SYNTHESIZING CALCITE AND DOLOMITE FOR MN/CR RELATIVE SENSITIVITY CORRECTIONS: A PROGRESS REPORT.
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Introduction: The carbonates calcite ($CaCO_3$) and dolomite (($Ca,Mg)CO_3$) are common alteration products in aqueously altered carbonaceous chondrites and some ordinary chondrites. Carbonates have been reported in CAIs, as isolated matrix fragments, and as veins in chondrule rims and matrix. The common occurrence of carbonates makes them potentially useful in constraining the relative chronology of aqueous alteration on the parent bodies of primitive chondrites.

The short-lived radionuclide ^{53}Mn has a half-life of 3.7 Myr (^{53}Mn decays to ^{53}Cr), making it suitable for dating materials formed within the first ~20 Myr of Solar System history. Natural carbonates form without appreciable amounts of Cr, while Mn is mildly compatible, often resulting in high Mn/Cr ratios. Much of the ^{53}Mn-^{53}Cr chronology is based on in situ analyses via secondary ion mass spectrometry (SIMS). In SIMS analyses, standards are required to correct for instrument mass fractionation and for the relative ionization efficiency of Mn compared to Cr. The difference in ionization efficiency can be corrected using relative sensitivity factor (RSF) by comparing SIMS Mn/Cr ion ratios to a "true" ratio measured independently, typically by electron microprobe analysis (EPMA). However, there are no natural carbonate standards because Cr is incompatible in calcite and dolomite, and historically, San Carlos olivine has been used as a standard for carbonates [e.g., 1–3]. This has led unreliable Mn-Cr ages, as the RSF of Mn and Cr is matrix and time dependent, and the RSF can be significantly different between olivine and calcite [4,5], and possibly even between dolomite and calcite [6].

There has been recent progress in synthesizing Mn- and Cr-doped calcite [4], and some preliminary work has been done on dolomite [6]. Artificially doping natural carbonates with Cr and Mn via ion implantation is also being investigated [e.g., 7]. While promising, many reference materials are zoned or are microcrystalline aggregates. Synthesizing large, homogeneous, single crystals of carbonates would improve this aspect of Mn-Cr analyses. A major problem of incorporating Cr is that it needs to be reduced (Cr^{2+}) to replace Ca or Mg, but it readily oxidizes to Cr^{6+}. We took the approach of [8] by instead attempting to incorporate Cr as CrO_4^{-2} in the CO_3^{-2} location.

Here, we present a progress report in synthesizing calcite and dolomite doped with natural concentrations of Mn and trace Cr. The goal is to provide matrix-matched standards for accurate ^{53}Mn-^{53}Cr chronology of meteoritic carbonates by SIMS.
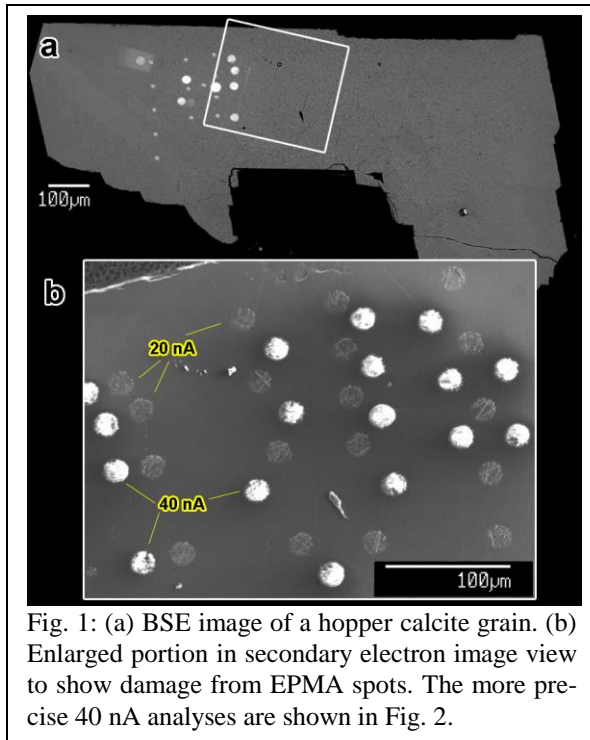
Calcite Synthesis: We synthesized calcite using passive diffusion, in which compounds diffuse through a medium to approach saturation of a desired phase [9]. The method was previously shown to produce calcite and aragonite [10]. Here, two 15 mL beakers were three-quarters filled with compounds dissolved in deionized (DI) water; 1.7M $CaCl_2$ in one beaker, the other with 2.5M $(NH_4)_2CO_3$ and ~0.38M $Na_2Cr_2O_7$. The small beakers were then set inside a 600 mL beaker. The remaining headspace of the 15mL beakers was capped by a barrier solution of HCl, which was also used to fill the large beaker to ~350 mL, several centimeters above the rims of the small beakers. Manganese was added as 0.001M $MnCl_2$ to the buffer solution. The buffer solution was made to be a pH ~3, as this initial condition reportedly yielded the best calcite crystal morphologies [10]. Experiments were run 10 to 24 days. Resulting crystals were gently scraped from beaker walls and decanted into filter paper, rinsed with DI water, and air dried.

