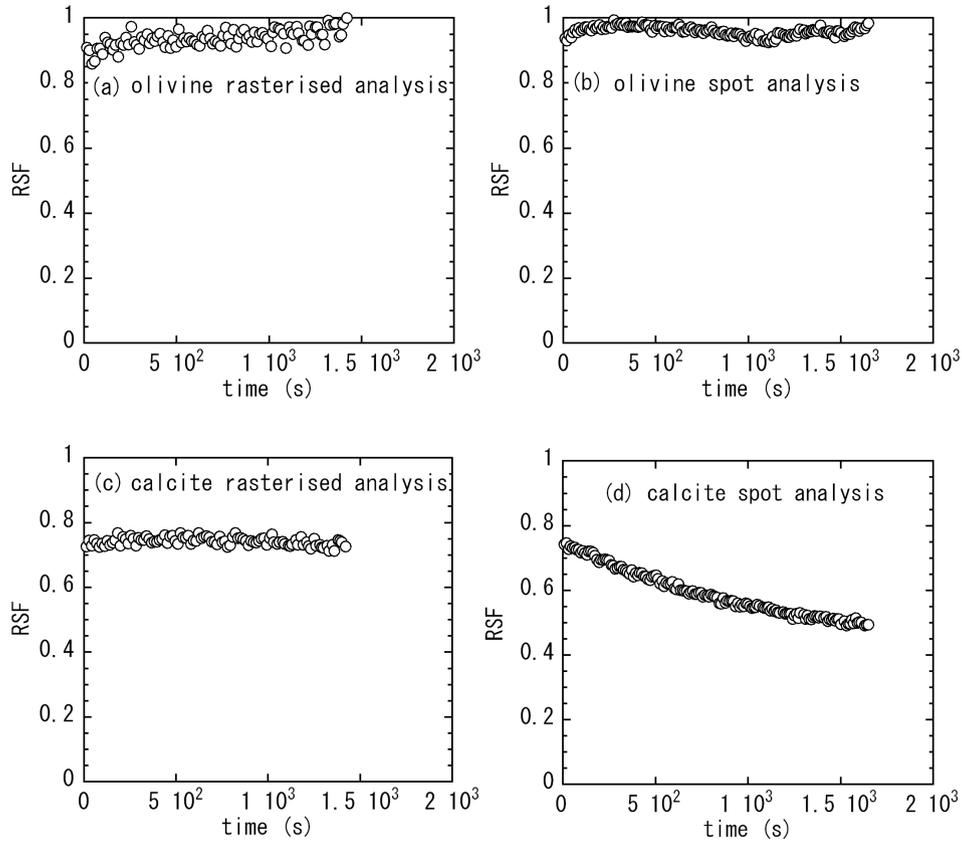


Fig. 3. Relative Mn/Cr sensitivity for olivine rasterised analysis (a), olivine spot analysis (b) calcite rasterised analysis (c) and calcite spot analysis (d).

Table 1. Mn/Cr relative sensitivity factors and Cr isotopic ratios

	RSF(Mn/Cr)		$^{53}\text{Cr}/^{62}\text{Cr}$		N*
	average	2 $\sigma$ std. deviation	average	2 $\sigma$ std. deviation	
olivine (rasterised)	0.93	0.03	0.1120	0.0012	4
olivine (spot)	0.95	0.02	0.1127	0.0004	2
calcite (rasterised)	0.79	0.05	0.1108	0.0007	8
calcite (spot)	0.63	0.04	0.1103	0.0003	12

\*Number of analyses.

The errors are estimated from the reproducibility of repeated measurements.

however, seems to be larger than that of Hoppe *et al.* (2007), which may be attributable to slight difference in the NanoSIMS measurement conditions.

## DISCUSSION

Although Mn and Cr concentrations in the synthetic calcite are slightly zoned, the depth profile for the spot analysis (Fig. 2d) is much steeper than that expected from a probable concentration gradient along the crater depth.

Besides, Ca concentrations are practically constant everywhere in the calcite grains. Therefore, the depth profile for the spot calcite analysis (Fig. 2d) is not explained by real changes in concentrations of these elements. We suggest that the decreases in these counting rates are mainly caused by charge-up of the calcite. Calcite is known to be a very poor electric conductor. We suspect that deep calcite craters were strongly, positively charged-up. The charge-up increases the accelerating voltage of positive secondary ions, causing decrease in the transmission of

the secondary ion optics. The nearly flat depth profile for rasterised calcite analysis (Fig. 2c) suggests that the aspect ratio of the crater is important in determining the degree of charge-up. Since the rasterised calcite analyses give nearly time-independent  $\text{Mn}^+/\text{Cr}^+$  RSF, one may think that this mode of measurement rather than the spot analyses should be adopted for Mn–Cr chronological studies. In chondritic carbonates, however, the area available for Mn–Cr dating is limited, making rasterised analyses impractical.

