

A PROGRESS REPORT ON THE MN/CR RELATIVE SENSITIVITY FOR CARBONATE MEASURED WITH A NANOSIMS. N. Sugiura¹, K. Ichimura¹, W. Fujiya¹ and N. Takahata², ¹Department of Earth and Planetary Sci., University of Tokyo, Tokyo 113-0033, Japan. Sugiura@eps.s.u-tokyo.ac.jp, ²Ocean Research Institute, University of Tokyo, Tokyo 164-8639, Japan.

Introduction: ^{53}Mn which decays to ^{53}Cr was present in the early solar system. The ^{53}Mn - ^{53}Cr system is useful for measuring time spans of various events such as solidification of achondrites [1] and aqueous activities on carbonaceous chondrite parent bodies [2]. ^{53}Mn - ^{53}Cr ages of Mn-bearing carbonates measured by secondary ion mass spectrometry (SIMS) have been reported for many CI and CM chondrites [3]. However, the $^{55}\text{Mn}^+/\text{Cr}^+$ relative sensitivity factor (RSF; defined by $(^{55}\text{Mn}^+/\text{Cr}^+) / (^{55}\text{Mn}/^{53}\text{Cr})$) which is necessary for calculating Mn/Cr ratios on isochron diagrams has not been reported for carbonates. In many previous studies, RSFs of silicates were used as a proxy. This is due to difficulties in determining RSFs of carbonates because natural terrestrial carbonates do not contain significant amounts of chromium. Therefore, accuracies of previously reported Mn-Cr ages of carbonates are questionable. We synthesized a Mn-, Cr- bearing carbonate for RSF determination. Preliminary results were presented in [4]. This is a progress report on a RSF for a synthetic calcite measured by SIMS.

Experimental: Ca-carbonate crystals were grown following the method described by [5]. The carbonate grains were set in an epoxy resin and polished for scanning electron microscopic (SEM) observation and SIMS measurements. Crystal structure of the Ca-carbonate was examined by electron backscatter diffraction (EBSD). A ThermoNoran PhaseID system attached to a SEM (Hitachi, S-4500) was used for EBSD acquisition. The accelerating voltage was 20kV.

Chemical compositions of the carbonate grains were measured with an energy-dispersive spectrometer (EDS) attached to a SEM (JEOL, 5310).

SIMS measurements were made using a NanoSIMS 50 at the Ocean Research Institute, the University of Tokyo. A primary O⁻ beam ~1 nA in intensity and ~5 μm in diameter was used. $^{43}\text{Ca}^+$, $^{52}\text{Cr}^+$, $^{53}\text{Cr}^+$ and $^{55}\text{Mn}^+$ secondary ions were analyzed in a combined peak jumping/multi detection mode. $^{43}\text{Ca}^+$, $^{52}\text{Cr}^+$ and $^{55}\text{Mn}^+$ ions were measured with 3 electron multipliers (EM) at a magnetic field. $^{53}\text{Cr}^+$ was measured at another magnetic field with the EM used for the $^{52}\text{Cr}^+$ measurement. The counting times at the first and second magnetic fields were 2 and 5 seconds, respectively. The waiting times before start counting at these fields were 2 seconds. One analysis consisted of 100 to 150 cycles of magnetic field jumping and took about ~1500 seconds.

At an early stage of this study, it was noticed that the Mn/Cr relative sensitivity was dependent on the depth of the crater produced by the primary-ion bombardment. To investigate this depth dependence, both spot analyses that produced deep craters and rasterised analyses that produced shallow craters were made. In the latter analyses, the primary beam was rasterised over a 20 μm x 20 μm area. Presputtering times were 5 minutes and 15 minutes for the spot analyses and rasterised analyses, respectively.

In addition to the synthetic carbonate, San Carlos olivine grains were measured under the same condition, to see if olivine was a good proxy for carbonate.

Results : The typical size of the synthetic carbonate grains is ~300 μm in diameter. According to the EBSD, the crystals are calcite. Mn and Cr concentrations are high at the grain center and decrease toward the rim. SIMS measurements were made near the center of 2 grains (grain A and grain B) where both Mn and Cr concentrations are nearly constant. The Cr and Mn concentrations around the SIMS spots in the grain A ranged from 0.19 to 0.26 atomic % and from 0.21 to 0.24 atomic %, respectively, whereas those in the grain B ranged from 0.13 to 0.16 atomic % and from 0.14 to 0.18 atomic %, respectively. The differences between the two grains are mainly due to difference in the distance of the polished surface from the center of the spherical carbonate grain where the Cr and Mn concentrations are the highest. The ranges within a grain are due to Mn and Cr zoning within the polished surface.

$^{43}\text{Ca}^+$, $^{52}\text{Cr}^+$, $^{53}\text{Cr}^+$ and $^{55}\text{Mn}^+$ count rates are nearly constant for a measurement that lasts ~1500 seconds, for a rasterised analysis of olivine, a rasterised analysis of carbonate and a spot analysis of olivine. In contrast, a spot analysis of carbonate shows steep decrease in the count rates of these ions. In addition, the decrease of Cr^+ is less steep compared with that of Mn^+ .

