# Chemical abundances in Ryugu, nugget effect, and cosmic composition

Nicolas Dauphas[1], Tetsuya Yokoyama[2], Ryota Fukai[3], Tomohiro Usui[3], Shogo Tachibana[4], Maria Schönbächler[5], Andrew M. Davis[1], Hisayoshi Yurimoto[6], The Hayabusa2-initial-analysis chemistry team, The Hayabusa2-initial-analysis core.

[1]*Origins Lab, Dept. of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, USA*
[2]*Dept. of Earth & Planetary Sciences, Tokyo Institute of Technology, Japan*
[3]*Dept. of Solar System Sciences, ISAS, JAXA*
[4]*Dept. of Earth and Planetary Science, University of Tokyo, Japan*
[5]*Inst. für Geochemie und Petrologie, ETH Zürich, Switzerland*
[6]*Dept. of Earth and Planetary Sciences, Hokkaido University, Japan*

Approximately 99.86% of the mass of the solar system is locked up in the Sun, which is largely inaccessible and whose composition is only known through spectroscopy and analysis of solar wind. Much of our knowledge of the chemical and isotopic compositions of the bulk solar system comes from analysis of meteorites, and among those CI (Ivuna-type) carbonaceous chondrites, which contain most elements except the most volatile ones in proportions that match estimates from solar photosphere observations [1,2]. CI chondrites are rare and most of them have been in meteorite collections for many decades (the largest one, Orgueil, fell in 1864), where they have been exposed to moisture, airborne and handling contaminants. The Hayabusa2 mission sampled ~5.4 g of pristine material from Ryugu, a Cb-type asteroid [3]. Laboratory analyses of the returned sample show that Ryugu is related to CI chondrites and probably originated from the outskirts of the solar system [4-7]. The only known contaminant for Ryugu samples is Ta in the projectile used to liberate dust and fragments from Ryugu's surface [8]. Given their pristine nature, Ryugu samples are ideally suited to constrain the composition of outer-solar system material, which we take as a proxy for the solar composition. A caveat to estimating the solar composition using Ryugu or CI chondrites is that these may contain extraneous refractory dust compared to other inner solar system objects. This was most clearly demonstrated with rare earth elements (REEs), as carbonaceous chondrites all show Tm anomalies relative to non-carbonaceous chondrites [9,10], presumably due to the presence of refractory dust with a group II REE pattern characterized by large positive Tm anomalies produced by evaporation/condensation processes in the solar nebula [11]. At this stage, it is unclear if the Sun would contain the same complement of refractory dust as CI chondrites, or if inner solar system objects are more representative.
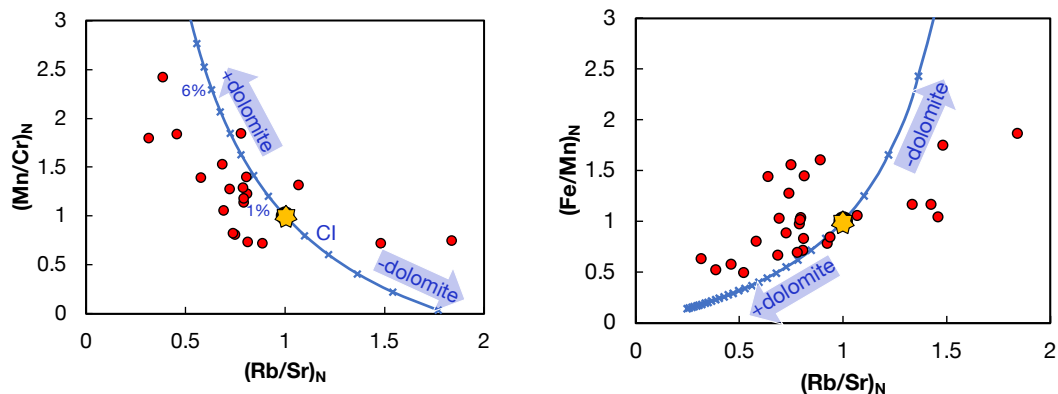


**Fig. 1.** Correlations between Mn/Cr, Fe/Mn, and Rb/Sr ratios. The yellow star is the CI composition. The red points are bulk fragment measurements for Ryugu [4,7]. The curves are calculated mixing curves between bulk CI and dolomite in CI chondrites [12,13].

