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PLANETARY SCIENCE

Water circulation in Ryugu asteroid affected the distribution of nucleosynthetic isotope anomalies in returned sample

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Studies of material returned from Cb asteroid Ryugu have revealed considerable mineralogical and chemical heterogeneity, stemming primarily from brecciation and aqueous alteration. Isotopic anomalies could have also been affected by delivery of exogenous clasts and aqueous mobilization of soluble elements. Here, we show that isotopic anomalies for mildly soluble Cr are highly variable in Ryugu and CI chondrites, whereas those of Ti are relatively uniform. This variation in Cr isotope ratios is most likely due to physicochemical fractionation between ⁵⁴Cr-rich presolar nanoparticles and Cr-bearing secondary minerals at the millimeter-scale in the bulk samples, likely due to extensive aqueous alteration in their parent bodies that occurred 5.2^{+1.8}_{-1.4} Ma after Solar System birth. In contrast, Ti isotopes were marginally affected by this process. Our results show that isotopic heterogeneities in asteroids are not all nebular or accretionary in nature but can also reflect element redistribution by water.

INTRODUCTION

Hayabusa2 is a JAXA sample return mission that targeted the Cb type asteroid (162173) Ryugu. The spacecraft collected 5.4 g of asteroid samples during two touchdown sequences: TD1, the first landing during which surface material was collected, and TD2, the second landing during which a mixture of surface and impact-ejected subsurface materials were collected (1, 2). Chemical and isotopic analyses (3, 4) as well as detailed mineralogical observations (5) of Ryugu samples revealed that Ryugu is composed of materials most similar to the CI (Ivuna-type) chondrites. CI chondrites are volatile- and organic-rich meteorites whose chemical compositions most closely resemble the elemental abundances in the solar photosphere with some notable exceptions (lithium and highly volatile elements) (6). Unlike meteorites, however, Ryugu samples are unaffected by terrestrial contamination (3), and they are particularly valuable for unraveling the earliest history of the Solar System as they retain primitive chemical characteristics.

The combination of mass-independent deviations in ⁵⁴Cr/⁵²Cr and ⁵⁰Ti/⁴⁷Ti ratios (expressed as ε⁵⁴Cr and ε⁵⁰Ti deviations from a terrestrial standard in parts per 10⁴ after correction of mass fractionation by internal normalization to fixed ⁵⁰Cr/⁵²Cr and ⁴⁹Ti/⁴⁷Ti ratios, respectively) provides fundamental insights into the nucleosynthetic origins of components in extraterrestrial materials. Variations in ε⁵⁴Cr and ε⁵⁰Ti, which are known as nucleosynthetic isotope anomalies, point to a heterogeneous distribution in the solar nebula of components synthesized in multiple stellar environments before the formation of the Solar System (7–10). Ryugu samples are most similar to CI chondrites in terms of nucleosynthetic isotopic variability in Ca, Ti, Cr, Fe, and Zn (3, 4, 11, 12). Nonetheless, Cr isotopic analyses reported so far reveal some variability in the ε⁵⁴Cr values among four bulk Ryugu samples that exceeds the documented dispersion of literature values for CI chondrites (3, 4). Ryugu and CI chondrites are breccias (13), begging the question of whether the ε⁵⁴Cr heterogeneity documented in Ryugu

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is an accretionary feature reflecting the presence of extraneous clasts with non-CI parentage, or if it reflects secondary processes such as parent-body alteration.

Variations in $^{53}\text{Cr}/^{52}\text{Cr}$ ratios in meteorites can be produced in part by the decay of the now extinct short-lived nuclide ^{53}Mn [$T_{1/2}$ (half-life) = 3.7×10^6 years], which can be used to date nebular and planetary processes associated with Mn-Cr fractionation in the early Solar System (14, 15). In situ ^{53}Mn - ^{53}Cr analyses of carbonates in Ryugu samples revealed that dolomite precipitated by 5 Ma after formation of calcium-aluminum-rich inclusions (CAIs) (3, 4, 16). Examination of ^{53}Mn - ^{53}Cr isotope systematics in bulk Ryugu samples can potentially provide complementary information to those in situ analyses as closure of the system at the bulk scale would be associated with large-scale fluid circulation while in situ measurements could potentially be reset by prolonged stagnant water-rock interactions.

To elucidate the origin of Ryugu materials and post-accretionary chemical processes on the Ryugu parent body, the present study focuses on the mass-independent Cr and Ti isotope variations as well as ^{53}Mn - ^{53}Cr isotope systematics in several bulk Ryugu samples. Specifically, we report results of such analyses in bulk aliquots of five Ryugu samples, two from TD1 (A0106 and A0106-A0107) and three from TD2 (C0107, C0108, and C0002). For comparison with the Ryugu samples, the compositions of several carbonaceous chondrites (including two CI chondrites, Orgueil and Alais) with comparable sample sizes to Ryugu are also reported.

RESULTS

Table 1 summarizes the values of $^{55}\text{Mn}/^{52}\text{Cr}$, $\epsilon^{53}\text{Cr}$, $\epsilon^{54}\text{Cr}$, and $\epsilon^{50}\text{Ti}$ in the Ryugu samples and carbonaceous chondrites obtained in this study. The $^{55}\text{Mn}/^{52}\text{Cr}$ ratio was measured by inductively coupled plasma mass spectrometry (ICP-MS) at Tokyo Tech. The Cr and

Ti isotopic analyses were conducted in three different laboratories [Tokyo Tech, University of Tokyo, and Arizona State University (ASU)] using established methods (Materials and Methods); the ϵCr values were obtained by thermal ionization mass spectrometry (TIMS) at Tokyo Tech and by multi-collector (MC)-ICP-MS at ASU, while the ϵTi values were obtained by MC-ICP-MS at University of Tokyo and at ASU. The measured values in each laboratory agree within the uncertainties for the Ryugu and carbonaceous chondrite samples (tables S1 to S3). The ϵCr and ϵTi values reported in Table 1 are the averages of the mean value of the replicate measurements for a given sample performed at each laboratory.

