

Nucleosynthetic s-Process Depletion in Mo from Ryugu samples returned by Hayabusa2

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Supplementary Information

The Supplementary Information includes:

- Experiments
- Results of Allende
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Experiments

Four bulk Ryugu samples (A0106 and A0106-A0107 from Chamber A, C0107 and C0108 from Chamber C) and two Allende samples (Allende A and Allende B) were examined in this study. The Ryugu sample A0106-A0107 was a powdered material prepared from a mixed aggregate of A0106 (1.6 mg) and A0107 (27 mg), such that 94% of this material was composed of A0107. The sample C0108 was a powdered material retrieved from a sealed cell used in the XRF analysis (Yokoyama *et al.*, 2023).

The Ryugu samples A0106 and C0107 were residues obtained after extracting soluble organic matter (SOM) using hexane, dichloromethane, and methanol (Yoshimura *et al.*, 2023). To estimate the removal rate of Mo in individual extraction processes with the organic solvents, we conducted a SOM extraction test using 43.73 mg of powdered Tagish Lake (C2 ungrouped). Tagish Lake has similar lithologies and mineralogies to CI chondrites and Ryugu, although Tagish Lake has sparse chondrule-like objects and altered CAIs. The Mo yields in individual organic solvents are listed in Table S-2. The total amount of Mo removed by the three-step SOM extraction procedures were less than 0.2%. An earlier leaching experiment on CI chondrite Orgueil (Dauphas *et al.*, 2002) showed that the Mo isotopic compositions of the first leachate (8.5 M CH₃COOH, 20 °C, 1 day) were generally within uncertainties of the terrestrial value. Therefore, we conclude that the Mo isotopic compositions of Ryugu samples A0106 and C0107 were not significantly modified by the SOM extraction steps.



The weight of each Ryugu sample dedicated for acid digestion was 23.88, 22.24, 14.61, and 12.78 mg for A0106-A0107, C0108, A0106, and C0107, respectively. Additionally, we examined two aliquots of the Smithsonian Allende powder (USNM 2359, Split 20, Position 31; 19.94 and 32.46 mg, 52.4 mg in total).

Sample digestion and the first and second steps of the chemical separation were conducted at the Tokyo Institute of Technology (Tokyo Tech), of which the details are described in Yokoyama *et al.* (2023). The powdered samples were weighed in Teflon vials and heated with a mixture of 0.25 mL HF and 0.25 mL HNO₃ at 180 °C for 5 days and dried. After digestion, a mixture of 0.1 mL HNO₃ and 0.1 mL HCl was added to each sample, heated at 110 °C for two days, and dried. Then, a mixture of 0.35 mL HNO₃, 0.1 mL H₂O₂, and 0.2 mL H₂O was added to each sample, heated at 90 °C for two days, and dried. The dissolved sample was conditioned with 1 mL 1.5 M HBr, which was loaded onto 0.1 mL of an anion exchange resin (AG1-X8, 200–400 mesh, BioRad). Major element cuts containing Mo were collected with 0.45 mL 1.5 M HBr. The major element cut was dried and conditioned with 1 mL 0.4 M HCl–0.5 M HF, which was loaded onto 1 mL of anion exchange resin. Molybdenum was separated from most of the other elements by this step (Nagai and Yokoyama, 2014). The Mo recovery yields during chemistries performed at Tokyo Tech were ~85%.

After the initial Mo separation at Tokyo Tech, the samples were transferred to the University of Maryland (UMd). Because the separated samples contained insufficient Mo for measuring isotope ratios individually to a meaningful precision, the four Ryugu samples and the two Allende samples were respectively combined at UMd. The composite samples were dissolved in 0.5M HCl–0.5 M HF, and Mo was further purified using anion exchange column chemistry as described in (Nagai and Yokoyama, 2014). The column separations were repeated to reduce Zr and Ru abundances. Approximately 50 ng and 55 ng of Mo were purified from ~70 mg of the Ryugu powdered samples and ~50 mg of the Allende sample powder, respectively. The Mo recovery yields during chemistries performed at UMd were ~90%.