Yokoyama *et al*. [4] and Nakamura E. *et al*. [7] reported high precision chemical composition analyses of Ryugu fragments by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS), the gold standard for such analyses. Those measurements show that Ryugu has almost unfractionated chemical abundances relative to CI chondrites, strengthening the case for a link between Cb-asteroid and CI chondrites. The fragments analyzed are relatively small (from ~0.2 to ~30 mg) and show significant departures relative to CI chondrites that are unrelated to volatility. This is true even in the largest fragments analyzed, which show significant enrichments in REEs, Ca, Sr, Ba, P, and Mn [4]. Chemical abundance variations have been seen previously in chondrites that presumably reflect heterogeneous distribution (and unrepresentative sampling) of phases highly enriched in some elements [9]. This is known as a nugget effect and represents a limit in the precision that can be attained in bulk rock analyses. Carbonate and phosphate phases have been found in Ryugu samples [4,6,7] and could be responsible for the chemical variations seen in bulk fragment analyses.

A nugget effect for REEs associated with the presence of phosphate was identified in carbonaceous and ordinary chondrites [9]. There are several telltale signatures of such a nugget effect. The first one is that in elemental ratio plots, "bulk" analyses should define mixing curves between the true bulk and the mineral composition. In ordinary and carbonaceous chondrites, the presence of phosphate nuggets was identified as a negative correlation between La/Lu ratios and Eu/Eu* (=observed Eu/interpolated Eu) anomalies (phosphates in ordinary chondrites have high La/Lu and negative Eu/Eu* anomalies) [9]. The phosphates in Ryugu lack these characteristic features and are more difficult to detect [7]. Ryugu fragments are rich in dolomite, which has high Mn/Cr, low Rb/Sr, and low Fe/Mn. In Fig. 1, we plot CI-normalized Mn/Cr and Fe/Mn against Rb/Sr. As shown, the ratios are correlated, and the variations observed can be well 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 [9]. As shown in Fig. 2, 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 [9]. 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/digested, the dispersion ($2\sigma$) 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 a due to non-representative sampling of mineral phases highly enriched in some elements. This artifact can be remediated by homogenizing a larger sample mass (~1 g), which is important to constrain the "cosmic" composition, and test if previous estimates based on CI chondrites are reliable.
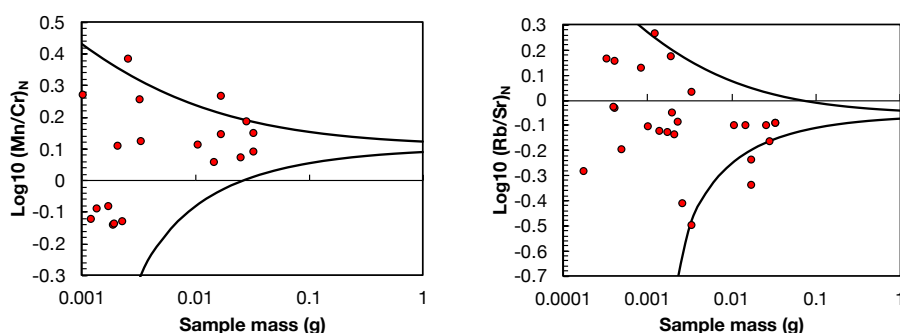


**Fig. 2.** Elemental ratios sensitive to carbonate nugget effects against mass homogenized/digested. If a nugget effect is present, we would expect the dispersion to decrease as the inverse of the square root of the mass of sample homogenized/digested (black envelope) [9]. As shown, this seems to be the case.

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**The Hayabusa2-initial-analysis chemistry team:** T. Yokoyama, K. Nagashima, I. Nakai, E.D. Young, Y. Abe, J. Aléon, C.M.O'D. Alexander, S. Amari, Y. Amelin, K. Bajo, M. Bizzarro, A. Bouvier, R. W. Carlson, M. Chaussidon, B.-G. Choi, N. Dauphas, A. M. Davis, T. Di Rocco, W. Fujiya, R. Fukai, I. Gautam, M. K. Haba, Y. Hibiya, H. Hidaka, H. Homma, P. Hoppe, G.R. Huss, K. Ichida, T. Iizuka, T.R. Ireland, A. Ishikawa, M. Ito, S. Itoh, N. Kawasaki, N. T. Kita, K. Kitajima, T. Kleine, S. Komatani, A. N. Krot, M.-C. Liu, Yuki Masuda, K.D. McKeegan, M. Morita, K. Motomura, F. Moynier, A. Nguyen, L. Nittler, M. Onose, A. Pack, C. Park, L. Piani, L. Qin, S.S. Russell, N. Sakamoto, M. Schönbächler, L. Tafla, H. Tang, K. Terada, Y. Terada, T. Usui, S. Wada, M. Wadhwa, R.J. Walker, K. Yamashita, Q.-Z. Yin, S. Yoneda, H. Yui, A.-C. Zhang, H. Yurimoto.

**The Hayabusa2-initial-analysis core:** S. Tachibana, T. Nakamura, H. Naraoka, T. Noguchi, R. Okazaki, K. Sakamoto, H. Yabuta, H. Yurimoto, Y. Tsuda, S. Watanabe.