THE RYUGU REFERENCE POWDER (RRP): A CONSORTIUM STUDY OF ELEMENTAL AND ISOTOPIC SOLAR SYSTEM ABUNDANCES.

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Introduction: The Hayabusa 2 spacecraft sampled ~5.4 g of asteroidal materials from Cb-type asteroid Ryugu, and returned the samples to the Earth in December 2020 [1]. Initial analysis of Ryugu materials revealed a mineralogical and chemical kinship to the CI (Ivuna-type) carbonaceous chondrites [e.g., 2-4], whose composition is similar to the solar photosphere for non-volatile elements [5]. Tantalum stands out with a large excess in Ryugu samples but this is due to contamination from the Ta projectile used in sample collection [2-3]. Isotopic analyses of Ryugu materials showed that Ryugu and CI chondrites presumably originated from the outskirts of the solar system [6-8]. The pristine nature of Ryugu, excluding Ta, makes the returned samples ideal to constrain the composition of outer-solar system material, which is deemed to be a proxy for the solar composition.

Here, we propose to establish a new consortium to estimate solar elemental and isotopic abundances based on analyses of Ryugu samples. The present study summarizes the elemental abundances in bulk Ryugu samples published to date, evaluates the compositional variability, and compares the results to those of CI chondrites. The ultimate goal of the consortium is to determine the reference values for elemental and isotopic abundances of the bulk Ryugu material, which will be used by multi-disciplinary communities including earth and planetary sciences, astronomy, physics, and chemistry.

Reported Ryugu data: Fig. 1 presents the CI-normalized abundances of 18 selected elements in Ryugu samples reported by [2] and [3]. The diamond and circle data points are those measured by X-ray Fluorescence (XRF) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in [2], respectively, using two samples (~25 mg powder mass each) collected from both touchdown sites TD#1 and TD#2 [1]. The boxplots show the variation of analytical data for 16 individual Ryugu particles (7 from TD#1, 9 from TD#2) with digested masses of 0.2–3 mg [3]. The results obtained by the two studies are generally in good agreement with each other, whereas some elements including P, Ca, Mn, Sr, La, Gd, and Yb obtained by [3] show large relative dispersion compared to the other elements.

The observed variation in some elements most likely stems from the presence of aqueously formed secondary minerals in Ryugu including carbonates and phosphates, in which some specific elements (e.g., P, Mn, Sr, and REEs) are strongly partitioned when these minerals precipitate. The modal abundance of carbonate (0.43–6.93%) and phosphate (0.16–1.88%) minerals vary from grain to grain in Ryugu [3], such that the obtained elemental abundances for small-size samples are controlled by the heterogeneous distribution of those minerals (*i.e.*, a nugget effect). Similar variability can be observed for the abundances of P and Ca in fragments of CI chondrites, which result from the varying mineralogical compositions of the measured fragments [9]. Even in ~25 mg of Ryugu samples, the influence of carbonate and phosphate minerals can be seen for P, Ca, and Mn (Fig. 1), as the two bulk samples (TD#1 and TD#2) showed > 20% differences in the abundances of these elements. Therefore, estimating solar composition using currently available Ryugu elemental abundances is challenging due to the nugget effect of carbonates and phosphates, and possibly other accessory minerals.

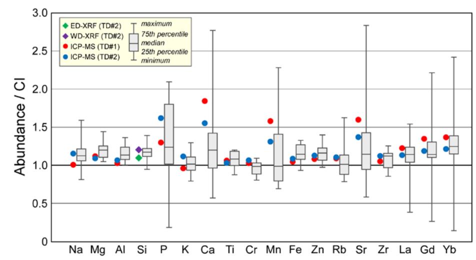

Fig. 1 CI-normalized elemental abundances in bulk Ryugu samples. Diamonds (XRF) and circles (ICP-MS) are those obtained using ~25 mg of powdered Ryugu samples [2]. Boxplots were created from the ICP-MS data of 16 individual Ryugu grains with digested masses of 0.2–3 mg except for Si that was measured by electron probe [3].

Nugget effect: A nugget effect associated with the presence of phosphate was identified for REEs in carbonaceous and ordinary chondrites [10]. There are several telltale characteristics of such a nugget effect. First, "bulk" analyses should define mixing curves between the true bulk and the mineral composition in elemental ratio plots. Because phosphates in ordinary chondrites have high La/Lu and negative Eu/Eu* anomalies (Eu* = observed Eu/interpolated Eu), the presence of phosphate nuggets in ordinary chondrites was identified as a negative correlation between La/Lu ratios and Eu/Eu* [10]. In contrast, phosphates in Ryugu lack these characteristic features and are more difficult to detect [3]. Ryugu fragments are rich in dolomite, which has high Mn/Cr, low Rb/Sr, and low Fe/Mn. As shown in Fig. 2, in Ryugu samples these ratios are well correlated, and the variations observed can be explained by admixture or removal of dolomite at the percent level.