The five different Ryugu samples display variable $\epsilon^{53}\text{Cr}$ values (from $+0.09 \pm 0.05$ to $+0.33 \pm 0.04$) that are generally correlated with the $^{55}\text{Mn}/^{52}\text{Cr}$ ratio (Fig. 1), suggesting radiogenic ingrowth of ^{53}Cr due to ^{53}Mn decay. Triplicate measurements of the CI chondrite Orgueil show subtle differences in $^{55}\text{Mn}/^{52}\text{Cr}$ and $\epsilon^{53}\text{Cr}$ values, although each sample was prepared from a single powdered aliquot of this chondrite (table S4). Such differences are also observed for another CI chondrite, Alais. Except for C0002, all Ryugu samples have $^{55}\text{Mn}/^{52}\text{Cr}$ ratios that are higher than those of the CI chondrites, while the range of $\epsilon^{53}\text{Cr}$ in these four Ryugu samples ($+0.25 \pm 0.03$ to $+0.33 \pm 0.04$) overlaps with that of CI chondrites ($+0.15 \pm 0.05$ to $+0.31 \pm 0.06$) (Fig. 1). The three C2 chondrites (Tarda, Tagish Lake, and Murchison) have identical $\epsilon^{53}\text{Cr}$ values and $^{55}\text{Mn}/^{52}\text{Cr}$ ratios within error. The Allende CV3 chondrite has the lowest $^{55}\text{Mn}/^{52}\text{Cr}$ and $\epsilon^{53}\text{Cr}$ values among all the samples analyzed in this study. The $^{55}\text{Mn}/^{52}\text{Cr}$ and $\epsilon^{53}\text{Cr}$ values for the carbonaceous chondrites analyzed here are generally consistent with those reported in previous studies as summarized in (17).

The five Ryugu samples show a relatively large variation in $\epsilon^{54}\text{Cr}$ ($+1.22 \pm 0.06$ to $+2.22 \pm 0.13$), but the range in $\epsilon^{50}\text{Ti}$ ($+1.63 \pm 0.11$ to $+1.94 \pm 0.14$) is small compared to the analytical uncertainties (Fig. 2). This is also the case for CI chondrites, which have variable

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Table 1. Cr and Ti isotopic ratios and $^{55}\text{Mn}/^{52}\text{Cr}$ ratios of Ryugu samples and carbonaceous chondrites. See Materials and Methods for the definition of $\epsilon^{53}\text{Cr}$, $\epsilon^{54}\text{Cr}$, and $\epsilon^{50}\text{Ti}$.

Samples	Sample mass	Digestion method	$^{55}\text{Mn}/^{52}\text{Cr}$	$\epsilon^{53}\text{Cr}^*$	$\epsilon^{54}\text{Cr}^*$	$\epsilon^{50}\text{Ti}^*$
<i>Ryugu</i>						
A0106-A0107 [†]	23.88 mg	Acid	1.166 ± 0.015	0.32 ± 0.03	1.23 ± 0.06	1.65 ± 0.16
C0108 [†]	22.24 mg	Acid	0.914 ± 0.014	0.25 ± 0.03	1.22 ± 0.06	1.94 ± 0.14
A0106 [‡]	14.61 mg	Acid	1.508 ± 0.005	0.33 ± 0.04	1.66 ± 0.07	1.63 ± 0.11
C0107 [‡]	12.78 mg	Acid	1.144 ± 0.003	0.26 ± 0.04	1.87 ± 0.14	1.86 ± 0.14
C0002	6.85 mg	Alkali fusion	0.673 ± 0.002	0.09 ± 0.05	2.22 ± 0.13	
A0022 [§]	0.444 mg	Acid			1.49 ± 0.16	
C0081 [§]	0.457 mg	Acid			1.77 ± 0.10	
Average Ryugu				0.27 ± 0.02	1.52 ± 0.04	1.77 ± 0.07
<i>Carbonaceous chondrites</i>						
Orgueil-1 (CI1)	20.82 mg	Acid	0.834 ± 0.021	0.31 ± 0.06	0.84 ± 0.14	2.12 ± 0.17
Orgueil-2 (CI1)	10.40 mg	Acid	0.782 ± 0.030	0.22 ± 0.06	1.49 ± 0.14	1.93 ± 0.14
Orgueil-3 (CI1)	9.67 mg	Alkali fusion	0.771 ± 0.003	0.15 ± 0.05	1.47 ± 0.13	
Alais-1 (CI1)	21.98 mg	Acid	0.807 ± 0.019	0.27 ± 0.05	0.90 ± 0.10	2.03 ± 0.14
Alais-2 (CI1)	10.15 mg	Acid	0.788 ± 0.032	0.24 ± 0.09	1.50 ± 0.17	1.85 ± 0.14
Alais-3 (CI1)	7.85 mg	Alkali fusion	0.779 ± 0.002	0.17 ± 0.05	1.52 ± 0.13	
Tarda (C2-ung)	25.10 mg	Acid	0.589 ± 0.010	0.22 ± 0.06	0.99 ± 0.14	2.65 ± 0.14
Tagish Lake (C2-ung)	24.29 mg	Acid	0.622 ± 0.014	0.20 ± 0.05	1.00 ± 0.11	2.61 ± 0.18
Murchison (CM2)	24.76 mg	Acid	0.574 ± 0.011	0.17 ± 0.04	0.94 ± 0.08	2.90 ± 0.12
Allende (CV3)	64.68 mg [¶]	Acid	0.454 ± 0.001	0.02 ± 0.03	0.85 ± 0.08	3.36 ± 0.27

*Average of the mean value of the replicate measurements for a given sample performed at each laboratory (tables S1 to S3). †Including extra measurements for $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$ in addition to those reported in (3). See tables S1 and S2. ‡SOM (soluble organic matter) extracted residues. §Data from (4). ||Weighted average considering the mass of each sample. ¶Average of the mean value of the replicate measurements for Allende-1 (24.92 mg) and Allende-2 (39.76 mg).

$\epsilon^{54}\text{Cr}$ (+0.84 ± 0.14 to +1.52 ± 0.13) but relatively homogeneous $\epsilon^{50}\text{Ti}$ (+1.85 ± 0.14 to +2.12 ± 0.17). Compared to Ryugu, the other four carbonaceous chondrites (Tarda, Tagish Lake, Murchison, and Allende) display lower $\epsilon^{54}\text{Cr}$ and higher $\epsilon^{50}\text{Ti}$ values, presenting a negative correlation between $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$. Except for the $\epsilon^{54}\text{Cr}$ values of Orgueil-1 and Alais-1, the $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$ values for the carbonaceous chondrites analyzed in this study are generally in good agreement with those reported in the previous studies (table S5 and Fig. 2).