Mn/Cr RSFs as a function of time (crater depth) are shown in Figs.1a-d. It can be seen that (1) RSFs for calcite are smaller than those for San Carlos olivine, and (2) the RSF for calcite spot analysis is time (depth) dependent.

Discussion: Time-averaged RSFs are 0.93 ± 0.03 , 0.95 ± 0.02 , 0.81 ± 0.05 and 0.66 ± 0.04 for olivine rasterised analysis, olivine spot analysis, calcite rasterised analysis and calcite spot analysis, respectively. The

attached errors are 2σ standard deviation for repeated measurements. The Mn/Cr RSF (0.95 ± 0.02) for the San Carlos olivine spot analysis is close to that (~ 0.93) reported by [6] who also made the measurements with a NanoSIMS. The Mn/Cr RSF (0.66 ± 0.04) is significantly smaller than that for San Carlos olivine. The difference in the RSF between calcite and olivine spot analyses corresponds to an age difference of ~ 1.9 Ma. This age difference is quite significant because it is more than twice the half life (~ 0.7 Ma) of ^{26}Al that is the main heat source in the early solar system. The amount of radioactive ^{26}Al in a meteorite parent body at the time of carbonate formation becomes less than one quarter of that estimated using the olivine RSF of ~ 0.95 . This strongly affects the formation process of carbonate minerals and the subsequent thermal history in the parent body. The exact reason why the RSF is time (depth) dependent is not known at present.

References:

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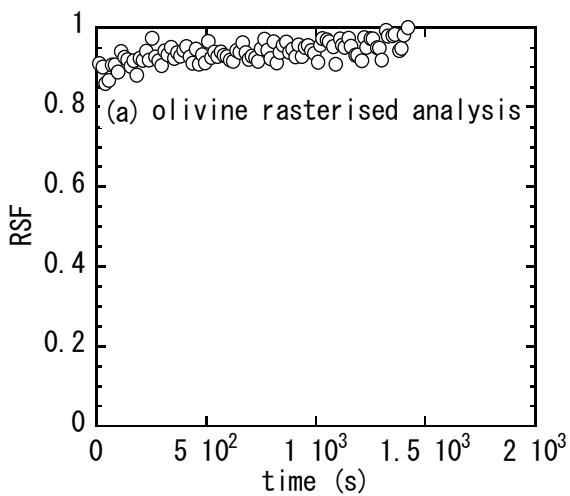


Fig.1a

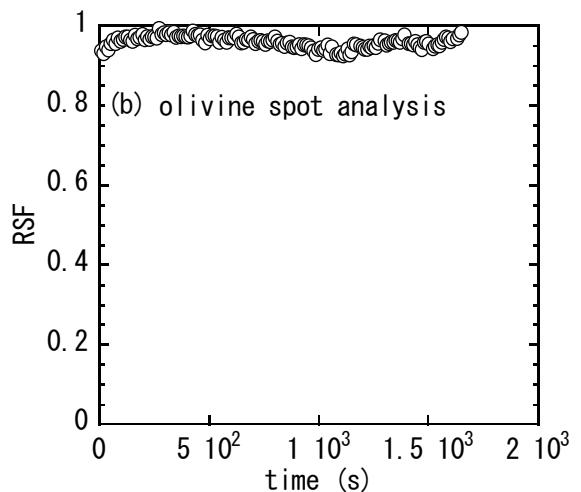


Fig.1b

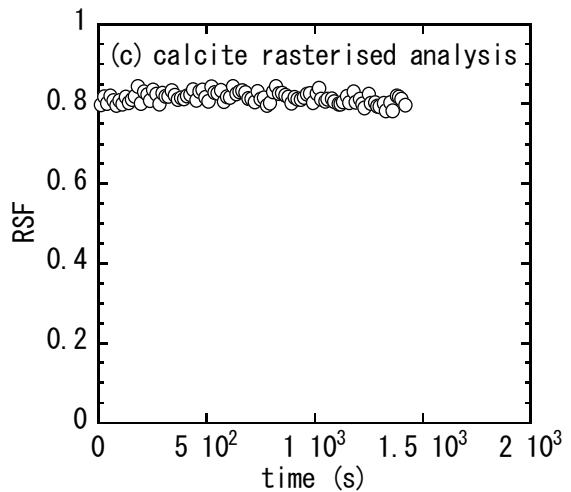


Fig.1c

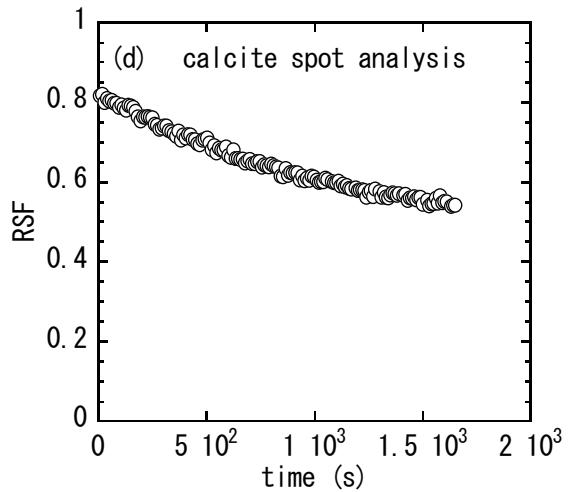


Fig.1d