

NEW SYNTHETIC CARBONATES FOR INVESTIGATION OF MANGANESE-CHROMIUM CHRONOLOGY BY SECONDARY ION MASS SPECTROMETRY. Patrick H. Donohue^{1*}, Gary R. Huss¹, and Kazuhide Nagashima¹; ¹Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, Hawai'i 96822, USA (*phd2@hawaii.edu)

Introduction: The short lived radionuclide ⁵³Mn decays to ⁵³Cr with a half-life of 3.7 million years. This system is important for dating early solar system processes [e.g., 1,2]. Meteoritic carbonates typically contain minor Mn but very little Cr, and so have high Mn/Cr ratios, making them good candidates for ⁵³Mn-⁵³Cr dating. But small crystal sizes require *in situ* measurement techniques such as secondary ion mass spectrometry (SIMS). In SIMS measurements, the ionization efficiency of Mn and Cr are different, meaning the measured Mn/Cr ratio is not the true ratio. Thus a correction factor, known as the relative sensitivity factor or RSF, is needed. The RSF is obtained by measuring a standard with known Mn/Cr ratio. Historically, San Carlos olivine has been used because there were no good natural or synthetic carbonate standards. But recent work has shown there are significant matrix effects on the ionization efficiency of Mn and Cr between olivine and carbonates, and even among olivines of different compositions [2,3]. These matrix effects lead to erroneous results. A synthetic calcite standard created by [3] was a good step forward in obtaining accurate Mn/Cr measurements by SIMS. Another group is investigating Mn and Cr ion implantation to synthesize standards [4].

Here we update our efforts to produce synthetic carbonates with known Mn and Cr contents. We have produced crystalline calcite with Mn and Cr contents easily measurable by electron microprobe (EMP), and we are working on other common meteoritic carbonates (e.g., dolomite, breunnerite). Calcite is compositionally zoned, but some sectors are large enough (~100 × 100 μm) for several SIMS measurement sessions. In addition, we have created several batches of carbonates with different amounts of Mn, Cr, and Fe to assess the compositional effects on the RSF.

Low-T Carbonate Synthesis: We synthesized calcite in two ways: *Constant addition* and *Free drift*. Both methods were typically left to run for 7 to 10 days. Our *Constant addition* technique was previously described in [5]. Briefly, three solutions were prepared. The first was a 150 mL CaCl₂ and MnCl₂ mix. The second 150 mL solution contained (NH₄)₂CO₃. These were slowly pumped into a third, low pH (~3-4) 200 mL solution which contained Na₂Cr₂O₇ solution. Concentrations were such that the fully mixed solution ideally had ~2600 ppm CO₃²⁻, 600 ppm Ca, 10 ppm Mn, and 1000 ppm Cr. The *Free drift* setup involves a reservoir of powdered (NH₄)₂CO₃ in an enclosed beaker with several smaller beakers of reactant solutions. The solutions were dissolved CaCl₂, MnCl₂, and CrCl₂, resulting in

similar reactant concentrations to those in the *constant addition* method. In one series we also added variable amounts of FeCl₂ to the reactants. The breakdown of (NH₄)₂CO₃ produced CO₃²⁻(g) that diffused into the solutions and reacted with the cations to produce calcite.

High-T Carbonate Synthesis: Dolomite and magnesite were synthesized by recrystallization of calcite in solution at elevated temperature. Small amounts of Mn- and Cr-bearing calcite seeds (~0.1 g, ~500 μm) were mixed with 10-15 mL of CaCl₂-MgCl₂ solutions to yield a Mg/Ca ratio of ~0.4 to 1.2. These solutions were poured into a 125 mL PTFE acid digestion vessel jacketed with a stainless steel pressure vessel (purchased from Parr instruments). The sealed assembly was placed in a commercial oven set to 215 °C (±3 °C variance) for 100-200 hours. Experiments were ended by decanting the cooled solutions through filter paper and rinsing the residue with DI water.

Characterization of the Resulting Carbonates: Crystals from select experiments were mounted in epoxy in wells on top of 0.25 inch stainless steel cylinders, and polished. Chemical compositions of the carbonates were measured by EMP using a 10 nA beam defocused to a 10 μm circular spot. Because the electron beam damages the carbonates, SIMS measurements were made near the electron-probe spots, not on the same spots.

SIMS Analysis: SIMS measurements were made using the University of Hawai'i Cameca ims 1280 ion microprobe. A ~100 pA ¹⁶O⁻ primary ion beam, accelerated to 13 keV and focused to a ~5×6 μm spot was used to sputter positive ions of ⁵²Cr, ⁵³Cr, ⁵⁵Mn, and ⁴⁰Ca¹⁶O from the sample. The secondary ion mass spectrometer was operated at 10 keV in combined multi-collection and peak-jumping mode. ⁵²Cr⁺ and ⁵³Cr⁺ were measured on a multicollector L2 electron multiplier (EM) and the monocollector (mono) EM respective for 45 seconds, followed by peak jumps to put ⁵⁵Mn⁺ and ⁴⁰Ca¹⁶O⁺ on the mono EM for 2 second each. The mass resolving power for L2 was ~4200, and that for the mono EM was ~6000, sufficient to resolve ⁵²CrH⁺ from ⁵³Cr⁺.