DISCUSSION

^{53}Mn - ^{53}Cr systematics of Ryugu samples

Figure 1 shows a plot of $\epsilon^{53}\text{Cr}$ versus $^{55}\text{Mn}/^{52}\text{Cr}$ for the five Ryugu samples and six carbonaceous chondrites analyzed in this study. Four of five Ryugu samples (A0106, A0106-A0107, C0107, and C0108) plot to the right of the carbonaceous chondrites, while the C0002 sample has $^{55}\text{Mn}/^{52}\text{Cr}$ and $\epsilon^{53}\text{Cr}$ values lower than those of CI chondrites. The regression line for the five Ryugu samples yields a slope of $(^{53}\text{Mn}/^{55}\text{Mn})_i = (2.6 \pm 0.7) \times 10^{-6}$, corresponding to the CAI relative age of $5.2_{-1.4}^{+1.8}$ Ma when the D'Orbigny angrite is used as an anchor (18, 19). Considering the small sample masses used in this study (<24 mg each), the variability in $^{55}\text{Mn}/^{52}\text{Cr}$ and $\epsilon^{53}\text{Cr}$ values among the different Ryugu samples likely stems from the

lithological differences between these samples. These differences appear to be largely controlled by the abundance of secondary carbonates with elevated Mn/Cr ratios as evidenced by the correlation between CI-normalized Mn/Cr and Fe/Mn ratios for bulk Ryugu samples (fig. S1). Therefore, the ^{53}Mn - ^{53}Cr age obtained in this study most likely represents the timing of carbonate precipitation in Ryugu samples during parent body aqueous alteration.

The ^{53}Mn - ^{53}Cr age of bulk Ryugu fragments obtained in this study [$(^{53}\text{Mn}/^{55}\text{Mn})_i = (2.6 \pm 0.7) \times 10^{-6}$] is in good agreement with that of carbonates in Ryugu samples reported in (3) [$(^{53}\text{Mn}/^{55}\text{Mn})_i = (2.55 \pm 0.35) \times 10^{-6}$; $5.2_{-0.7}^{+0.8}$ Ma] but is younger than those reported in (16) [$(^{53}\text{Mn}/^{55}\text{Mn})_i = (6.8 \pm 0.5) \times 10^{-6}$; 0.4 ± 0.4 Ma], ($^{53}\text{Mn}/^{55}\text{Mn})_i = (6.1 \pm 0.9) \times 10^{-6}$; 1.0 ± 0.8 Ma], and in (4) [$(^{53}\text{Mn}/^{55}\text{Mn})_i = (4.14 \pm 0.68) \times 10^{-6}$; $2.6_{-0.8}^{+1.0}$ Ma]. This is opposite to expectations as bulk rock samples should have been closed to exchange earlier than carbonates measured in situ. All previously reported ^{53}Mn - ^{53}Cr ages were determined by in situ measurements of carbonates (mostly dolomites) using secondary ion mass spectrometry (SIMS). The age difference between the three studies may be due to the use of different standard materials in each study, resulting in different instrumental correction factors (relative sensitivity factors) used to determine the Mn/Cr ratio of the carbonates. In this study, the Mn/Cr ratios of the Ryugu samples were measured by ICP-MS without the matrix

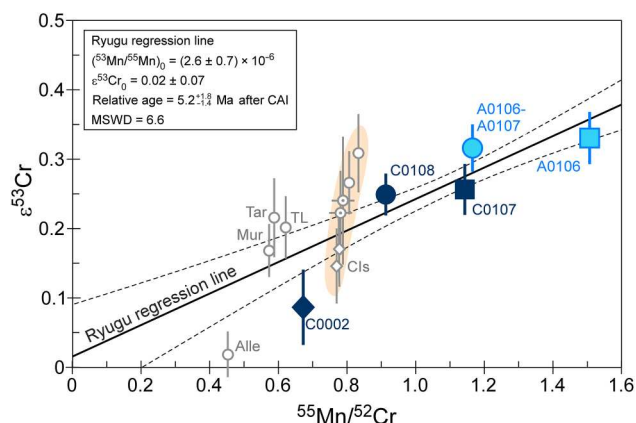


Fig. 1. ^{53}Mn - ^{53}Cr isotope systematics of Ryugu (large symbols) and carbonaceous chondrites (small gray symbols) measured in this study. Circle and diamond symbols represent acid-digested and alkali fusion-digested samples, respectively. Square symbols represent SOM extracted samples digested by acids. Mur, Murchison; Tar, Tarda; TL, Tagish Lake; Alle, Allende. Cls are Orgueil and Alais. The bold line and dotted curves represent a regression line for the five Ryugu samples and the error envelopes, respectively, which were determined using an algorithm of the ISOPLOT software (49). The regression line for the carbonaceous chondrites is shown in fig. S5. MSWD, mean square weighted deviation.

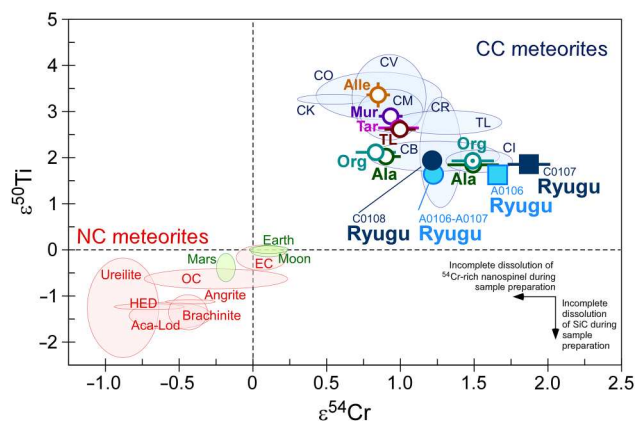


Fig. 2. $\epsilon^{50}\text{Ti}$ versus $\epsilon^{54}\text{Cr}$ diagram for Ryugu and meteorites. Ellipses represent the 2SD of the literature data for each meteorite group (table S5), with two-sigma rejection of outliers in the literature data. Abbreviations Mur, Tar, TL, and Alle are the same as Fig. 1, and Org and Ala stand for Orgueil and Alais, respectively. HED and Aca-Lod represents Howardite-Eucrite-Diogenite and Acapulcoite-Lodranite, respectively. Vertical and horizontal arrows indicate the isotopic shifts due to the incomplete dissolution of presolar SiC and ^{54}Cr -rich nanospinel grains, respectively.

matching problem commonly encountered in SIMS measurements. However, a subtle dispersion of Ryugu data points is observed around the ^{53}Mn - ^{53}Cr isochron (Fig. 1), as indicated by the relatively large mean square weighted deviation ($= 6.6$). This may be due to the incorporation of carbonates that precipitated at different times (20) or the presence of non-isochronous materials in bulk Ryugu samples that are unrelated to the precipitation of carbonates.

