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The Solar System calcium isotopic composition inferred from Ryugu samples

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Abstract

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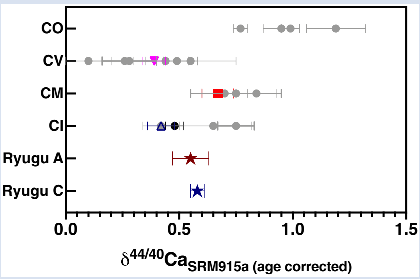

The Hayabusa2 spacecraft has returned samples from the Cb-type asteroid (162173) Ryugu to Earth. Previous petrological and chemical analyses support a close link between Ryugu and CI chondrites that are presumed to be chemically the most primitive meteorites with a solar-like composition. However, Ryugu samples are highly enriched in Ca compared to typical CI chondrites. To identify the cause of this discrepancy, here we report stable Ca isotopic data (expressed as $\delta^{44/40}Ca_{SRM915a}$) for returned Ryugu samples collected from two sites. We found that samples from both sites have similar $\delta^{44/40}Ca_{SRM915a}$ (0.58 ± 0.03 ‰ and 0.55 ± 0.08 ‰, 2 s.d.) that fall within the range defined by CIs. This isotopic similarity suggests that the Ca budget of CIs and Ryugu samples is dominated by carbonates, and the variably higher Ca contents in Ryugu samples are due to the abundant carbonates. Precipitation of carbonates on Ryugu likely coincided with a major episode of aqueous activity dated to have occurred ~5 Myr after Solar System formation. Based on the pristine Ryugu samples, the average $\delta^{44/40}Ca_{SRM915a}$ of the Solar System is defined to be 0.57 ± 0.04 ‰ (2 s.d.).

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Introduction

In December 2020, the JAXA Hayabusa2 spacecraft returned to Earth with the first samples collected from a Cb-type asteroid, (162173) Ryugu (Tachibana *et al.*, 2022; Yada *et al.*, 2022). Chemical, mineralogical, petrological, and isotopic analyses of these samples suggest that they are closely related to CI chondrites. In particular, their bulk Cr and Ti isotopic signatures and the chemical abundances of most elements are within the range of CI chondrites (Nakamura E. *et al.*, 2022; Yokoyama *et al.*, 2022). Among meteorites, CI chondrites have chemical compositions that most closely resemble the Sun; therefore, they are the most representative samples of the solar nebula composition with the exception of volatile elements (Palme *et al.*, 2014).

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Given that the Ryugu samples did not experience any terrestrial alteration, they are likely the chemically most pristine Solar System samples available estimating the original isotopic compositions of most elements in the Solar System (Yokoyama *et al.*, 2022).

Despite many aspects of similarities with the CIs, the Ryugu samples display an apparent excess of Ca by over 50 %, which may be related to a heterogeneous distribution of carbonates (dolomite and calcite) (Nakamura T. *et al.*, 2022; Yokoyama *et al.*, 2022) between Ryugu, Orgueil and other CIs. Calcium is a major constituent of carbonates and can be isotopically fractionated during aqueous alteration and carbonate precipitation, leading to more than 1 ‰ variations in the $^{44}Ca/^{40}Ca$ ratio in terrestrial carbonates (*e.g.*, Fantle and Tipper, 2014; Blättler and Higgins, 2017). In addition, Ca exhibits large isotopic variations among bulk carbonaceous chondrites (CC), with the $^{44}Ca/^{40}Ca$ ratio spanning a range of 1 ‰. This range is likely related to a combination of the variable modal abundances of refractory inclusions among CC (Hezel *et al.*, 2008) that can be enriched in the lighter Ca isotopes by several per mille (Niederer and Papanastassiou, 1984; Huang *et al.*, 2012) and the heterogeneous distribution of carbonates (Simon and DePaolo, 2010; Valdes *et al.*, 2014; Dauphas and Pourmand, 2015). Therefore, stable Ca isotopes could be useful for investigating the origin of Ca excess in Ryugu samples compared to CIs.

Here we have analysed the stable Ca isotopic compositions of Ryugu samples collected from the first and second touchdown sites, using the collision cell equipped multicollection inductively-coupled plasma mass spectrometer (CC-MC-ICP-MS), Nu Sapphire.

