NUCLEOSYNTHETIC CR-TI ISOTOPE ANOMALIES IN RYUGU SAMPLES. T. Yokoyama1, M. Wadhwa2, T. Izuka3, V. Rai1, I. Gautam4, Y. Hibiya3, Y. Masuda5, M.K. Haba6, R. Fukai7, R. Hines2, N. Phelan2, The Hayabusa2-initial-analysis Chemistry Team and Core. 1Tokyo Institute of Technology (tetsuya.yoko@eps.sci.titech.ac.jp), 2Arizona State University, 3The University of Tokyo, 4ISAS/JSEC, JAXA.

Introduction: Hayabusa2 collected 5.4 g of asteroid samples from the Cb-type asteroid Ryugu during two touchdown sequences: TD1, the first landing, which collected surface material, and TD2, the second landing, which collected a mixture of surface and impact-ejected subsurface materials [1]. Analyses of the returned samples revealed that Ryugu is composed of materials most similar to CI chondrites, including in terms of nucleosynthetic isotopic data in Ca, Ti, Cr, Fe, and Zn [2-5]. Nonetheless, Cr isotopic analyses reported to date show some variability in ε54Cr values (deviation of 54Cr/52Cr ratios from a terrestrial standard in parts per 10⁴) among four bulk Ryugu samples that exceeds the documented dispersion of literature values for CI chondrites [2, 3]. Ryugu and CI chondrites are breccias, raising the question of whether the ε54Cr heterogeneity documented in Ryugu is an accretionary feature reflecting the presence of extraneous clasts of non-CI parentage, or whether it reflects secondary processes such as parent-body alteration. To elucidate the origin of Ryugu materials and post-accretional chemical processes on the Ryugu parent body, this study focuses on the mass-independent Cr and Ti isotope variations as well as 53Mn-53Cr isotope systematics in five Ryugu samples, two from TD1 (A0106 and A0106-A0107) and three from TD2 (C0107, C0108, and C0002). For comparison, the compositions of several carbonaceous chondrites with comparable sample sizes to the Ryugu samples are also reported.

Experiments: The Ryugu and chondrite samples were digested with acids (HF, HNO3, HCl, and H2O2) as described in [2], except for one Ryugu (C0002) and two CI samples, which were digested by alkali fusion using Na2CO3. The Mn/Cr ratios of the dissolved samples were measured with a quadrupole-type ICP-MS (iCAP TQ; Thermo Fisher Scientific) at Tokyo Tech. After the five-step sequential chemical separation by column chromatography [2], the Cr isotopic compositions in the samples were measured by TIMS at Tokyo Tech (Triton-Plus; Thermo Fisher Scientific) and by MC-ICP-MS (Neptune XT; Thermo Fisher Scientific) at Arizona State University. The Ti isotopic data were obtained by MC-ICP-MS at University of Tokyo (Neptune-Plus; Thermo Fisher Scientific) and at Arizona State University.

Results and Discussion: Figure 1 shows a plot of ε53Cr versus 55Mn/52Cr for the five Ryugu samples and six carbonaceous chondrites analyzed in this study. The regression line for the five Ryugu samples yields a slope of (53Mn/52Mn)i = (2.6±0.8)×10⁻⁶, corresponding to the CAI relative age of 5.2 (+1.8/-1.4) Ma using the D’Orbigny angrite as an anchor [6]. Considering the small sample masses used in this study (< 24 mg each), the variability in the 53Mn/52Cr and ε53Cr values among the different Ryugu samples are likely due to the lithological differences between these samples, and largely controlled by the abundance of secondary carbonates. Therefore, the 53Mn-23Cr age obtained in this study most likely represents the timing of carbonate precipitation in Ryugu samples during parent body aqueous alteration.

Figure 2 shows a plot of ε50Ti versus ε54Cr for the Ryugu samples and carbonaceous chondrites obtained in this study. Although the ε50Ti values of the Ryugu samples and CI chondrites are consistent with previously reported CI data, the ε54Cr values of these samples vary beyond the range of those previously reported for CIs. The observed variability in ε54Cr values among the Ryugu samples and CI chondrites is an intrinsic property of the individual samples, most likely reflecting the heterogeneous distribution of 54Cr-rich and 54Cr-poor phases at the mm-scale. Exposure to galactic cosmic rays or incomplete digestion of presolar grains could also induce variations in ε54Cr 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.

As shown in Fig. 3, ε54Cr data are weakly negatively correlated with ε53Cr values in the bulk Ryugu samples.
and CI chondrites. 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 [7]. Previously documented $^{54}$Cr-rich presolar grains have a slightly lower $^{53}$Cr/$^{54}$Cr ratio than the solar value, so mixing between the C0002 Ryugu sample and these grains would result in a positive correlation in Fig. 3 (dashed line). Therefore, radiogenic ingrowth of $^{53}$Cr from the decay of $^{53}$Mn is required to explain the anticorrelation between the samples with elevated $\varepsilon^{53}$Cr values and Ryugu C0002, which has the lowest $\varepsilon^{53}$Cr value. The simplest explanation for the anticorrelation is that it represents a mixing line between $^{53}$Cr-rich/$^{54}$Cr-poor labile Cr in secondary phases such as dolomite and the complementary $^{53}$Cr-poor/$^{54}$Cr-rich component documented in previous studies during leaching of carbonaceous chondrites [e.g., 8]. These observations suggest that the mm-scale $\varepsilon^{54}$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 $\varepsilon^{54}$Cr value and $^{54}$Cr-rich Cr-oxide nanoparticles. Pervasive aqueous alteration in the Ryugu parent body released Cr with a negative $\varepsilon^{54}$Cr value from chemically labile phases (e.g., olivine, amorphous silicates), whereas $^{54}$Cr-rich presolar nanoparticles were largely unaffected. Chromium dissolved in the aqueous fluid was incorporated into the secondary phases (e.g., dolomite) at ~5 Ma after the birth of the Solar System (Fig. 1). This process led to physicochemical fractionation between the $^{54}$Cr-rich presolar nanoparticles and secondary minerals at a mm-scale in the bulk samples, resulting in $\varepsilon^{53}$Cr–$\varepsilon^{54}$Cr variations in the bulk fragments.

Overall, the observed Cr isotopic variability in the bulk Ryugu samples and CI chondrite samples shows that isotopic heterogeneities in asteroids are not all nebular or accretionary in nature, as they can also reflect elemental redistribution by aqueous fluid.


Fig. 2 $\varepsilon^{50}$Ti–$\varepsilon^{54}$Cr diagram for Ryugu and meteorites. Ellipses represent the 2SD of the literature data for each meteorite group.

Fig. 3 $\varepsilon^{54}$Cr–$\varepsilon^{53}$Cr diagram for Ryugu and CI chondrites. Dashed line represents the mixing line between Ryugu (C0002) and the $^{54}$Cr-rich presolar nanoparticles [9]. Thin dotted line is the mixing line between C0002 and the $^{54}$Cr-rich nanoparticles assuming that the particles have a terrestrial $^{50}$Cr/$^{52}$Cr ratio.