Another telltale signature of a nugget effect is that the dispersion in elemental ratios should decrease as the inverse of the square root of the mass of sample homogenized [10]. As shown in Fig. 3, the dispersions in elemental ratios are consistent with a sampling problem associated with a nugget effect. The dispersion in elemental ratios can be calculated if the nugget size, abundance, and composition are known [10]. Because these are poorly constrained for carbonates, we calculated instead the dispersion for the smaller fragments digested and calculated the predicted dispersion for larger masses. Having established that unrepresentative sampling of carbonate is likely responsible for the dispersion in specific elemental ratios, we can predict the expected dispersion if large sample masses are digested. We thus estimate that for 1 g of Ryugu sample homogenized, the dispersion (2σ) of the bulk Mn/Cr and Rb/Sr ratios will be better than ~±5%. Elements that are not concentrated in specific minerals will be much less affected by this uncertainty. Our analysis shows that much of the dispersion in chemical composition between Ryugu grains is due to non-representative sampling of mineral phases highly enriched in some elements.

Sample processing protocols: The scatter in chemical compositions in published Ryugu data [2, 3] was most likely caused by a nugget effect of carbonates and phosphates. This nugget effect can be mitigated by homogenizing a larger sample mass (~1 g). This approach is important to constrain the "cosmic" composition, and test if previous estimates based on CI chondrites stored in museums for decades to centuries are reliable.

The first step is to produce a homogenous powder from a large sample (*i.e.*, the Ryugu Reference Powder; RRP). This procedure must be done in a clean glovebox with ultra-purified N_2 gas to avoid exposure of fresh sample surface to the terrestrial atmosphere. The homogenized powder will be equally divided into ~10 portions, half of which will be saved for future studies, as was done with the Allende Reference Powder, albeit at a different scale [13]. Individual portions will be distributed to several teams of the consortium for multiple purposes to obtain the abundances of all analyzable elements. It should be noted that the Ryugu data reported to date lack abundances of some elements such as Hg and halogen excluding chlorine [2]. The chemical and isotopic compositions measured by all consortium teams (consortium solicitation announced later by JAXA) will be evaluated statistically to produce a recommended RRP composition. For comparison, we plan to apply the above protocols to gram-level aliquots of CI chondrites (*e.g.*, Orgueil, Ivuna) in parallel with the analysis of Ryugu samples.

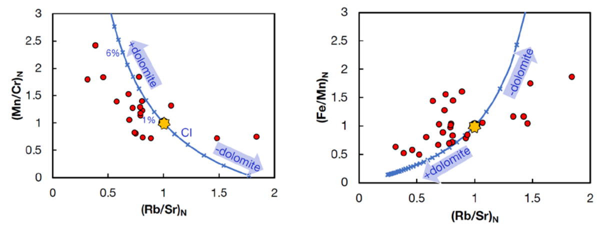

Fig. 2 Correlations between Mn/Cr, Fe/Mn, and Rb/Sr ratios for bulk Ryugu samples obtained by [2-3]. The star is the CI composition [5]. The curves are calculated mixing curves between bulk CI and dolomite in CI chondrites [11-12].

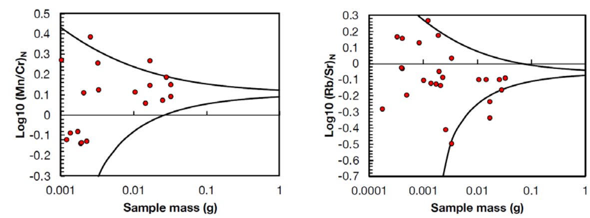

Fig. 3 Elemental ratios sensitive to carbonate nugget effects against mass homogenized/digested. If a nugget effect is present, we would expect the dispersion to decrease as the inverse of the square root of the mass of sample homogenized/digested (black envelope) [10].

References: [1] Tachibana S. et al. (2022) *Science, 375,* 1011–1016. [2] Yokoyama T. et al. (2022) *Science,* eabn7850. [3] Nakamura E. et al. (2022) *Proc. Jap. Acad. B, 98,* 227–282. [4] Nakamura T. et al. (2022) *Science,* eabn8671. [5] Lodders K. (2021) *Space Sci. Rev., 217,* 44. [6] Ito M. et al. (2022) *Nature Astron. 6,* 1163-1171. [7] Hopp T. et al. (2022) *Sci. Adv., 8,* eadd8141. [8] Kawasaki N. et al. *Sci Adv., 8,* eade2067. [9] Morlok A. et al. (2006) *Geochim. Cosmochim. Acta, 70,* 5371–5394. [10] Dauphas N. and Pourmand A. (2015) *Geochim. Cosmochim. Acta, 163,* 234–261. [11] Endreß M. and Bischoff, A. (1996) *Geochim. Cosmochim. Acta, 60,* 489–507. [12] Macdougall J.D. et al. (1984) *Nature, 307,* 249–251. [13] Jarosewich, E. et al. (1987) *Smithsonian Contrib. Earth Sci.* 1–49.