Samples and Methods

The samples returned by the Hayabusa2 spacecraft consist of ∼5 g of materials from the Ryugu asteroid recovered during two touchdowns (Tachibana *et al.*, 2022; Yada *et al.*, 2022). Approximately 3 g of samples representing the surface materials of Ryugu were collected during the first touchdown and stored in Chamber A. Approximately 2 g of samples likely representing a mixture of materials from the surface and subsurface were collected into Chamber C at a site that was close to the crater formed by the Small Carry-on Impactor, a kinetic impact experiment of the Hayabusa2 mission (Saiki *et al.*, 2017; Arakawa *et al.*, 2020). Two Ryugu samples, A0106-A0107 (Chamber A) and C0108 (Chamber C), were analysed in this study (for information on the mineralogy see https://jaxa.repo.nii.ac.jp/?action=repository_uri&item_id=48255&file_id=31&file_no=1).

Sample A0106-A0107 was prepared from a mixed aggregate of A0106 (1.6 mg) and A0107 (27.3 mg). In addition to the Ryugu samples, fusion-crust free bulk samples of six CC, Orgueil (CI1), Alais (CI1), Tarda (C2-ungrouped), Tagish Lake (C2-ungrouped), Murchison (CM2), and Allende (CV3), were analysed in the same way for comparison. See Table S-1 for the weights and providers of the meteorite samples. All samples were dissolved in PFA vials with a mixture of concentrated HF and HNO_3 at the Tokyo Institute of Technology (Yokoyama *et al.*, 2022).

After dissolution, aliquots of ∼0.15 % of the solutions containing ∼5 μg of Ca were transferred and dedicated for our study. All the sample aliquots were dried and redissolved in 0.4 ml of 4 mol/L HNO_3 in preparation for Ca chemical purification and isotopic measurements at the Institut de Physique du Globe, following Dai *et al.* (2022) (see Supplementary Information).

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We report both the mass dependent deviation and the radiogenic ingrowth on ^{40}Ca from the decay of ^{40}K. For mass dependent deviation, the data are reported as $\delta^{x/y}$Ca:

$$\delta^{x/y}\text{Ca} = \left(\frac{(^{x}\text{Ca}/^{y}\text{Ca})_{\text{sample}}}{(^{x}\text{Ca}/^{y}\text{Ca})_{\text{SRM915b}}} - 1\right) \times 10^3,$$

with x and y = 40, 42, 43 or 44. Since most of the published Ca isotope data are measured against the SRM 915a standard, the $\delta^{44/40}$Ca values reported here are re-normalised to SRM915a to facilitate comparison.

The radiogenic ingrowth on ^{40}Ca is reported using the epsilon notation,

$$\varepsilon^{40}\text{Ca} = \left(\frac{(^{40}\text{Ca}/^{44}\text{Ca})_{\text{n sample}}}{(^{40}\text{Ca}/^{44}\text{Ca})_{\text{n SRM915b}}} - 1\right) \times 10^4,$$

with $(^{40}\text{Ca}/^{44}\text{Ca})_n$ representing the ^{40}Ca/^{44}Ca ratio corrected from the mass dependent isotopic fractionation after being normalised to the ^{42}Ca/^{44}Ca ratio using the exponential law and ^{42}Ca/^{44}Ca = 0.31221 (Russell *et al.*, 1978).

The effect of concentration mismatch on the Sapphire is more significant than on traditional MC-ICP-MS (Moynier *et al.*, 2021), and all the samples were analysed with Ca concentrations within 1 % of the standard.

Results and Discussion

The Ca isotopic compositions of the two Ryugu samples and the six CC are reported in Table 1, along with literature values for the chondrites where available. The radiogenic ingrowth on ^{40}Ca from ^{40}K decay was corrected using the K and Ca abundances of the samples (from Yokoyama *et al.*, 2022) and $\delta^{44/40}$Ca (age corrected) ratios are also presented in Table 1. The following discussion focuses on these corrected mass dependent isotopic variations. The $\delta^{44/40}$Ca difference between SRM915b and SRM915a is 0.72 ‰ (Heuser and Eisenhauer, 2008). Neither the Ryugu samples nor the meteorites analysed here show any ^{40}Ca anomalies (after age corrections), which is consistent with the literature (*e.g.*, Simon and DePaolo, 2010; Huang and Jacobsen, 2017).

In a plot of $\delta^{44/42}$Ca *vs.* $\delta^{44/40}$Ca (age corrected), the data fall along a mass dependent line, regardless of whether the slope for equilibrium fractionation (1/2.1 as shown in Fig. 1) or kinetic fractionation is used. Likewise, variations between $\delta^{44/42}$Ca and $\delta^{44/43}$Ca are mass dependent within error (Fig. S-2). Therefore, the Ca isotopic variations observed among the samples analysed primarily reflect mass dependent isotopic fractionation.