The total procedural blanks for the chemistries performed at Tokyo Tech are listed in Table S-3. A0106-A0107 and C0108, and A0106 and C0107 were processed in round 1 and 2, respectively. Although



the blanks for round 2 do not include the SOM extraction steps, Mo blanks in 2 mL of each organic reagent were measured (Table S-3). All three organic reagents used in SOM extraction contain little Mo. Because the four Ryugu samples were combined at UMd, the total Mo blank during the process at Tokyo Tech is estimated to be 5.7 ng. The additional blank added at UMd as a result of further processing is estimated to be 0.4 ng. Assuming the blanks have terrestrial isotopic composition, blank corrections change the $\epsilon^i\text{Mo}$ values of the Ryugu composite sample and Allende further above the CC line.

Molybdenum isotopic compositions were measured using a *Neptune Plus* multi-collector inductively-coupled plasma mass spectrometer (MC-ICP-MS, *Thermo Fisher*) at UMd. Ion beams of ^{92}Mo , ^{94}Mo , ^{95}Mo , ^{97}Mo , and ^{98}Mo were analyzed on Faraday collectors coupled with $10^{11} \Omega$ amplifiers. Isobaric interferences from Zr and Ru were collected by monitoring ^{91}Zr and ^{99}Ru using $10^{13} \Omega$ amplifiers. Due to the limited number of $10^{11} \Omega$ amplifiers, ^{100}Mo was not measured. Because the samples consisted of limited Mo, an X-skimmer cone and H-sample cone combination was used for greatest sensitivity. The purified Mo solutions (50 ppb in 0.5 M HNO_3 -0.05 M HF) were introduced into the MC-ICP-MS using an *Aridus 2* (*CETAC Technologies*) desolvating nebulizer. The 50 ppb solutions gave signals of 2 V on ^{98}Mo for over 100 cycles with 8.4 s integration times. Sample analyses were bracketed by measurements of an *Alfa Aesar* Mo standard solution. A terrestrial sample of 200 Ma molybdenite (Highland Valley) was measured in the same session as the Ryugu sample to assess the accuracy and precision of the measurements. The Highland Valley molybdenite was digested with HNO_3 and HCl and processed through a primary column before the measurements. The sample was previously measured numerous times in the UMd laboratory using thermal ionization mass spectrometry in negative ionization mode (N-TIMS) using a *Thermo Fisher Triton Plus* (Birmingham *et al.*, 2018).

The results for the molybdenite are summarized in Table S-4. The Mo isotopic ratios are reported as $\epsilon^i\text{Mo}$ values ($\epsilon^i\text{Mo} = [(^i\text{Mo}/^{96}\text{Mo})_{\text{sample}}/(^i\text{Mo}/^{96}\text{Mo})_{\text{standard}} - 1] \times 10^4$) for ^{92}Mo , ^{94}Mo , ^{95}Mo , and ^{97}Mo . The results for the molybdenite were in good agreement with the previous measurements. The analytical reproducibilities (2SD) as estimated by repeated analyses of equivalent quantities of Highland Valley ($n = 6$)



to the Ryugu and Allende samples are ± 0.6 for $\epsilon^{92}\text{Mo}$, ± 0.3 for $\epsilon^{94}\text{Mo}$, ± 0.3 for $\epsilon^{95}\text{Mo}$, and ± 0.1 for $\epsilon^{97}\text{Mo}$. It should be noted that these 2SDs are minimum estimates for the true external reproducibility. Because the Ryugu and Allende samples have complex matrices, the samples required more complex digestion and separation steps than the molybdenite. Due to the coexistence of Zr and Ru in the measured Mo samples for Allende (Zr/Mo = 0.0011, Ru/Mo = 0.0004) and Ryugu (Zr/Mo = 0.0010, Ru/Mo = 0.0002), relatively, large interference corrections were made on the obtained $\epsilon^{92}\text{Mo}$, $\epsilon^{94}\text{Mo}$, $\epsilon^{95}\text{Mo}$, and $\epsilon^{97}\text{Mo}$ values, which were -11 ϵ , -20 ϵ , 3 ϵ , and 3 ϵ for Allende and -10 ϵ , -18 ϵ , 3 ϵ , and 3 ϵ for Ryugu.

