^{53}Mn-^{53}Cr ages of dolomite in Ryugu samples and the thermal history of the Ryugu parent body.

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Introduction: Previous studies have provided several lines of evidence that Ryugu materials underwent extensive aqueous alteration in the Ryugu parent body [1-3]. They have a variety of secondary minerals such as phyllosilicates, carbonates, magnetite, and sulfides, which can shed light on the conditions of aqueous alteration. In particular, dolomite ($CaMg(CO_3)_2$), the major carbonate mineral in Ryugu, is an important mineral whose oxygen isotopic composition records the formation temperature as well as fluid compositions [1,2,4-6] and ^{53}Mn-^{53}Cr age (^{53}Mn decays to ^{53}Cr with a half-life of 3.7 Myr) provides chronological information [1,2,6]. Previous studies have tried measuring the ^{53}Mn-^{53}Cr age of Ryugu dolomite using secondary ion mass spectrometry (SIMS), however, they have faced a problem about calibration of the observed $^{55}Mn^+/^{52}Cr^+$ ratios to true $^{55}Mn/^{52}Cr$ ratios, resulting in systematic biases of initial $(^{53}Mn/^{55}Mn)_0$ ratios, and thus, erroneous ages. Here, we report the ^{53}Mn-^{53}Cr age of Ryugu dolomite measured using synthetic dolomite standards to appropriately calibrate $^{55}Mn^+/^{52}Cr^+$ ratios [7,8].

Experimental: We analyzed two Ryugu samples A0203 and C0192. These particles were embedded in epoxy and polished without using water. We carried out Mn-Cr isotope analysis using the NanoSIMS 50 at Max Planck Institute for Chemistry in Mainz. An O^- primary ion beam of ~100 pA in intensity and ~300 nm in size was generated by the Hyperion source and rastered over 3 x 3 μm^2 areas. We acquired a series of secondary ion images of $^{43}Ca^+$, $^{52}Cr^+$, $^{55}Mn^+$, $^{57}Fe^+$ (in magnetic field #1) and $^{53}Cr^+$ (in magnetic field #2) detected using electron multipliers in a combined multi-collection peak-jumping mode. According to the secondary ion images, we integrated ion signals only from dolomite grains. The measurement time was ~980s and ~4900s for magnetic fields #1 and #2, respectively. We used the synthetic dolomite standards Dol#0, Dol#2 and Dol#6, which contain sufficient amounts of Mn and Cr, and Fe of 0 mol% (below detection limit), 2 mol%, and 6 mol% (in total cations), respectively, to obtain the relative sensitivity factor (RSF: $(^{55}Mn^+/^{52}Cr^+)_{SIMS}/^{55}Mn/^{52}Cr)_{true}$) [8]. We took a special care to analyze the standards and Ryugu samples under the same conditions, which is critical for accurate ^{53}Mn-^{53}Cr dating of carbonate [8].

Results and discussion: We found that the RSF values of the synthetic dolomites ranged from 0.84 to 1.00 and increased with their Fe contents as observed by previous studies [6,8]. The initial $(^{53}Mn/^{55}Mn)_0$ ratios of dolomites in A0203 and C0192 are $(2.13 \pm 0.96) \times 10^{-6}$ and $(4.79 \pm 0.69) \times 10^{-6}$, respectively. If we use the D'Orbingy angrite as an anchor to covert the initial $(^{53}Mn/^{55}Mn)_0$ ratios to absolute ages [9,10], then we can calculate the absolute ages of 4560.7 (+2.0/-3.2) Ma and 4565.0 (+0.7/-0.8) Ma for the A0203 and C0192 dolomites, respectively. These ages correspond to 6.6 Myrs and 2.3 Myrs after the birth of the solar system as defined by the Pb-Pb age of CV CAIs [11]. Note that these relative ages depend on the choice of time anchors: if we use an initial $(^{53}Mn/^{55}Mn)_0$ ratio of 8.09×10^{-6} and the half-life of ^{53}Mn of 3.80 Myr proposed by Desch et al. [12], then the formation ages of the A0203 and C0192 dolomites will change to 7.3 Myr and 2.9 Myr after the birth of the solar system, respectively. Although it is difficult to compare our ages and those reported by previous studies due to the $^{55}Mn^+/^{52}Cr^+$ calibration problem, Sugawara et al. [8] tried updating the age of the Ryugu A0058 dolomite using the synthetic dolomite standards. The updated age is 4562.8 (+1.0/-1.2) Ma, which is intermediate between our ages. Thus, it is clear that dolomite did not grow in all parts of the Ryugu parent body synchronously but has a range of formation ages. Fujiya et al. [13] argued on the basis of oxygen isotopes that Ryugu dolomite formed during retrograde cooling when temperature was decreasing, and the A0203 dolomite formed at temperature as low as 15°C whereas the C0192 dolomite formed at higher temperature. Using the information about dolomite formation obtained, we will construct a thermal evolution model of the Ryugu parent body in future.

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