The meteorite data reported here are consistent with literature values (Fig. 2 and Table 1), but it should be noted that literature Ca isotopic values are variable, especially for Orgueil and Allende. The variability may reflect interlaboratory bias, but more likely it reflects isotopic heterogeneity at the sample scale analysed. This is particularly the case for Allende, which contains abundant calcium-aluminum-rich inclusions (CAIs). Since our Allende sample was obtained from the Smithsonian Museum's large batch of homogenised powder, and our measured Ca isotopic composition falls in the middle of the range previously reported, it is likely representative of the bulk (Fig. 2). For Orgueil, part of the interlaboratory variability may be controlled by the variable distribution of secondary phases produced by aqueous alteration since Ca may be isotopically fractionated during alteration and carbonate precipitation (Blättler and Higgins, 2017). However, none of the studies that report Ca isotopic data include the Ca contents of their Orgueil analyses. We report here the first $\delta^{44/40}$Ca values for Tarda and

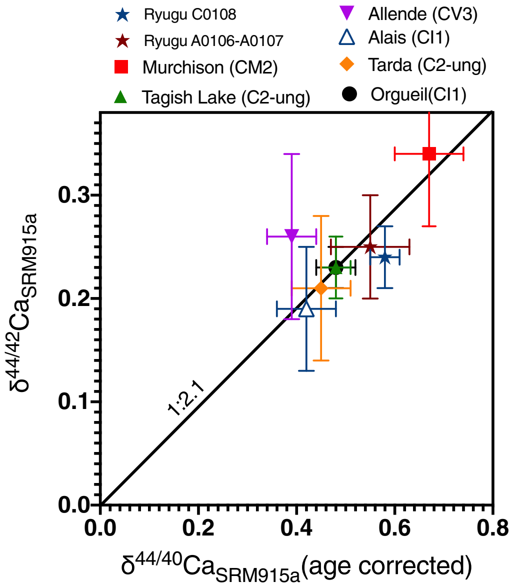

Figure 1 The $\delta^{44/42}$Ca values plotted against $\delta^{44/40}$Ca values for the various samples analysed in this study, including the Ryugu samples. All the samples fall on a mass dependent line within error. Error bars represent 2 sigma standard deviation.

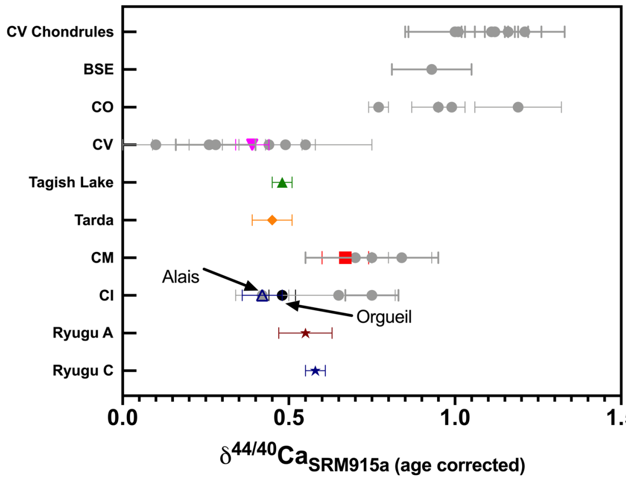

Figure 2 A comparison of age corrected $\delta^{44/40}$Ca values for the samples analysed here (in colour, see Fig. 1) and from the literature (grey). Ryugu samples from Chambers A and C are similar within error and fall within the range defined by the CI chondrites. The literature data are from Table 1, BSE estimate from Kang *et al.* (2017) and chondrules data from Amsellem *et al.* (2017). Error bars are 2 x standard deviation.

Tagish Lake, which are within error of one another and overlap with Orgueil.

The two Ryugu samples have Ca isotopic compositions within error of one another ($\delta^{44/40}$Ca = 0.58 ± 0.03 ‰ for C0108 and 0.55 ± 0.08 ‰ for A0106-A0107; uncertainties represent 2 s.e. for n = 5 and 6, respectively). They are also within the range of published $\delta^{44/40}$Ca values for CIs (Fig. 2). Notably, Ryugu sample A0106-A0107 (Ca/Al ~ 1.9) has almost twice the amount of Ca compared to the average CI (Ca/Al ~ 1.06) (Fig. 3), and ~20 % more than Ryugu sample C0108 (Ca/Al ~ 1.55). If the excess Ca in A0106-A0107 is mainly stored in secondary carbonates (Yokoyama *et al.*, 2022 and our discussion below), then these carbonates must contribute significantly to the bulk Ca

Table 1 Calcium isotopic data from this study and literature (Simon and DePaolo, 2010; Valdes *et al.*, 2014; Amsellem *et al.*, 2017; Huang and Jacobsen, 2017). 2 s.d. = 2 x standard deviation and 2 s.e. = 2 x standard error (2sd/$\sqrt{n}$). n is number of measurements.