Variation of $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$ values in Ryugu samples

Figure 2 shows a plot of $\epsilon^{50}\text{Ti}$ versus $\epsilon^{54}\text{Cr}$ for the Ryugu samples and carbonaceous chondrites obtained in this study. One Ryugu sample (C0002) and two CI chondrites (Orgueil-3 and Alais-3) that were digested by the alkali fusion method are not plotted in this figure because $\epsilon^{50}\text{Ti}$ values were not measured. The ellipses in this figure represent the 2SDs of $\epsilon^{50}\text{Ti}$ and $\epsilon^{54}\text{Cr}$ values from the literature data for the various meteorite groups and terrestrial samples (table S5). Although Ryugu samples chemically and mineralogically resemble CI chondrites (3), the Ryugu fragments have variable Cr isotopic compositions. The $\epsilon^{54}\text{Cr}$ values previously reported for two Ryugu samples (A0106-A0107 and C0108) (3) are slightly lower than CIs and plot in the region of CB or CR chondrites. Conversely, one TD2 sample (C0107) has an $\epsilon^{54}\text{Cr}$ value higher than the mean value for CIs, and another TD2 sample digested by the alkali fusion method (C0002, not shown in Fig. 2) has a much higher $\epsilon^{54}\text{Cr}$ value (of $+2.22 \pm 0.13$; Table 1) than other chondrites. It should be noted that the $\epsilon^{50}\text{Ti}$ values for the four Ryugu samples are within the range of previously reported CI data (table S5). The $\epsilon^{54}\text{Cr}$ values for two CI chondrite fractions analyzed in this study (Orgueil-1 and Alais-1) are somewhat lower than the values previously reported for CIs, while the other two fractions of these same CIs (Orgueil-2 and Alais-2) have $\epsilon^{50}\text{Ti}$ and $\epsilon^{54}\text{Cr}$ values consistent with literature data. In addition, two other CI chondrite fractions decomposed by the alkali fusion method have $\epsilon^{54}\text{Cr}$ values consistent with literature data (Orgueil-3 = $+1.47 \pm 0.13$, Alais-3 = $+1.52 \pm 0.13$; Table 1). The $\epsilon^{50}\text{Ti}$ and $\epsilon^{54}\text{Cr}$ values for the other carbonaceous chondrites (Murchison, Tagish Lake, and Allende) are in good agreement with previously reported values. Therefore, apparent discrepancies with literature data affect exclusively $\epsilon^{54}\text{Cr}$ values in some Ryugu and CI samples.

The observed variability in $\epsilon^{54}\text{Cr}$ values among the Ryugu samples and CI chondrites is an intrinsic property of individual samples, most likely reflecting the heterogeneous distribution of ^{54}Cr -rich and ^{54}Cr -poor phases at a millimeter scale. This interpretation is supported by the variation in $\epsilon^{54}\text{Cr}$ values of CI chondrites measured in sample aliquots of <100 mg (fig. S2). Previous studies of the Cr isotopic composition of acid leachates and residues from CI chondrites aid in constraining the anomalous ^{54}Cr carriers residing in CI chondrites and Ryugu. Sequential acid leaching of bulk CI chondrites showed that most of the earlier fractions obtained by mild acid leaching (e.g., acetic acid and cold and dilute HNO_3) were characterized by negative $\epsilon^{54}\text{Cr}$ values down to -8 (21–23). In contrast, the $\epsilon^{54}\text{Cr}$ values increased gradually with acid strength, reaching the largest value of approximately $+100$ or more at a step where hot HCl and/or HF were used. Therefore, phases with negative $\epsilon^{54}\text{Cr}$ values are considered to be distributed in easily leachable minerals in the Ryugu samples and CI chondrites.

Exposure to galactic cosmic rays or incomplete digestion of presolar grains could also induce variations in $\epsilon^{54}\text{Cr}$ values that would not be intrinsic to the samples, but we can rule out these processes because they fail to quantitatively account for the variations documented here. The cosmogenic production of Cr isotopes via spallation of Fe and Ni isotopes has been commonly observed in extraterrestrial samples with long cosmic-ray exposure (CRE) ages (>100 Ma) and elevated Fe/Cr and Ni/Cr ratios (24–26). Noble gas analyses indicate short CRE ages of 5 Ma for Ryugu samples (27). Given the Fe/Cr ratio of ~ 70 and the short CRE age of 5 Ma for bulk Ryugu samples, the correction for the Fe spallation effect by a

traditional method (22, 28) resulted in -0.0043 for $\epsilon^{54}\text{Cr}$, which is negligible.

As described below, incomplete dissolution of samples containing refractory presolar grains can also be ruled out as an explanation for the measured $\epsilon^{54}\text{Cr}$ variations in bulk Ryugu samples. Presolar grains are micrometer- to submicrometer-sized minerals that condensed in stellar outflows that predated Solar System formation (29). Incomplete dissolution of acid-resistant presolar grains documented in Ryugu (30, 31) can potentially result in biased results that are not representative of the bulk isotopic composition. The Ryugu sample C0002 was decomposed by an alkali fusion method that can completely dissolve acid-resistant presolar grains. It shows a distinctly higher $\epsilon^{54}\text{Cr}$ value ($+2.22 \pm 0.13$) compared to those of the other Ryugu samples dissolved by acids ($+1.22 \pm 0.06$ to $+1.87 \pm 0.14$) (Table 1). Therefore, if incomplete dissolution had occurred, then the undissolved phase would need to be enriched in ^{54}Cr . NanoSIMS imaging of acid residues from CI chondrites revealed the presence of Cr-oxide particles with large ^{54}Cr excesses up to $\epsilon^{54}\text{Cr} = +5.6 \times 10^5$ (32–34). Most of the Cr-oxide particles likely carrying excess ^{54}Cr were smaller than 100 nm and were fully digested by hot HCl treatment (33) and thus could not survive the acid digestion performed in this study. Although some large Cr-oxide grains (up to 300 nm) were found in the CI acid residues, these grains are rare (10 of 60,000 Cr-rich grains identified in the images) and less anomalous in ^{54}Cr ($\epsilon^{54}\text{Cr} = +8200 \pm 8200$, 1SD) compared to the most anomalous ^{54}Cr -rich presolar grain (34). Therefore, incomplete dissolution of Cr-oxide particles with large ^{54}Cr excesses cannot explain the observed $\epsilon^{54}\text{Cr}$ variation in the bulk Ryugu samples. The incomplete dissolution scenario requires the presence of an undefined ^{54}Cr -rich phase that is at least as acid-resistant as SiC, although presolar SiC grains are highly depleted in Cr ($\sim 1 \mu\text{g/g}$) (35) and their contribution to bulk analyses is negligible.

