SAMPLING MASS AND CHEMICAL HETEROGENEITIES AMONG RYUGU SAMPLES RETURNED BY THE HAYABUSA2 MISSION.
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Introduction: The Hayabusa spacecraft returned samples from the S-type asteroid Itokawa, demonstrating that it was related to LL chondrites [1,2]. The mass recovered was limited, and all studies relied on *in situ* techniques to characterize the samples. The Hayabusa2 mission sampled the C-type asteroid Ryugu at two sites and brought ~5.4 g of asteroidal material back to the Earth on December 5, 2020 [3]. The large sample mass recovered by Hayabusa2 opens its study to macroscopic techniques, including bulk chemical and isotopic analyses. The petrographic, chemical, and isotopic characteristics of Ryugu samples point to a relationship with CI chondrites [3,4]. To further evaluate how Ryugu compares to known meteorites and possibly re-evaluate cosmic abundances of the elements based on a sample that has not experienced any sort of terrestrial alteration, the initial-analysis-chemistry-team conducted destructive, chemical, and isotopic analyses of two bulk Ryugu samples (<25 mg each) from the two touchdown sites [4].

A question posed by analyses of precious returned samples is what is the mass required to obtain a representative composition? While CI chondrites and Ryugu appear to be homogeneous at first sight, microscopic examination reveals the presence of chemically diverse clasts and secondary alteration phases such as carbonate, pyrrhotite, phosphate, and magnetite that can be heterogeneously distributed at the sampling scale [4,5].

Previous studies have investigated the issue of sample representativity for meteorites using many fragments of the same sample [6-8], but this is not possible with irreplaceable samples such as those recovered from Ryugu. We use here an alternative approach of computing the predicted dispersion in chemical and isotopic compositions of bulk samples based on a mathematical description of the nugget effect previously applied to REE abundances in meteorites [9]. This is a preliminary report as we are in the process of characterizing the chemical compositions of individual phases, a critical input in this calculation. The same approach can be used in the future to guide sample allocation strategy in sample return missions such as OSIRIS-REx and MMX.

The nugget effect: Previous work has shown that chondrites are susceptible to the nugget effect, for example for REEs that are highly concentrated in heterogeneously distributed phosphate grains [9]. The compositions of two Ryugu samples (A0106-0107 from the first sampling site in Chamber A; C0108-1 and C0108-2 two aliquots from the same homogenized powder from the second sampling site in Chamber C) and three carbonaceous chondrites (Tagish Lake, C2-ung; Murchison, CM2; Allende, CV3) were examined by ICP-QMS after acid digestion [4,10]. The Ryugu samples have chemical compositions that closely match CI chondrites. Detailed examination of the data however reveals departures that cannot be easily explained by analytical error and could be due instead to sample heterogeneity. For example, the Ryugu samples have high REE/Al (Al is used here for normalization as it is lithophile and fluid-immobile), high Mn/Cr, and low Rb/Sr ratios that can potentially be due to heterogeneous distribution of apatite and carbonate grains/veins.

Assuming that the nuggets are equant, of constant diameter, and randomly distributed, which is not necessarily the case in Ryugu samples (carbonates for example tend to form clusters), an elemental ratio $R = C_2/C_1$ will follow a normal distribution whose mean is the true ratio and dispersion is given by the formula [9],

$$\sigma_R \simeq \frac{r}{(1+rf)^2}\sqrt{\frac{f\rho_{\mathrm{matrix}}\pi d^3}{6m}}\left|R_{\mathrm{nugget}} - R_{\mathrm{matrix}}\right|, \quad (1)$$

where $r = C_{1,\mathrm{nugget}}/C_{1,\mathrm{matrix}}$, f is the nugget volume fraction, d is the nugget diameter, m is the mass homogenized, and *matrix* refers to all non-nugget material. This standard deviation represents the uncertainty in assessing the bulk composition due to limited sample mass. This equation shows that the nugget effect will be more prevalent for elements that show a larger concentration/elemental ratio contrast between nugget and matrix, and are concentrated in

