

PREPARATION OF SYNTHETIC DOLOMITE FOR DETERMINATION OF MN/CR RELATIVE SENSITIVITY . K. Ichimura¹ and N. Sugiura¹, ¹Department of Earth & Planetary Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan (ichimura@eps.s.u-tokyo.ac.jp)

Introduction: Applying ⁵³Mn-⁵³Cr systematics to carbonate minerals in CI and CM chondrite is effective for understanding alteration processes on their parent asteroids [e.g. 1]. Secondary ion mass spectrometry (SIMS) is often used for analyzing carbonates, and the relative sensitivity factor (RSF) of Mn to Cr is obtained using a synthetic calcite-type standard [1-3]. Recently, a large range in the RSFs of other carbonates was suggested [4]. The synthetic standard was limited to calcite-type that is only one end-member composition so far. Dolomite-type standard samples that contain similar amounts of Mg and Ca are yet to be prepared. Here, we report on the detail of preparation of Mn and Cr containing dolomite-type polycrystal that is expected to be used as a standard for SIMS.

Preparation of CaMg(CO₃)₂: There seem to be some difficulties on producing dolomite-type standards. The first one is the low growth rate of dolomite at mild condition of polytetrafluoroethylene (PTFE) vessel at 473 K used for the hydrothermal method at this time. To make matters worse, Mn in solution is “negative catalyst” that delay the crystal growth [5]. The second one is low content of Cr in the crystals. We found that earlier precipitation of Cr₂O₃ and stichtite-type clay (Mg₆Cr₂(CO₃)(OH)₁₆•4H₂O [6]) reduced the Cr concentration of reaction solution and prevented to partition a large amount of Cr into later forming dolomite. The third problem is low densities of produced polycrystal. In a past study, we synthesized dolomite-type samples by two step reaction where metastable Ca carbonates such as vaterite-type and aragonite-type are converted to dolomite-type in Mg containing solutions [7]. However, the product was unfortunately found to be unsuitable for a standard because stable secondary beam of SIMS was not obtained [8]. The reason seems to be low porosity of the polycrystal. In this study, we applied a conventional method for synthesis of dolomite-type [9] and used biuret as an additive of catalysis [10] to improve the growth rate. Hydrazine chloride was added in order to prevent undesirable oxidation of Mn²⁺ and Cr^{2+/3+} in solution. To prevent formation of stichtite-type clay and to get favorable solvent effect [11,12], some organic solvents were used instead of water.

Typical raw materials were as follows: CaCl₂ · 2H₂O, MgCl₂ · 6H₂O, MnCl₂ · 4H₂O, CrCl₃ · 6H₂O, urea, N₂H₄ · HCl, NaCl, Mn metal, 36% HCl, biuret, ethylene glycol, 4.2, 4.7, 0.2, 0.29, 1.45, 5, 1.5, 0.065,

0.14, 2, 46.5 each in gram, respectively. The materials were mixed under inert gas condition and put into a PTFE vessel with a stainless jacket. After resting for 1 h during reaction of Mn and acid to produce H₂ gas inside the vessel, it was transferred into an oven at 473 K and kept for 170 h. Product CaMg(CO₃)₂ precipitates were filtered, and washed with ethanol and distilled water and dried in a vacuum oven. Dried particles were embedded in epoxy resin and polished.

Characterization of crystals: Crystal structures were characterized using powder x-ray diffractometer (XRD). Field-emission type electron probe microscope (FE-SEM) equipped with an electron backscattered diffraction (EBSD) detector was used for analyzing each grain.

Measurement of Mn and Cr concentrations: Polished sections of samples were measured using field emission type electron probe micro analyzer (FE-EPMA) at acceleration voltage of 12 kV with beam current of 12 nA. Analyses were made with 5 μm diameter. Counting times were 30 s (peak) and 15 s (upper and lower background, in each) for Mn and Cr, 10 s (peak) and 5 s (background) for other elements.

Results and discussions: Figure 1 shows a X-ray diffraction pattern of a product. There are peaks of dolomite-type and aragonite-type. Crystallinity of dolomite-type seems low in view of the broad peaks. The components ratio of crystals was estimated to ~80% dolomite-type and ~20% aragonite-type calculated from a whole powder pattern fitting (WPPF) program of RIGAKU. The result was confirmed with an observation of SEM. Because the atomic ratio of Ca/Mg in the reagent slurry was 1.25, aragonite-type crystals were produced by excess calcium.

SEM observation showed that there were isolate spherical particles or congregated, and their sizes range from 10 to 100 μm. A few particles more than 80 μm in diameter were found in an area of 1 mm². Figure 2 shows one of the particles. Clear EBSD patterns were not obtained from any particles of dolomite-type in this study. This result implies each particle is composed of very fine (< 0.1 μm) crystals. In some cases, density of particles tends to be low at the center, and hollow spheres are also found. The spherical shape of particles seems to be attributed to a micelle that induces self-assembly into microsphere [12]. Further transformation from precursor phase [13] may induce hollow spheres.

Figure 3 shows elemental composition of a particle (Fig. 2). Elemental compositions of most particles

show gradients inside them. Ca/Mg ratios usually become low towards the rim. Ca/Mg atomic ratios range 1-2 in the core and 0.8-2 in the rim. Cr concentrations are nearly constant in the central part of a particle. However, near the rim where Mg concentrations are high, Cr concentrations are sometimes very high (Fig. 3, middle). The Mn/Cr ratio of this particle at the central part is homogeneous within the error (6% at 2σ). The valence of chromium is not determined so far. Divalent chromium seems preferable for a replacement of the same valence Ca or Mg. However, trivalent chromium may incorporate in analogy with europium [14]. We plan to use these particles for determination of accurate Mn/Cr relative sensitivities of SIMS in the near future.

