

Mn/Cr relative sensitivity factors of SIMS determined for synthetic Mn-, Cr-, and Fe-bearing dolomites

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Dolomite [CaMg(CO₃)₂] is a carbonate mineral commonly found in aqueously altered carbonaceous chondrites and contains some amounts of Mn and Fe. Dolomite in meteorites formed in the early solar system and incorporated a short-lived radionuclide ⁵³Mn that decays to ⁵³Cr with a half-life of 3.7 million years [1]. Thus, the timescale of aqueous alteration and the formation age of parent bodies can be constrained by ⁵³Mn-⁵³Cr dating of meteoritic dolomite.

The Mn-Cr dating of dolomite has commonly been performed using secondary ion mass spectrometry (SIMS). For SIMS analyses, the relative sensitivity factor (RSF) defined as a Mn⁺/Cr⁺ ion intensity ratio divided by a Mn/Cr elemental ratio must be evaluated using a standard material with the same composition as the meteoritic carbonate to be analyzed to correct the matrix effect. However, because carbonates in the natural environment contain little Cr, it is challenging to utilize a proper Cr-bearing dolomite standard, and therefore, the previously reported Mn-Cr ages of meteoritic dolomite may have systematic uncertainties. To overcome this problem, the synthesis of Mn- and Cr-bearing dolomite has been attempted [8,9], although dolomite crystallization proceeds only under hydrothermal conditions, making it difficult to incorporate Cr. Alternatively, Mn- and Cr-bearing calcite [CaCO₃] [10], which can be synthesized in aqueous solution at room temperature, has been used [2-5], but the RSFs of calcite and dolomite may be different. Recently, natural dolomite to which Cr ions were implanted was produced as a Cr-bearing dolomite standard [11,12]. However, the depth of the implantation was within 1 μm from the sample surface, and thus, the analytical conditions of this standard and meteoritic dolomite were much different, which may lead a systematic error on the obtained Mn-Cr ages.

In this work, we synthesized Mn-, Cr-, and Fe-bearing dolomites via amorphous carbonates. Amorphous calcium carbonate (ACC), which can incorporate large amounts of incompatible elements for crystal phases, crystallizes into calcite by heating [e.g., 13]. Applying this method, we synthesized Mn-, Cr-, and Fe-bearing dolomites via amorphous calcium magnesium carbonate (ACMC) with FeO contents of (i) 0 wt%, (ii) 0.95 wt%, and (iii) 3.17 wt%. Also, we synthesized Mn- and Cr-bearing calcite from ACC for comparison with previous studies [10].

We produced ACMCs by mixing a 0.2 M Na₂CO₃ solution and a 0.2 M (Mg, Ca, Cr, Mn, Fe) Cl₂ solution. The ACMCs were dehydrated at 270-300 °C and crystallized to dolomite by heating at 310-420 °C under a 1-22 bar CO₂ atmosphere. The heated samples were washed with ultrapure water and dried in a vacuum desiccator. The run products were identified as single-phase dolomite by powder X-ray diffraction (XRD). We observed the dolomites with a field emission scanning electron microscope (FE-SEM) and found that they were from several 10s nanometer- to submicron-sized particles. Also, a Mn-, and Cr-bearing calcite was synthesized via ACC [13]. The Mn-, Cr-, and Fe-bearing dolomite and Mn- and Cr-bearing calcite particles were separately put in a tungsten carbide piston cylinder and pressed using a hydraulic press to produce pellets. These pellets were embedded in resin, and their surfaces were polished and then coated with carbon. Electron probe micro analysis confirmed that the ⁵⁵Mn/⁵²Cr ratios of the dolomites were (i) 1.32 ± 0.02 (2SE, n = 185), (ii) 5.46 ± 0.14 (2SE, n = 391), and (iii) 2.70 ± 0.06 (2SE, n = 220), and that of the calcite was 0.86 ± 0.01 (2SE, n = 200).

Then, we analyzed the synthesized carbonates and a natural olivine from San Carlos using SIMS. Secondary ions of ^{43,44}Ca⁺, ^{52,53}Cr⁺, ⁵⁵Mn⁺, and ⁵⁷Fe⁺ were produced with a ~1 nA O⁻ primary ion beam focused to ~10 μm in diameter. The RSFs of olivine and calcite were 0.93 and ~0.75, respectively, consistent with previous studies [2-5, 10] (Fig. 1). We found that the RSFs of Fe-bearing dolomites increase with their FeO contents from ~0.81 to ~1.00, which is also consistent with the previous study [12] (Fig. 2). The observed variation in the RSFs between Fe-bearing dolomites and calcite could result in a systematic error on the ages of meteoritic dolomites by 1.6 Myr. We noted, however, that the reproducibility was worse when we used a primary ion beam with a lower intensity of 150 pA, probably due to the influence of the surface topography. This indicates that it is important to keep analytical conditions the same between the standard and meteoritic dolomites.

