Synthesis of Mn-, Cr-bearing calcite, dolomite, and magnesite for Mn-Cr dating of carbonates

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Carbonate minerals are often observed in CI, CM, and CR chondrites. Carbonate minerals formed by aqueous alteration on asteroids and are important materials because their formation ages can be measured by ^{53}Mn-^{53}Cr dating (half-life: 3.7 Ma) (e.g., Fujiya et al., 2012).
Secondary Ion Mass Spectrometry (SIMS) is normally used for Mn-Cr dating of carbonates. In SIMS analyses, measurements of a standard material with the same crystal structure and chemical composition as carbonates are necessary because of the matrix effect. Sugiura et al. (2010) synthesized Mn- and Cr-bearing calcite ($CaCO_3$) in aqueous solution because natural carbonate minerals do not incorporate Cr. However, quantitative analysis of Mn and Cr is difficult because precipitation in aqueous solution results in zoning of Mn and Cr concentrations during crystallization. In this study, we try to synthesize calcite, dolomite, and magnesite containing Mn and Cr homogeneously.

Incompatible elements for calcite may be incorporated into amorphous calcium carbonate (ACC). ACC crystalizes to calcite at high pressure or temperature, where large amounts of incompatible elements such as Sr, U, and Pb can homogeneously be distributed (Matsunuma et al., 2014; Miyajima et al., 2019). In this study, we applied this method to Mn and Cr. We mixed cold 0.1M Na_2CO_3 and 0.1M (Ca, Mn, Cr) Cl_2 aqueous solutions to produce ACC. The ACC was subsequently separated by vacuum-filtration, and was dried in a vacuum desiccator for one day. The ACC crystallized to calcite by heating under IW-buffer at 400 ℃ for two hours. The material before and after heating were confirmed as ACC and calcite, respectively, by using powder X-ray diffraction (XRD). Then, the calcite was embedded in resin and its surface was polished. We conducted semi-quantitative analysis of Mn and Cr by using SEM-EDS. Manganese and Cr were homogeneously incorporated into the calcite grains with Mn/Ca and Cr/Ca ratios of 1.47 ±0.09 and 0.96 ±0.07 (2 σ), respectively.
Next, we produced amorphous carbonates with Ca/Mg ratios of ~1 and 0 using the same method as the Mn-, Cr-bearing calcite. However, these did not crystallize to dolomite and magnesite by heating. Then, we tried to produce dolomite and magnesite via hydrothermal synthesis. We put an aqueous solution with amorphous carbonate in autoclave and heated it at 200℃ for three days. Dolomite and magnesite were successfully synthesized, and in the future, we will try to dope Mn and Cr into the synthesized dolomite and magnesite.

Keywords: amorphous calcium carbonate, standard, Mn-Cr dating