Influence of aqueous alteration on $\epsilon^{54}\text{Cr}$ values in Ryugu samples

As illustrated in Fig. 3, $\epsilon^{54}\text{Cr}$ values are weakly negatively correlated with $\epsilon^{53}\text{Cr}$ values in the bulk Ryugu samples and CI chondrites.

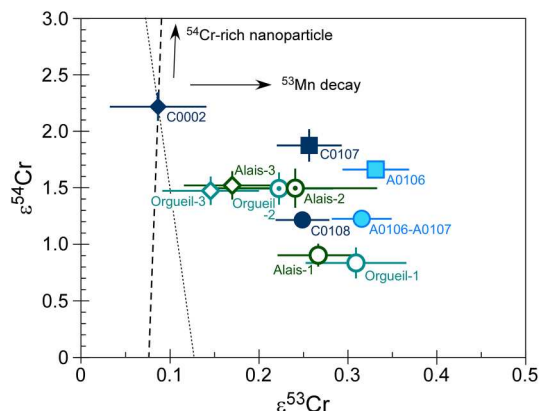


Fig. 3. $\epsilon^{54}\text{Cr}$ versus $\epsilon^{53}\text{Cr}$ diagram for Ryugu and CI chondrites. Dashed line represents the mixing line between the Ryugu sample (C0002) and the ^{54}Cr -rich presolar nanoparticles (34). Thin dotted line is the mixing line between C0002 and the ^{54}Cr -rich nanoparticles assuming that the particles have a terrestrial $^{50}\text{Cr}/^{52}\text{Cr}$ ratio.

Such a negative correlation can be observed in acid leachates and residues of CM chondrites, suggesting the coexistence of ^{53}Cr -rich/ ^{54}Cr -poor and ^{53}Cr -poor/ ^{54}Cr -rich components in the chondrites (36). Previously documented ^{54}Cr -rich presolar grains have a slightly lower $^{53}\text{Cr}/^{52}\text{Cr}$ ratio than the solar value, on average, but show large excesses at mass 50, which may or may not be due to ^{50}Cr , so mixing between the Ryugu sample (C0002) and these grains would result in a positive correlation between $\epsilon^{53}\text{Cr}$ - $\epsilon^{54}\text{Cr}$ (dashed line in Fig. 3) if one uses a terrestrial $^{50}\text{Cr}/^{52}\text{Cr}$ ratio in the internal normalization of the Cr isotope measurements. Therefore, radiogenic ingrowth of ^{53}Cr from the decay of ^{53}Mn is required to explain the anticorrelation between the samples with elevated $\epsilon^{53}\text{Cr}$ values and Ryugu C0002, which has the lowest $\epsilon^{53}\text{Cr}$ value (Fig. 3). The most straightforward explanation to the negative correlation between $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ is that it represents a mixing line between ^{53}Cr -rich/ ^{54}Cr -poor labile Cr in secondary phases represented by dolomite and the complementary ^{53}Cr -poor/ ^{54}Cr -rich component documented in previous studies during leaching of carbonaceous chondrites. Another observation that corroborates this interpretation is that ^{53}Cr -rich/ ^{54}Cr -poor samples tend to have Ti/Cr ratios that are higher than that of Ryugu C0002 (fig. S3), indicating that these samples presumably have lithologies that are enriched in Ti-bearing secondary phases (e.g., magnetite and pyrrhotite) that coprecipitated with dolomite during the aqueous alteration of the parent body.

These observations suggest that the millimeter-scale $\epsilon^{54}\text{Cr}$ variability in the bulk Ryugu samples and CI chondrites was primarily caused by the fluid-driven decoupling via parent body aqueous alteration between Cr in chemically labile phases with a slightly negative $\epsilon^{54}\text{Cr}$ value and ^{54}Cr -rich Cr-oxide nanoparticles. Pervasive aqueous alteration in the Ryugu parent body released Cr with a negative $\epsilon^{54}\text{Cr}$ value from chemically labile phases (e.g., olivine and amorphous silicates), whereas ^{54}Cr -rich presolar nanoparticles were largely unaffected. Chromium dissolved in the aqueous fluid was incorporated in secondary dolomite as well as magnetite and pyrrhotite at ~ 5 Ma after Solar System birth (Fig. 1). This process led to physicochemical fractionation between the ^{54}Cr -rich presolar nanoparticles and secondary minerals at a millimeter scale in the bulk samples, resulting in $\epsilon^{53}\text{Cr}$ - $\epsilon^{54}\text{Cr}$ variations in bulk fragments.

The above scenario is supported by a mass balance calculation using the abundances of Ti, Cr, and Mn in the bulk Ryugu samples, CI chondrites, and the secondary minerals (dolomite, magnetite, and pyrrhotite) in Ryugu (37), as well as the $\epsilon^{53}\text{Cr}$ and $\epsilon^{54}\text{Cr}$ values in these samples (Supplementary Text). The result shows that the ^{53}Cr -rich/ ^{54}Cr -poor samples contain more secondary minerals of dolomite by 3.2% and magnetite + pyrrhotite by 4.2% compared to the most ^{53}Cr -poor/ ^{54}Cr -rich Ryugu sample C0002, and the secondary minerals were calculated to have a negative value of $\epsilon^{54}\text{Cr} = -19$ (table S6). Such variations in mineral abundances are within the observed range of secondary mineral abundances in Ryugu fragments: carbonate = 0.63 to 6.93%, magnetite = 0.47 to 6.47%, and Fe-sulfide = 1.11 to 5.24% (4). Unlike $\epsilon^{54}\text{Cr}$, the variation of $\epsilon^{50}\text{Ti}$ values in the bulk Ryugu samples and CI chondrites is relatively small. Overall, the observed Cr isotopic variability in the bulk Ryugu samples and CI chondrites shows that isotopic heterogeneities in asteroids are not all nebular or accretionary in nature as can also reflect elemental redistribution by aqueous fluid.