The depth profiles of  $^{43}\text{Ca}^+$  and  $^{55}\text{Mn}^+$  are nearly identical whereas those of  $\text{Cr}^+$  are less steep (Fig. 2d). If the charge-up of the crater is the sole cause of the decrease in the ion yields with time, then the depth profiles (Fig. 2d) should be identical for all ions. Therefore, the difference in the depth profiles between  $\text{Cr}^+$  on the one hand and  $\text{Ca}^+$  and  $\text{Mn}^+$  on the other, suggests that the numbers of ions extracted from the crater change with time (and depth). It may be that a fraction of secondary ions becomes neutral atoms during the extraction from a deep crater. If the fraction is smaller for Cr than for Mn (possibly due to difference in Cr and Mn valence states, although the Cr valence state is not known for the calcite), then shallower Cr depth profile relative to Mn could be explained. More studies on the  $\text{Cr}^+$  ion yield together with  $\text{CrO}^+$  and  $\text{CrO}_2^+$  yields are certainly needed for substantiating this speculation.

The  $\text{Mn}^+/\text{Cr}^+$  RSF ( $0.95 \pm 0.02$ ) for the San Carlos olivine spot analysis is close to that ( $\sim 0.93$ ) reported by Hoppe *et al.* (2007) who also made measurements with a NanoSIMS. Rasterised analysis and spot analysis of the olivine give identical RSFs within the attached errors. These observations suggest that the  $\text{Mn}^+/\text{Cr}^+$  RSFs for silicates are not strongly dependent on the measurement conditions as far as the same ion probe is used. However, the time-averaged RSF ( $0.63 \pm 0.04$ ) for calcite spot analysis is significantly lower than that ( $0.95 \pm 0.02$ ) for the spot olivine analysis. The time-averaged RSF ( $0.79 \pm 0.05$ ) for rasterised calcite analysis is also lower than that ( $0.93 \pm 0.03$ ) for the rasterised olivine analysis. The difference in the RSF between calcite and olivine spot analyses corresponds to an age difference of  $\sim 2.2$  Ma. This age difference is quite significant because it is nearly three half lives ( $3 \times 0.7$  Ma) of  $^{26}\text{Al}$  that is the main heat source for planetesimals in the early solar system. The amount of radioactive  $^{26}\text{Al}$  in a meteorite parent body at the time of carbonate formation becomes  $\sim 1/8$  of that estimated using the olivine RSF of  $\sim 0.95$ . This strongly affects the formation process of carbonate minerals and the subsequent thermal history in the parent body.

Previously reported  $^{53}\text{Mn}$ – $^{53}\text{Cr}$  ages of meteoritic calcite should be younger by  $\sim 2.2$  Ma, if they were measured under the same condition as described here and a RSF of  $\sim 0.95$  were used. There are, however, many fac-

tors that could affect the RSF. For example, measurements made with conventional ion probes like Cameca-6f and Cameca-1270 where the primary beam size tends to be large and the incident angle is  $30^\circ$ , would make craters shallower than those of NanoSIMS. In such cases, appropriate RSFs may be larger than 0.63 if the other conditions are the same. If measurement time is longer than that used in this study, appropriate RSFs may be smaller because RSFs decrease with time. Therefore, we emphasize that it is essential to measure both meteoritic carbonates and a standard carbonate under exactly the same condition.

## CONCLUSIONS

We found that  $^{43}\text{Ca}^+$ ,  $^{52}\text{Cr}^+$ ,  $^{53}\text{Cr}^+$  and  $^{55}\text{Mn}^+$  counting rates from spot analyses of calcite decrease with time (and depth of crater) in SIMS using a NanoSIMS 50. This is interpreted mainly as due to charge-up of the deep crater formed by SIMS. The relative  $\text{Mn}^+/\text{Cr}^+$  sensitivity is also time-dependent. It may be necessary to use a time-dependent RSF for chronological studies of meteoritic carbonates. The time-averaged RSF for the calcite spot analysis is significantly lower than that for San Carlos olivine. The instrumental isotopic fractionation of the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio measured with a NanoSIMS 50 seems to be different between the calcite and San Carlos olivine.

The exact reason why the relative  $\text{Mn}^+/\text{Cr}^+$  sensitivity is time-dependent is not known. We speculate that it may be related to the valence state of Cr, but the Cr valence state is not known for our calcite sample. Some carbonaceous chondrites contain dolomite rather than calcite. It is important to determine the dolomite  $\text{Mn}^+/\text{Cr}^+$  RSF because it may be different from that of calcite.

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