References: [1] Fujiya W. et al. (2012) *Nat. Commun.*, 3: 627. [2] Sugiura N. et al. (2010) *Geochem. J.*, 44, e11-e16. [3] Jilly C. E. (2014) *Meteoritics & Planetary Sci.*, 49, 2104-2117. [4] Steele R. C. J. et al. (2014) 77th Annual Meteorit. Society Meeting, Abstract #5438.

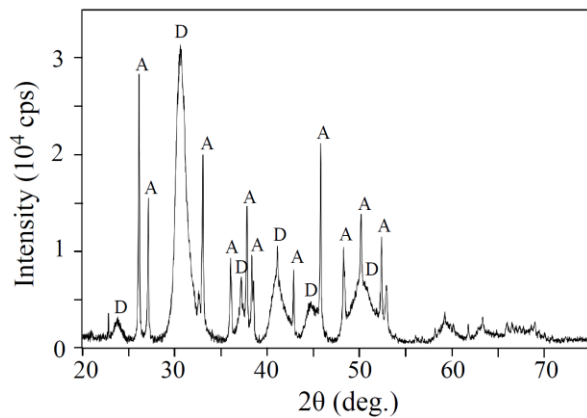


Figure 1 X-ray powder pattern of synthesized material. A and D in the figure show aragonite and dolomite, respectively.

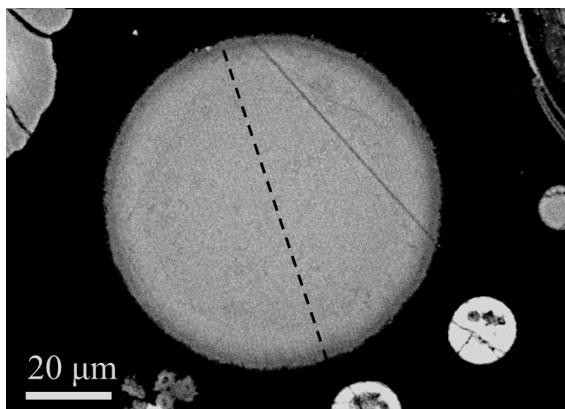


Figure 2 Backscattered electron image of a synthesized particle of $\text{MgCa}(\text{CO}_3)_2$ doped with Mn and Cr. EPMA measurements were made along the broken line.

[5] Lumsden D. N. et al. (1989) *Geochim. Cosmochim. Ac.* 53: 2325-2329. [6] Theiss et al. (2013) *Clay Minerals*, 48: 143-148. [7] Isobe H. and Takayama N. (2004) *Abstracts, 2004 Japan Earth and Planetary Science Joint Meeting*, K038-P010. [8] Fujiya W., in private communications. [9] Medlin W. L. (1959) *Am. Mineral.*, 44: 979-986. [10] Mitsushio H. et al. (1983) *Proc. First Int. Symp. Hydrothermal Reactions*, 730-737. [11] Flaten E. M. et al. (2009) *J. Cryst. Growth*, 311: 3533-3538. [12] Qi R.-J. and Zhu Y.-J. (2006) *J. Phys. Chem. B*, 110: 8302-8306. [13] Suzuki et al. (2006) *Cryst. Growth Des.*, 6: 2004-2006. [14] Fernandes M. M. et al. (2008) *J. Colloid Interface Sci.* 321: 323-331.

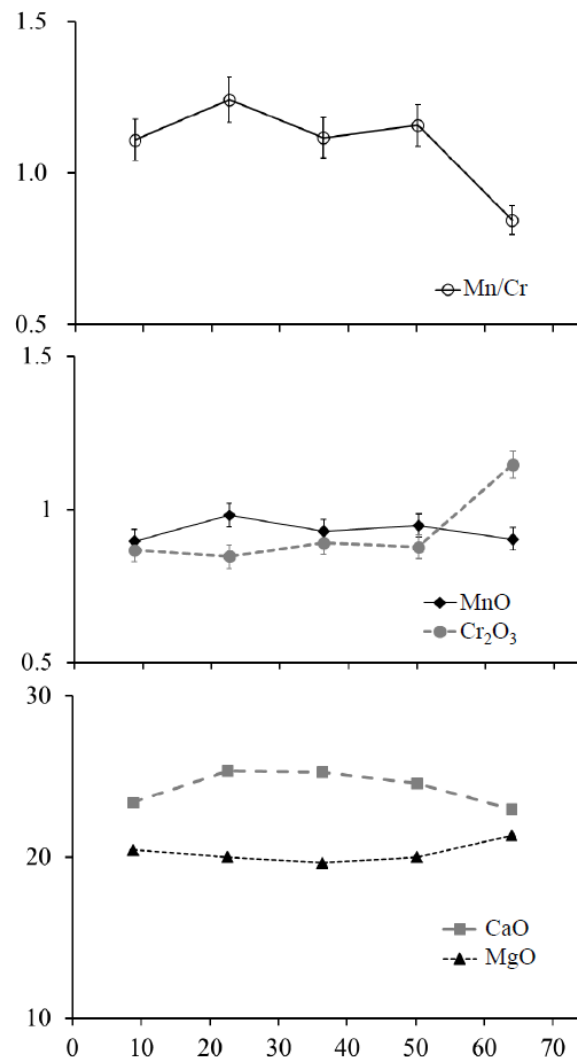


Figure 3 Elemental compositions across a synthetic grain 74 μm in diameter.