Representative Cr and Ti isotopic compositions in returned Ryugu samples

The present study found that Ryugu samples < 24 mg have variable $\epsilon^{54}\text{Cr}$ values that exceed the dispersion of previously reported values for CI chondrites. However, the variation in $\epsilon^{50}\text{Ti}$ values is relatively small, and the data obtained agree well with the literature values for CIs. To obtain representative isotopic compositions of the returned Ryugu materials, we calculated the weighted means of the $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$ values by the sample mass dissolved for the isotopic measurements (Table 1). Two $\epsilon^{54}\text{Cr}$ values determined by (4) were included in the calculation. The calculated $\epsilon^{54}\text{Cr}$ and $\epsilon^{50}\text{Ti}$ values, corresponding to a total of ~90 mg of bulk Ryugu sample, are consistent with the CI values (fig. S4), further corroborating the isotopic similarity between Ryugu and CI chondrites. Therefore, we conclude that the source materials of Ryugu and CI chondrites share a common genetic heritage, consistent with previous studies (3–5, 11, 12, 38, 39).

The stable isotopic compositions of extraterrestrial samples are valuable tools in determining the origin and evolution of extraterrestrial materials. However, small-scale sample heterogeneity can lead to biased results in the isotopic compositions, specifically for unequilibrated materials with a petrologic grade of 1 or 2. Most studies have focused on solar nebula or planetary processes to explain isotopic heterogeneities in meteorites, and our results show that parent-body aqueous alteration can create spurious isotopic anomalies. To obtain unbiased isotopic compositions in future analyses of returned materials, such as for the OSIRIS-REx mission, it is strongly recommended that a thoroughly homogenized powder be prepared using at least ~100 mg of the material before dissolution and chemical processing.

MATERIALS AND METHODS

Samples

The samples investigated in this study are summarized in table S1. These include two Ryugu samples from the first touchdown site (small grain aggregates: A0106 and A0106-A0107), three Ryugu samples from the second touchdown site (small grain aggregates: C0107 and C0108; individual grain: C0002), two CI chondrites (Orgueil and Alais), two C2-ungrouped chondrites (Tarda and Tagish Lake), one CM chondrite (Murchison), and one CV chondrite (Allende).

The Ryugu sample A0106-A0107 was a powdered material prepared from a mixed aggregate of A0106 (1.6 mg) and A0107 (27 mg), such that 94% of this material was composed of A0107. The sample C0108 was a powdered material retrieved from a sealed cell used in the x-ray fluorescence analysis (3). The sample C0002 was a coarse-grained material (93.5 mg) embedded in an epoxy resin (EpoxiCure 2, Buehler). We used a small piece of this sample by extracting fragments from the resin using a tungsten carbide needle; total weight collected of this sample was 6.85 mg.

The Ryugu samples A0106 and C0107 were residues obtained after extracting soluble organic matter (SOM) using hexane, dichloromethane, and methanol (40). There are no systematic studies that report the removal rate of each element in individual extraction processes of carbonaceous chondrites with the organic solvents. Therefore, we have conducted an SOM extraction test using 43.73 mg of powdered Tagish Lake. This meteorite is a type 2 ungrouped carbonaceous chondrite that bears lithological and

mineralogical similarities to CI chondrites and Ryugu. Tagish Lake is a breccia at all scales, and its major constituent is a fine-grained opaque matrix consisting mainly of phyllosilicates (saponite and serpentine), Fe-Ni sulfides, magnetite, and sparse carbonates (41). Although there are subtle differences between Tagish Lake and Ryugu in terms of the presence of sparse chondrule-like objects and altered CAIs in the former, we consider Tagish Lake an analog of Ryugu for the SOM extraction test to evaluate the behavior of elements during this extraction process. As shown in table S7, which lists the yields of 16 elements in individual organic solvents, the total amounts of Ti, Cr, and Mn removed by the three-step SOM extraction procedures were less than 0.1%. The low solubilities of Ti, Cr, and Mn in the organic solvents used suggest that the isotopic systematics of Ti and Cr in the Ryugu samples A0106 and C0107 were not disturbed by the SOM extraction procedures.

Sample dissolution and chemical separation

Acid digestion

Four Ryugu samples (A0106, A0106-A0107, C0107, and C0108) and six carbonaceous chondrites were digested by acids, and chemical separations were conducted on these samples as described in (3). It is noted that the aliquots of purified Ti and Cr from A0106-A0107 and C0108 analyzed in this study were splits from the purified Ti and Cr obtained by (3) from these two samples. Briefly, the powdered samples were weighed in Teflon vials and heated with a mixture of HF and HNO_3 at 180°C. For the replicate analysis of two CI chondrites (Orgueil-2 and Alais-2), the vial was heated at 200°C at this step. After digestion with HF and HNO_3 , the samples were further treated with a mixture of HNO_3 and HCl, followed by treatment with a mixture of HNO_3 and H_2O_2 . After the final treatment with HNO_3 , the samples were dissolved in 5 ml of 0.5 M HNO_3 ; the five-step column chemistry procedures were then performed on 80% of this solution, while the remainder was used for the determination of elemental abundances and Mn/Cr ratios via ICP-MS.

Alkali fusion digestion

One Ryugu sample (C0002) and two CI chondrites (Orgueil and Alais) were digested by an alkali fusion method to determine the Cr isotopic ratios. The sample powder and an alkali flux (99.999% Na_2CO_3 , Merck Millipore) were mixed in a ratio of 1:5. The mixture was thoroughly homogenized in an agate mortar using an agate pestle, and then the mixture was transferred to a Zr-free, high-purity Pt crucible. The crucible was covered with a Pt lid and heated with a propane torch for 15 min by gradually increasing the gas power, reaching a temperature of over 1000°C. After cooling to room temperature, the fused sample was transferred to a clean Teflon vial with 1.5 ml of H_2O . Then, 2.0 ml of 6 M HCl was slowly added to facilitate complete sample dissolution. The sample solution was dried at 90°C and then redissolved in 5 ml of 0.5 M HNO_3 . Column chemistry procedures were subsequently performed on 90% of this solution, and the remainder was used for the determination of elemental abundances and Mn/Cr ratios via ICP-MS. The Cr procedural blank for the alkali fusion digestion was 1.8 ng and is negligible as compared to the total Cr in the decomposed sample (~16 μg).

