Chemical composition and variability of Ryugu samples, CI chondrites and Kainsaz assessed by quadrupole ICP-MS analyses

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Introduction. The similar relative abundances of non-atmophile elements between the Sun and rare CI chondrites suggest that CI chondrites represent the most primordial meteorites available for laboratory analyses. Samples returned from asteroid Ryugu by the Japanese Hayabusa2 mission resemble CI chondrites, were not altered on Earth, but affected by aqueous alteration [1-4].

This study aims to provide additional data on the elemental compositions and variabilities and representative sample masses for CI chondrites, Ryugu and the Kainsaz CO3 chondrite.

Samples. Data was obtained for five ~3 mg Ryugu samples from chamber A (1st touchdown), seven ~3 mg chips and 3, 4 and 50 mg bulk powder samples from the Kainsaz CO3 chondrite and ~50 mg powder aliquots from the CI chondrites Ivuna (2 x), Orgueil (3 x) and Y-980115. For quality control, Allende Smithsonian reference powder, JB-2, BHVO-2 and ~3 mg powder test samples from Allende, Ivuna, JB-2 as well as a Perkin Elmer multi element solution were analyzed.

Methods. The ~3 mg samples were digested in HF-HNO_3 at hotplates. The Ryugu samples and 5 out of 7 chips from Kainsaz were not ground before digestion to avoid material loss. Most 50 mg samples were digested in Parr pressure digestion vessels. Methods for quadrupole ICP-MS analyses and data evaluation are given in [5]. Samples were 4000-fold diluted and Rh and Re were used as internal standards. Most elements were determined in kinetic energy discrimination mode using He as a cell gas with CeO/Ce ~ 0.4%. (1.7% in standard mode). For each sample set, three to seven measurement sessions were run. Outliers were removed if > 4 sd and Ta data was rejected from four sessions that yielded unusual low Ta values. Four-point matrix matched calibration [5, 6] yielded a median correlation coefficient of 0.9999 as calculated from all elements and sessions. Repeatability judged from 121 analyses of Ivuna was 3.2% on average with Mn, Co, Cu, Rb, Y, Sr, Pb < 1.5% and 23% for Be being the worst case. In order to rigorously control blank contributions, seven blanks each were prepared along with the Ryugu and Kainsaz samples and four blanks with the 50 mg CI chondrite samples. Median blanks were subtracted. Maximum blanks for ~3 mg samples were: Ryugu and Ivuna: As, Sn and Sb 2 to 6%; Nb 10%; W 16%; Mo 29%; Kainsaz: Zn, As, Cd and Sn <3%; W 15%; JB-2: Zn, Nb, Sn and W 5 to 6 %; Mo 35%.

Results. Most CI chondrite, Allende Smithsonian, JB-2, BHVO-2 and Perkin Elmer solution data agrees within 10 to 20% with reference data [e.g., 7-13]. However, due to problems related to the calibration solutions (as observed in [6]), Sr, Mo, Sb, Ho, Ta, W and Bi are systematically too low. For the basalt reference samples, S, Se, Ag, Ir and Pt were not quantified and Ti, Cr, Ni, Te and As are off by about 20 to 60%. Except for U in Ivuna, results for 3 mg test samples agreed with results for the corresponding 50 mg samples to within better than 10% or within 10 to 20% for Se, Ag, Te (Ivuna), S, Ag, Ir, Pt (Allende) and As and Bi for JB-2 (S, Se, Ag, Ir and Pt not quantified in basalt reference materials). Three mg chips from Kainsaz display some heterogeneity and scatter around the data for the 50 mg bulk sample. However, the 50 mg bulk sample and 3 and 4 mg aliquots from the same powder display fractionated REE. The REE Kainsaz data shows that nugget effects in chondrites can affect larger samples more significantly than small mg samples. The Kainsaz 3 mg chip data displays reproducible, sometimes large enrichments in As, Sb and Pb of unknown origin.

Discussion. Ivuna and Mg normalized data reveal the following: Many elements in CI chondrites agree within ~2 %. Two out of three Orgueil samples display 20 to 50% enrichments in some refractory elements, most notably Zr, Hf, Th and Ba while Y-980115 is depleted in Cd, In, Tl and Bi as observed previously [5]. One Ryugu sample matches the CI chondrite REE pattern, the other four samples are enriched in light over heavy REE with variable REE/Mg. Two Ryugu samples are clearly enriched in Ca and Sr, one in Mn and Fe. Only one out of five Ryugu samples displays contamination of Ta from the projectile. Overall, the 3 mg Ryugu samples from chamber A display a clear CI chondrite affinity, but their chemical compositions are obviously affected by aqueous alteration as previously observed. For CI chondrites, Kainsaz and Ryugu, we estimated the representative sample mass needed to obtain elemental abundances to within 5% at the 95% confidence level, using the formula given in [10]: Representative sample mass = test portion mass * (standard deviation / (mean * standard error of the mean))^2 * student-t distribution factor.

For CI chondrites (n=4), the median representative sample mass corresponds to 452 mg; for ten elements, including Na, Zr, Hf, Ba, La, Ce and U, the representative sample mass was above 1 g. For Kainsaz, the median representative sample mass equals 74 mg and is above 1 g for S, As, Cd, Sb, Cs and Pb only. The median representative sample mass calculated for Ryugu corresponds to 99 mg with Mn, Ca and P being the least homogeneous elements with calculated representative sample masses of about 300, 400 and 500 mg. A complete table can be obtained from the author.

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