Sample names	$\delta^{40/44}Ca_{SRM915b}$	2 s.d.	$\delta^{42/44}Ca_{SRM915b}$	2 s.d.	$\delta^{43/44}Ca_{SRM915b}$	2 s.d.	$\varepsilon^{40}Ca$	2 s.e	n	$\delta^{44/40}Ca_{SRM915a}$	$\delta^{44/40}Ca_{SRM915a}$ (age corrected)
Ryugu C0108	0.22	0.03	0.12	0.03	0.04	0.07	−0.17	0.25	5	0.50	0.58
Ryugu A0106-A0107	0.23	0.08	0.11	0.05	0.06	0.07	0.09	0.22	6	0.49	0.55
Murchison	0.12	0.07	0.02	0.07	0.01	0.10	0.85	0.46	5	0.60	0.67
Murchison (Valdes+)											*0.84*
Murchison (Huang+.)										*0.72*	
Allende	0.36	0.05	0.10	0.08	0.06	0.13	1.47	0.79	4	0.36	0.39
Allende (Simon+)							*0.52*	*0.58*	*2*	*0.49*	*0.54*
Allende (Valdes+)											*0.55*
Allende (Amsellem+)											*0.26*
Allende (Amsellem+)											*0.10*
Allende (Amsellem+)											*0.44*
Allende (Huang+)										*0.28*	
Alais	0.41	0.06	0.17	0.06	0.10	0.08	0.56	0.34	6	0.31	0.42
Tarda	0.34	0.06	0.15	0.07	0.05	0.07	0.25	0.37	6	0.38	0.45
Tagish Lake	0.30	0.03	0.13	0.03	0.06	0.07	0.33	0.26	6	0.42	0.48
Orgueil	0.30	0.04	0.13	0.02	0.06	0.08	0.44	0.40	4	0.42	0.48
Orgueil (Amsellem+)											*0.45*
Orgueil (Valdes+)											*0.65*
Orgueil (Huang+)										0.75	

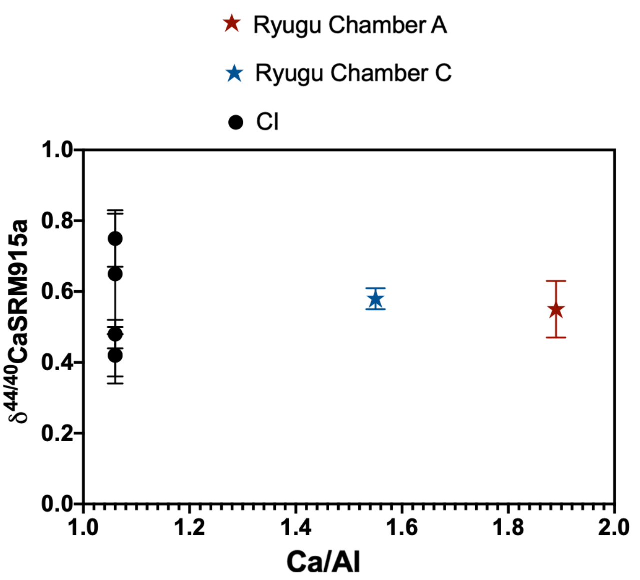

Figure 3 $\delta^{44/40}Ca$ plotted against the Ca/Al ratio of the samples. The Ca/Al ratios of bulk Chamber A and Chamber C samples from Yokoyama *et al.* (2022) are used for Ryugu samples in this work and are taken from the average value in Barrat *et al.* (2012) for Orgueil, as it was not available for specific samples used here.

isotopic composition. Therefore, our results imply that the Ca isotopic composition of the Ryugu samples and CIs are not significantly modified by the dissolution of primary Ca-bearing phases and precipitation as carbonates during aqueous alteration. One reason for the similar Ca isotopic compositions in Ryugu samples and CIs is that their Ca isotopic compositions are mostly dominated by the high abundance and the composition of the carbonates.