The 90% aliquot was dried and dissolved in 1 ml of 12 M HNO_3 . After centrifuging the solution, the supernatant was loaded onto 1.8 ml of extraction chromatographic resin ("DGA-Normal Resin"; 50 to 100 μm , Eichrom Technologies Inc., USA) in a polypropylene

column. Major elements including Cr were collected with the subsequent elution of 11 ml of 12 M HNO₃, followed by the collection of Fe with 12 ml of 3 M HNO₃–0.2 M HF. The first fraction containing major elements and Cr was dried and then dissolved with 1 ml of 1 M HNO₃–10% H₂O₂. Subsequent procedures for the chemical separation of Cr were the same as described in (3).

Mass spectrometry

Measurement of Mn/Cr ratios using ICP-MS

The Mn/Cr ratios of the Ryugu and chondrite samples were measured by a quadrupole-type ICP-MS (iCAP TQ; Thermo Fisher Scientific) at Tokyo Tech. After sample dissolution, an aliquot of the sample solution, removed before conducting the chemical separation procedure, was conditioned in 0.5 M HNO₃ with a dilution factor of 100,000. The sample solution was introduced into the ICP-MS through a MicroMist quartz nebulizer equipped with a Cyclonic quartz spray chamber at an uptake rate of 0.4 ml/min. The isotopes of ⁵²Cr and ⁵⁵Mn were monitored alternately with an integration time of 10 ms for each mass per scan, 100 scans per run, and 30 runs per measurement. The data were acquired in the SQ-HeKED (single quadrupole; helium collision gas; kinetic energy discrimination) mode, in which argon- and oxygen-based polyatomic interferences (e.g., ¹²C⁴⁰Ar, ¹⁶O³⁶Ar, and ³⁹K¹⁶O) were reduced. The Mn/Cr ratio of the sample was determined against the calibration curve created by measuring four standard solutions (Mn/Cr = 0.25, 0.5, 1.0, and 2.0). Analytical uncertainty of the Mn/Cr ratio was determined by the 2SE of 30 runs, which was less than 2.5%.

Chromium isotopic measurements using TIMS at Tokyo Tech

The Cr isotopic compositions in the Ryugu samples and carbonaceous chondrites were measured by a TIMS instrument (Triton-Plus; Thermo Fisher Scientific) installed at Tokyo Tech (table S1). The details of the measurement protocol are described in (42). Briefly, the purified Cr sample (2.5 to 3.0 μg per measurement) was loaded onto a prebaked single W filament together with Al and B-doped silica gel as an activator. The filament was first heated to 1000°C, followed by the gentle heating of the filament until a stable Cr⁺ beam was obtained at ~1200°C. The isotopic ratios of Cr (⁵⁰Cr/⁵²Cr, ⁵³Cr/⁵²Cr, and ⁵⁴Cr/⁵²Cr) were acquired by multistatic methods with a three-line cup setting. The effect of mass fractionation during the TIMS measurement was corrected with the exponential law by assuming that ⁵⁰Cr/⁵²Cr = 0.051859 (43). The ⁵³Cr/⁵²Cr and ⁵⁴Cr/⁵²Cr isotopic ratios in Ryugu and chondrite samples are reported in the ε unit defined as follows

$$\epsilon^i\text{Cr} = \left(\frac{i\text{Cr}/^{52}\text{Cr}_{\text{sample}}}{i\text{Cr}/^{52}\text{Cr}_{\text{NIST979}}} - 1 \right) \times 10^4 \quad i = 53, 54$$

Analytical uncertainties for the Ryugu samples are either the 2SD of multiple sample measurements or the largest analytical uncertainty in multiple campaigns of NIST SRM 979 measurements, whichever is larger.

Titanium isotopic measurements using MC-ICP-MS at University of Tokyo

The Ti isotopic compositions in the Ryugu and chondrite samples were measured by an MC-ICP-MS instrument (Neptune-Plus; Thermo Fisher Scientific) installed at the University of Tokyo (table S2). The purified Ti fraction was dried and dissolved in 0.5 M HNO₃–0.001 M HF to a concentration of 150 ng/ml. The dissolved sample was introduced into the MC-ICP-MS using a Cetac

Aridus II desolvating nebulizer with an uptake rate of ~0.15 ml/min. Measurements were performed using a Jet sample cone and an X skimmer cone with medium mass resolution, which resulted in ⁴⁸Ti signal intensities of ~2.5 × 10⁻¹⁰ A. All five Ti isotopes together with ⁴³Ca, ⁵¹V, and ⁵³Cr were monitored in a dynamic mode using Faraday cups. Amplifiers with 10¹¹ ohm resistors were connected to the Faraday cups monitoring Ti isotopes and ⁵¹V, whereas those with 10¹³ ohm resistors were used for ⁴³Ca and ⁵³Cr. Data were acquired from 40 cycles, 2 lines/cycle, 8.4 s integration per line, and 4-s idle time between lines. Instrumental mass fractionation was corrected relative to ⁴⁹Ti/⁴⁷Ti = 0.749766 (44) with an exponential law. Isobaric interferences on Ti isotopes from ⁴⁶Ca, ⁴⁸Ca, ⁵⁰V, and ⁵⁰Cr were corrected assuming that the mass bias factors of Ca, V, and Cr were identical to that of Ti. For the correction, the literature values of ⁵⁰V/⁵¹V = 0.0251 (45) and ⁵⁰Cr/⁵³Cr = 0.45732 (43) were used, whereas Ca isotope ratios were artificially modified to ⁴⁶Ca/⁴³Ca = 0.02365 and ⁴⁸Ca/⁴³Ca = 1.4039, which eliminates artificial isotopic anomalies for Ca-doped Ti standard solutions. Individual sample measurements were bracketed by analyses of an Alfa Aesar standard solution. The Ti isotopic ratios of samples were determined relative to the standard runs and are reported in the ε unit defined as follows

$$\epsilon^i\text{Ti} = \left(\frac{i\text{Ti}/^{47}\text{Ti}_{\text{sample}}}{i\text{Ti}/^{47}\text{Ti}_{\text{standard}}} - 1 \right) \times 10^4 \quad i = 46, 48, 50$$

Analytical uncertainties on the sample Ti isotope ratios were determined by propagating the internal precisions (2 SEs) and the dispersion of the mean of the bracketing standard analyses (2SE).