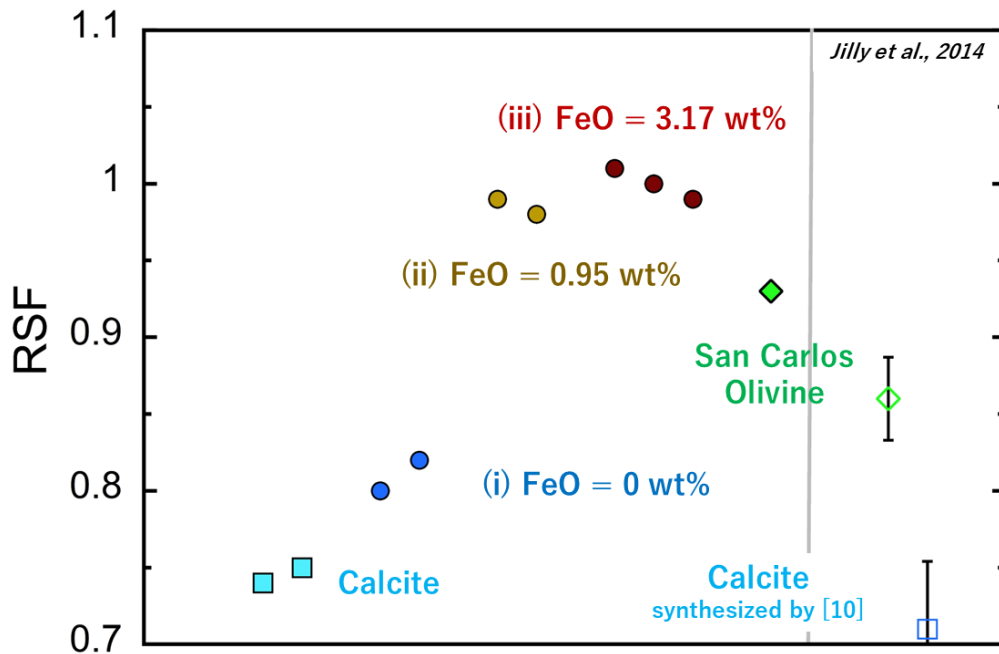


Fig.1. The relative sensitivity factors [RSF = $(^{55}\text{Mn}/^{52}\text{Cr})_{\text{SIMS}}/({}^{55}\text{Mn}/^{52}\text{Cr})_{\text{EPMA}}$] of synthetic dolomites, synthetic calcite, and San Carlos Olivine. RSFs obtained by Jilly et al. [4] are shown by open symbols for comparison.

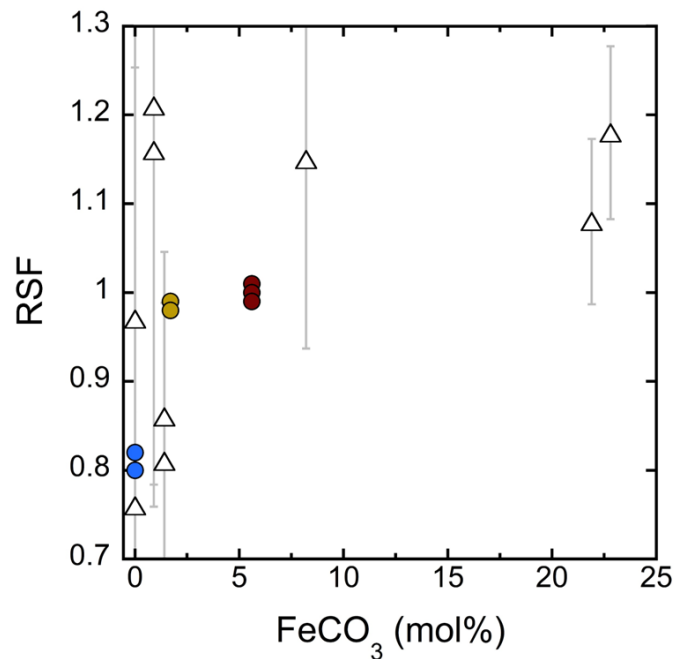


Fig. 2. The RSFs of synthetic dolomites as a function of Fe contents. RSFs obtained by McCain et al. [12] are shown by open symbols for comparison.

References

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