All ratios were calculated using the sum of the total counts, which reduces ratio bias induced by low denominator count rates [6]. Uncertainties on measurements were propagated from the mean of ratios because these give a more accurate account of variation during analyses. The RSF is calculated here as a ratio of the SIMS-measured ⁵⁵Mn/⁵²Cr ion ratio to the EMP-determined element ratio corrected for isotopic abundance:

$$\text{RSF} = \left(\frac{{}^{55}\text{Mn}^+ / {}^{52}\text{Cr}^+}{\text{SIMS}} \right) / \left(\frac{{}^{55}\text{Mn} / {}^{52}\text{Cr}}{\text{TRUE}} \right)$$

The RSF-corrected isotope ratio is:

$$({}^{55}\text{Mn}/{}^{52}\text{Cr})_{\text{RSF-corr.}} = ({}^{55}\text{Mn}^+ / {}^{52}\text{Cr}^+)_{\text{SIMS}} / \text{RSF}.$$

Results and Discussion: Products of the *constant addition* experiments are large (typically >500 μm) yellow to orange hemispherical calcite grains. Sector zonation is apparent in BSE view, with high Mn and Cr zones brighter in BSE compared to low Mn and Cr zones (Fig. 1a). Within some large zones the Mn and Cr abundance is relatively constant. Products of the *free drift* experiments were up to 300 μm diameter, concentrically zoned crystals, often with a low Mn and Cr core surrounded by a high Mn and Cr region, then a thin (~10 μm) outer rim with very high Cr and low Mn (Fig. 1b).

SIMS investigation of *constant addition* product MnCr-22 yielded reproducible RSFs over the investigated area, with an average RSF of 0.61 ± 0.08 (2σ uncertainty). Many of the *free drift* experiments produced spikes in count rates during analysis and several exhibited decoupling between Mn and Cr count rates, suggesting subsurface heterogeneity. The two Fe-bearing samples yielded considerably higher RSFs (>1) compared to MnCr-22, but the change was not correlated with Fe contents and further characterization is needed to determine if the difference is reproducible. Averages of decent measurements are summarized in Table 1. An analysis of previously characterized synthetic calcite [3] was within uncertainty of the average RSF of MnCr-22.

A SIMS measurement of San Carlos olivine yielded an RSF of 0.80 ± 0.15 . This is within uncertainty of prior measurements made under similar operating conditions (0.86 ± 0.06) [7], and higher than the calcite RSF. As has been previously demonstrated, using the RSF of non-matrix-matched standard in SIMS analyses would skew the interpretations of isotope systematics [2,3,7,8].

Dolomite experiments produced crystalline dolomite with measurable Mn and Cr contents (between 0.1 and 0.4 wt.%). Unfortunately, SIMS investigation revealed microscale heterogeneities and decoupling of Mn from Cr with depth, which disturbed the Mn/Cr ratio and frequently made for unreliable measurements. However, preliminary RSFs for five dolomite analyses

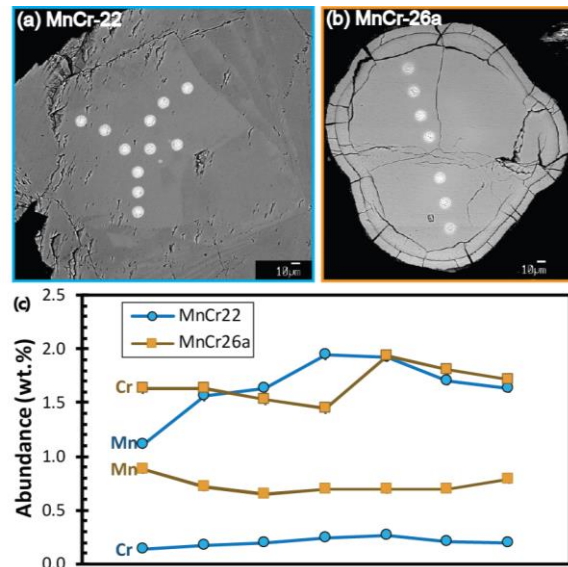


Fig. 1. BSE images of representative experimental products of (a) *constant addition*, contrast-enhanced to show zonation, and (b) *free drift* techniques. (c) EMP profiles from top-to-bottom of the two grains show minor chemical gradients.

yielded an average RSF identical to calcite, with a large associated uncertainty. Magnesite analyses also yielded RSFs consistent with those for calcite and dolomite.

Overall, the calcite produced by *constant addition* experiment technique produced the most reliable standard for RSF corrections. We successfully used the sample shown in Fig. 1a in a series of CM chondrite calcite measurements [9].

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Table 1. Average compositions and RSFs (2σ uncertainty) for synthesized carbonates.

phase	expt.	n	EMP			Fe (at.%)	SIMS		RSF			
			Mn (at.%)	Cr (at.%)			${}^{55}\text{Mn}/{}^{52}\text{Cr}$					
calcite	MnCr22	11	0.503	0.163	0.074	0.018	-	8.05	1.53	0.61	0.08	
	MnCr25c	1	0.525	0.023	0.626	0.013	-	0.60	0.01	0.60	0.03	
	MnCr26a	3	0.250	0.008	0.533	0.002	0.01	0.01	0.34	0.02	0.60	0.03
	MnCr27b	1	0.519	0.021	0.100	0.007	0.74	0.01	9.30	0.14	1.50	0.12
	MnCr27c	2	0.218	0.035	0.134	0.154	2.32	0.05	2.39	2.79	1.02	0.18
	Sugiura	1	0.167	0.015	0.163	0.008	0.02	0.01	0.89	0.01	0.73	0.04
dolomite	CaDo7	5	0.112	0.088	0.045	0.019	-	2.49	5.07	0.66	0.56	
magnesite	CaDo10	2	0.066	0.010	0.476	0.010	-	0.12	0.01	0.74	0.06	
olivine	San Carlos	1	0.038	0.002	0.005	0.001	-	7.95	0.03	0.80	0.15	