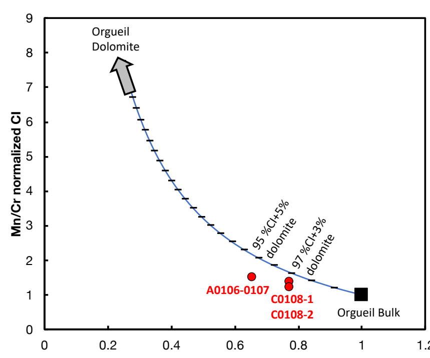

Fig. 1. Mn/Cr vs Rb/Sr in bulk samples of Ryugu measured by ICP-QMS from homogenized powders of 32 mg from chamber C for C0108-1 (22 mg) and C0108-2 (4 mg) and 29 mg from chamber A for A0106-0107 (24 mg). The blue curve is a mixing calculation between previously measured Orgueil bulk and Orgueil dolomite, with each tick mark representing 1% increments in the proportion of dolomite.

larger nuggets. We also see that the uncertainty in bulk determinations scales as the inverse of the square root of the mass of the sample analyzed (*e.g.*, to reduce this uncertainty by a factor of 2, one need to measure samples 4 times as large).

Results and Discussion: We have evaluated the effect of the heterogeneous distribution of carbonates on the bulk chemical composition of Ryugu samples, notably Rb/Sr and Mn/Cr ratios. We will expand that work to other elemental ratios before the conference. Samples C0108-1 and C108-2 measured from the same powdered batch have very similar Mn/Cr and Rb/Sr ratios. Tagish Lake, Murchison, and Allende give values that are very close to those previously reported in the literature. These two sets of observations support the view that the Mn/Cr and Rb/Sr determinations are precise and accurate. As shown in Fig. 1, the two Ryugu samples have Mn/Cr ratios that are significantly higher than Orgueil. They also have Rb/Sr ratios that are significantly lower than Orgueil. Dolomite in CI is very rich in Sr [11] and Mn [12], and the Ryugu samples have been found to contain large amounts of carbonates [4]. To test the idea that the shifts in Rb/Sr and Mn/Cr ratios of the Ryugu samples are due to addition of carbonates in the samples, we have calculated a mixing curve between Orgueil bulk and dolomite (Fig. 1). As shown, the low Rb/Sr and high Mn/Cr ratios measured in Ryugu samples can be explained by the addition of 3-5 vol% dolomite to Orgueil. The modal abundance of carbonates in Orgueil is highly variable, with previous studies reporting no detection to ~5 vol% [13]. Our estimates for Ryugu samples are therefore realistic.

The Mn/Cr ratios of the Ryugu samples are shifted by 20-50% relative to the reference CI composition. To test whether the high Mn/Cr and low Rb/Sr ratio of Ryugu samples are due to non-representative sampling of carbonate, we calculated the predicted uncertainty in the bulk ratio determination [9] assuming 4 vol% carbonate in CI and 100 μm carbonate grains (Fig. 2). This order-of-magnitude calculation shows that even with 30 mg homogenized samples, 5-10% relative uncertainty could be present. Further work is needed to test whether the heterogeneous distribution of accessory phases in Ryugu samples can explain some of the departures in chemical composition observed compared to CI meteorites, which has some bearing on other cosmochemical questions. Do bulk ^{53}Mn-^{53}Cr isochrons of bulk Ryugu fragments and carbonaceous chondrites date volatile element depletion in the nebula, or mobilization by fluids in the parent-bodies [10]? Are CI chondrites more representative of solar composition, despite their handling and possible contamination, because larger masses can be homogenized [7,8]? Can we correct for biases introduced by the nugget effect to obtain a representative bulk composition?

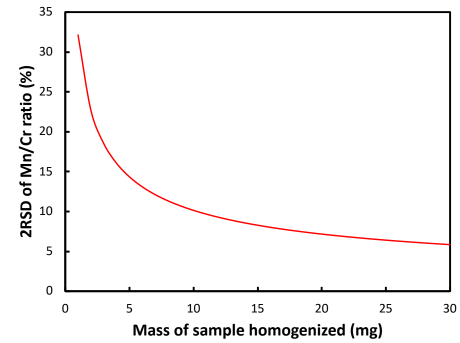

Fig. 2. Calculation of the nugget effect (Eq. 1; [8]) on the uncertainty in bulk Mn/Cr determination associated with the heterogenous distribution of Mn-rich Cr-poor dolomite in Orgueil (CI). RSD=relative standard deviation.

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