Dolomite Synthesis: We adapted the method of [11] to grow dolomite crystals doped with Mn and Cr. An aqueous solution (35 mL total) of 0.25M $CaCl_2$, 0.25M $MgCl_2$, 0.50M $(NH_4)_2CO_3$, 0.30M $Na_2Cr_2O_7$, and 0.050M $MnCl_2$ was mixed in a Teflon-lined capsule. The capsule was a commercial 125 mL acid-digestion bomb (Parr Instrument Co.) consisting of a stainless steel jacket with a Teflon liner. The sealed capsule was placed in an oven at 215°C for 470 hours. The resulting product was decanted through filter paper. Residue was rinsed with DI water and air dried.
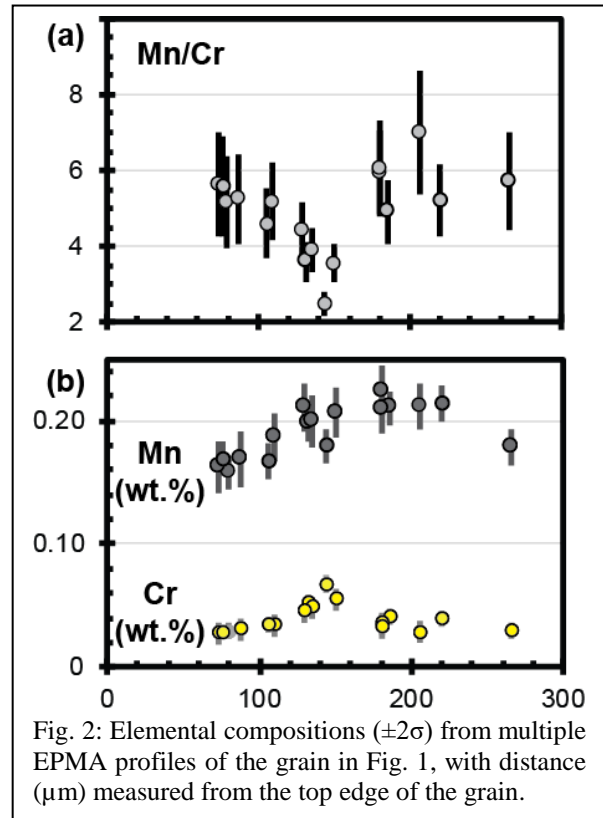
Sample Characterization: Loose grains of calcite and dolomite were analyzed by micro-Raman spectroscopy using 514.5 nm and 785 nm wavelength lasers. Samples were analyzed at 10× magnification for 10-30 s, using 24 mW power. Spectra were compared to natural aragonite and calcite, and reference spectra of dolomite and magnesiochromite (http://rruf.info).

Selected crystals were epoxied in 6.5 mm diameter rounds, polished to a 1 µm finish, and carbon coated. Compositional analyses were conducted using a JEOL JXA-8500F electron microprobe at the University of Hawai'i (UH). Preliminary analyses were conducted using a 10 µm diameter beam at 10 nA (visible as small white dots on Fig. 1a). However, the low abundance of Cr in calcite yielded high uncertainties in Mn/Cr ratios. Increasing the beam current produces better counting statistics, but may also damage the crystal. We found a 20 µm diameter beam and 40 nA beam current yielded sufficient counts while producing minimal damage to the grains. EPMA results will be used to calculate "true" Mn/Cr ratios in subsequent SIMS analyses.

Fig. 1: (a) BSE image of a hopper calcite grain. (b) Enlarged portion in secondary electron image view to show damage from EPMA spots. The more precise 40 nA analyses are shown in Fig. 2.

Fig. 2: Elemental compositions (±2σ) from multiple EPMA profiles of the grain in Fig. 1, with distance (µm) measured from the top edge of the grain.

Results and Discussion: Synthesis experiments produced abundant translucent calcite grains up to 1.5 mm in size and dolomite grains up to ~50 microns in diameter. Raman spectra of loose grains from the different experiments show typical calcite and dolomite peaks. The peaks are broader relative to pure crystals, suggesting some deformation of the crystal lattice. In synthetic calcite, additional Raman features between 800 and 1000 cm^{-1} are caused by Cr incorporation, with relative peak intensity corresponding to Cr concentration [12]. Chromate incorporation in dolomite is tentatively assigned to a broad peak at ~585 cm^{-1}.

Calcite morphology appears to be independent of Cr content, and strongly controlled by Mn abundance. Calcite grown in the presence of Cr, but with little Mn, exhibited rhombohedra and hopper morphology. With Mn and Cr, the dominant calcite morphology is multicrystalline and blocky, with grains slightly misoriented to each other. Increasing amounts of Mn produces smaller and more rounded grains. Multi-crystalline grains exhibit complex Mn and Cr sector zonation in cross section, not ideal for use as standards. Some larger hopper grains (Fig. 1) exhibit large regions (several hundred square µm) with little apparent variation in back-scattered electron (BSE) contrast. EPMA profiles show slight compositional gradients in Mn and Cr (Fig. 2). However, there are large regions across the crystal that could accommodate multiple SIMS spots. It is also promising that Mn is present at abundances similar to meteoritic calcite [e.g., 13]. With careful selection and characterization, these types of grains may be useful in determining RSFs for SIMS analyses.

Synthetic dolomite formed spherical crystal aggregates with blocky faces, primarily ~20 µm in size but with some faces reaching 50 µm. In cross section, dolomite was very porous and appears highly zoned in BSE contrast. Most of the Cr appears to have been sequestered into large grains (up to 1 mm) of CaCrO$_4$, which contain ~52 wt.% Cr. Thus, dolomite is not currently suitable for use as standards. However, analyzed dolomite grains contained up to 0.21 wt.% Mn and 0.27 wt.% Cr. Additional experiments are underway.

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