Titanium isotopic measurements using MC-ICP-MS at ASU

The titanium isotope compositions of aliquots of purified Ti from four Ryugu fractions (A0106, A0106-A0107, C0107, and C0108) and six carbonaceous chondrites (Orgueil-1, Alais-1, Tarda, Tagish Lake, Murchison, and Allende) were determined using an MC-ICP-MS instrument (Neptune XT; Thermo Fisher Scientific) in the Isotope Cosmochemistry and Geochronology Laboratory at ASU (table S3). The mass spectrometry protocols used for these measurements were similar to those reported previously (46, 47), although the sample solutions were run at lower concentrations in the current study. Titanium isotope analyses were conducted using a Jet sample cone and an H skimmer cone in high-resolution mode (i.e., with a mass resolving power > 8000). Samples were introduced via a Cetac Aridus3 desolvating nebulizer attached to a self-aspirating perfluoroalkoxy alkane (PFA) nebulizer with an uptake rate of 50 μl/min. Uptake and wash times of 60 and 90 s were used, respectively, between consecutive sample and standard measurements. Each run for a sample, standard, or blank comprised 20 cycles with an 8.4-s integration time per cycle. Purified Ti samples and standards were analyzed at a concentration of 250 ng/ml, and the typical sensitivity resulted in a ⁴⁸Ti signal of ~12 V at this concentration (using a 10¹¹ ohm resistor in the Faraday cup amplifier). Data were collected by switching between two different cup configurations: The intensities of ⁴⁴Ca, ⁴⁶Ti, ⁴⁷Ti, ⁴⁸Ti, and ⁴⁹Ti were measured in the first cup configuration, followed by measurement of ⁴⁷Ti, ⁴⁹Ti, ⁵⁰Ti, ⁵¹V, and ⁵²Cr intensities with the second cup configuration. Intensities of ⁴⁴Ca, ⁵¹V, and ⁵²Cr were used to correct for isobaric interferences on the Ti masses. All the cup amplifiers used 10¹¹ ohm resistors. All data reduction was performed offline.

Mass-independent titanium isotopic compositions were measured relative to the NIST 3162a Ti standard after correction for

instrumental and natural mass-dependent fractionation using sample-standard bracketing. Internal normalization was performed assuming a $^{49}\text{Ti}/^{47}\text{Ti}$ ratio of 0.749766 for the terrestrial standard (44) and using an exponential mass fractionation law. As described above, sample $^{50}\text{Ti}/^{47}\text{Ti}$ ratios are reported in the ϵ unit defined as follows, with renormalization to the Alfa Aesar standard (48)

$$\epsilon^{46}\text{Ti} = \left(\frac{^{46}\text{Ti}/^{47}\text{Ti}_{\text{sample}}}{^{46}\text{Ti}/^{47}\text{Ti}_{\text{NIST3162a}}} - 1 \right) \times 10^4 + 0.04$$

$$\epsilon^{48}\text{Ti} = \left(\frac{^{48}\text{Ti}/^{47}\text{Ti}_{\text{sample}}}{^{48}\text{Ti}/^{47}\text{Ti}_{\text{NIST3162a}}} - 1 \right) \times 10^4 - 0.10$$

$$\epsilon^{50}\text{Ti} = \left(\frac{^{50}\text{Ti}/^{47}\text{Ti}_{\text{sample}}}{^{50}\text{Ti}/^{47}\text{Ti}_{\text{NIST3162a}}} - 1 \right) \times 10^4 + 0.28$$

The external reproducibility (2SD) based on repeat measurements using analytical conditions described above of pure synthetic Ti standards as well as terrestrial rock and Allende meteorite standards in this laboratory is ± 0.15 for $\epsilon^{50}\text{Ti}$ (2SD).

Chromium isotopic measurements using MC-ICP-MS at ASU

Chromium isotopic measurements of purified Cr from (A0106, A0106-A0107, C0107, and C0108) and six carbonaceous chondrites (Orgueil-1, Alais-1, Tarda, Tagish Lake, Murchison, and Allende) were conducted on a Thermo Neptune XT MC-ICPMS at ASU using a Jet sample cone and an H skimmer cone in high-resolution mode (table S6). Samples were introduced through a Cetac Aridus3 desolvating nebulizer attached to a self-aspirating PFA with an uptake rate of 50 $\mu\text{l}/\text{min}$. An uptake time of 60 s and a wash time of 90 s were used between consecutive sample and standard measurements. Each run for a sample, standard, or blank comprised 50 cycles with an 8.4-s integration time. Purified Cr samples and standards were analyzed at a concentration of 400 ng/ml, and the typical sensitivity for ^{52}Cr was ~ 25 V at this concentration (using a 10^{11} ohm resistor in the Faraday cup amplifier). The intensities of ^{50}Cr , ^{52}Cr , ^{53}Cr , and ^{54}Cr were measured, along with ^{49}Ti , ^{51}V , and ^{56}Fe to monitor and correct for isobaric interferences. All the cup amplifiers used 10^{11} ohm resistors. All data reduction was performed offline.

Mass-independent Cr isotopic compositions are reported relative to the NIST SRM 979 Cr standard after correction for instrumental and natural mass-dependent fractionation using sample-standard bracketing and internal normalization to $^{50}\text{Cr}/^{52}\text{Cr}$ ($=0.051859$) using the exponential law (43). Chromium isotopic anomalies are reported in ϵ notation, i.e., parts per ten thousand deviation from the standard as defined above (see the TIMS section). The external reproducibility (2SD) based on repeat measurements of pure synthetic Cr standards as well as the Allende reference powder in this laboratory under the analytical conditions described above is ± 0.07 for $\epsilon^{53}\text{Cr}$ and ± 0.13 for $\epsilon^{54}\text{Cr}$.

Supplementary Materials

This PDF file includes:

Supplementary Text

Figs. S1 to S6

Tables S1 to S9

References

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Water circulation in Ryugu asteroid affected the distribution of nucleosynthetic isotope anomalies in returned sample

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