Several studies have quantified the modal abundances of minerals in CIs, but there is no systematic study and consensus on the Ca carriers. Calcium sulfates are usually not detected in CIs but can be present at up to ~1 vol. % (*e.g.*, Endress and Bischoff, 1996; Morlok, *et al.*, 2006). Even when present, they were suggested to have formed during terrestrial alteration (Gounelle and Zolensky, 2001). Ca-rich phosphates exist in CI chondrites (Morlok *et al.*, 2006), but they appear to be quite rare (0–0.05 vol. %; King *et al.*, 2015; Alfing *et al.*, 2019) and therefore are unlikely to have a strong control on the total Ca budget. Thus, carbonates are the most likely major carriers of Ca in CIs (Endress and Bischoff, 1996; Morlok *et al.*, 2006, Alfing *et al.*, 2019). Scanning electron microscopic (SEM) analyses of 18 sections of CIs (including Orgueil) point to an average carbonate abundance of ~5 vol. % and the carbonates are dominated by dolomite (Endress and Bischoff, 1996). However, analyses of CO_2 released by phosphoric acid dissolution of ~100 mg of Orgueil only returned ~0.1 wt. % of carbonate C (Alexander *et al.*, 2015), which is equivalent to ~0.8 wt. % carbonate (although carbonate abundance in Ivuna estimated by a similar method is three times higher). X-ray diffraction (detection limit ~1 vol. %) did not reveal carbonates in three Orgueil samples (from 50 to 200 mg), but 2 vol. % in Alais (200 mg) and 3 vol. % in Ivuna (50 mg) (King *et al.*, 2015), while Bland *et al.* (2004) detected no carbonates in Orgueil (200–300 mg samples). Given the variability in the modal mineralogy in the literature, Alfing *et al.* (2009) focused on phases >5 μm (which only represent ~6 vol. % of CIs) and found ~0.5 wt. % of carbonates in CIs. A variability in the abundance of carbonates in CIs is consistent with variable Ca concentrations (from 0.77 to 0.96 wt. %) measured even in large (0.5–1 g) Orgueil bulk samples (Barrat *et al.*, 2012). Considering that the most abundant carbonates in Orgueil are dolomites with ~20 wt. % Ca (Endress and Bishoff, 1996), the presence of ~4 wt. % carbonates in CIs would be sufficient to dominate their Ca budget, less if calcites or aragonites are involved. Despite the variability in carbonate abundances of CIs reported in the literature, we suggest that the major fraction of Ca in CIs is stored in carbonates.

Nakamura, T. *et al.* (2022) estimated the mineral abundances and compositions of the main phases of the Ryugu samples by SEM observations of two ~10 mm^2 sections from a sample from the second touchdown site (sample C0002) (see their Tables S6 and S7). No Ca sulfates were found in these sections, and a simple mass balance using their data shows that carbonates account for 75–80 % of the Ca budget, with apatite and phyllosilicates accommodating the remaining Ca more or less equally. This calculation may underestimate the Ca fraction in carbonates because the samples also contain small Ca carbonate grains (*e.g.*, Table S7 of Nakamura T. *et al.*, 2022), the abundances of which could not be quantified here. C0002 is the third largest sample among all returned grains containing the major lithology (Nakamura T. *et al.*, 2022), suggesting that the Ca budget in the Ryugu samples is dominated by carbonates. It should be noted that another study also found several vol. % of carbonate minerals in samples from both touchdown sites, with a large variability in Ca content between ~1 mg grains (Nakamura E. *et al.*, 2022) and a correlation between Ca content and the dolomite abundances of the grains (Fig. S-1). The two heaviest Ca isotopic compositions for Orgueil samples from Valdes *et al.* (2014) (0.65 ± 0.17 ‰, 2 s.d.) and Huang and Jacobsen (2017) (0.75 ± 0.11 ‰, 2 s.d.) may reflect different proportions of carbonates. Unfortunately, these two studies did not report the Ca contents of their Orgueil fractions, so it is not possible to test this hypothesis.

The similar Ca isotopic compositions between the two Ryugu samples and CIs are most simply explained if the Ca excesses observed in the bulk Ryugu samples are due to the heterogeneous distribution of carbonates, and if these carbonates have similar Ca isotopic compositions to the bulk samples. This explanation is consistent with an episode of fluid circulation and carbonate precipitation in the Ryugu samples that occurred 2.5 to 5 Myr after CAIs formation, as dated using ^{53}Mn-^{53}Cr chronometry in carbonate phases (Nakamura E. *et al.*, 2022; Yokoyama *et al.*, 2022). Hence, at present the average of the two Ryugu samples (0.57 ± 0.04 ‰, 2 s.d.) represents the best estimate of Ryugu's and Solar System Ca isotopic composition. Future work should test whether this value is representative of the whole body by analysing other Ryugu fragments containing fewer carbonate phases and less total Ca, such as the Ryugu material in section 5 from C0002 (Nakamura T. *et al.*, 2022), which only contains ~75 % of its Ca in carbonates.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2238.

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