Results of Allende

The Mo isotopic pattern of Allende is characterized by positive $\epsilon^i\text{Mo}$ values that decrease in the order of $^{92}\text{Mo} > ^{94}\text{Mo} > ^{95}\text{Mo} > ^{97}\text{Mo}$ with a kink at ^{94}Mo and ^{95}Mo (Fig. 1), suggesting a combination of both *s*-process deficit and *r*-process excess in Mo isotopes compared to the terrestrial standard. The $\epsilon^{92}\text{Mo}$, $\epsilon^{94}\text{Mo}$, and $\epsilon^{95}\text{Mo}$ values of Allende were slightly higher than the range of literature values (Dauphas *et al.*, 2002; Burkhardt *et al.*, 2011; Budde *et al.*, 2016; Render *et al.*, 2017), while the obtained $\epsilon^{97}\text{Mo}$ value was slightly lower than the literature values. The difference is not due to an inadequate interference correction of Zr^+ and Ru^+ ions, because the correction lowers the observed $\epsilon^{92}\text{Mo}$ and $\epsilon^{94}\text{Mo}$ values but increases the $\epsilon^{95}\text{Mo}$ value. Given the small sample size of the Allende sample examined in this study (52.4 mg), this difference most likely reflects compositional heterogeneities in Allende consistent with powders including greater or lesser proportions of chondrules, calcium aluminum inclusions (CAIs) and amoeboid olivine aggregates (AOAs). For example, chondrule fractions separated from Allende show *s*-deficit compositions ranging from + 1.42 to + 3.98 on $\epsilon^{95}\text{Mo}$ (Budde *et al.*, 2016). Therefore, the Allende samples measured in previous studies may have originally contained slightly lower proportions of chondrule-like materials than the Allende reference powder measured in this study. Previous studies have shown that Mo isotopic data for CC and NC meteorites define two distinct linear trends on the $\epsilon^{94}\text{Mo}$ - $\epsilon^{95}\text{Mo}$ diagram (Budde *et al.*, 2016; Poole *et al.*, 2017; Worsham *et al.*, 2017). The



Allende sample generally plots on the CC line (Fig. 2a) as is consistent with prior studies and validates our Mo isotope analysis methods using multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS). The observation that the datum plots slightly above the line, most likely due to an excess of *r*-process Mo, may indicate that the Allende sample aliquot analyzed was enriched in CAI material compared to the Allende samples measured in previous studies.

Mass balance calculation

For the calculations we assumed: 1) $\delta^{92}\text{Mo}$, $\delta^{94}\text{Mo}$, $\delta^{95}\text{Mo}$, $\delta^{97}\text{Mo}$, and $\delta^{98}\text{Mo}$ values for SiC to average -686, -662, -418, -356, and -167, respectively (*e.g.*, Stephan *et al.*, 2019; Liu *et al.*, 2019), 2) a SiC abundance of 25 ppm in bulk Ryugu, as determined from the total area of $\sim 39,000 \mu\text{m}^2$ in Ryugu thin section and pressed particles (Barosch *et al.*, 2022), 3) the measured Mo abundance of 1 $\mu\text{g/g}$ for the Ryugu sample (Yokoyama *et al.*, 2023), and 4) the range of Mo abundances previously reported for presolar SiC (10-100 $\mu\text{g/g}$; Nicolussi *et al.*, 1998). We note that the Mo concentration in presolar SiC is not well determined.

For MC-ICP-MS and TIMS measurements, all the $\epsilon^i\text{Mo}$ values were determined by applying the mass fractionation correction. On the other hand, in resonance ionization mass spectrometry, which is used for analyses of SiC grains, the mass fractionation can be corrected using external standards, and the remaining natural mass fractionation is negligible relative to large nucleosynthesis anomalies of SiC grains. Thus, the MC-ICP-MS and TIMS data need to be transformed to values without internal normalization so that they can be compared with SiC grain data (Lugaro *et al.*, 2023; Stephan and Davis, 2021). Using these values, the compositions of the mixture of Ryugu material and presolar SiC at each SiC mixing rate. The SiC mixing rate (Ryugu 1 mol vs. SiC X mol) was increased by 0.00002 for each step of the calculation.



Supplementary Tables

Table S-1 Bulk meteorite data from previous studies.

	$\epsilon^{92}\text{Mo}$	$\epsilon^{94}\text{Mo}$	$\epsilon^{95}\text{Mo}$	$\epsilon^{97}\text{Mo}$	$\epsilon^{100}\text{Mo}$
Allende (CV)					
Dauphas <i>et al.</i> (2002)	2.38 ± 0.57	1.95 ± 0.79	1.98 ± 0.50	1.62 ± 0.53	1.17 ± 0.50
Dauphas <i>et al.</i> (2002)	3.54 ± 0.67	2.62 ± 1.26	1.92 ± 0.67	0.91 ± 0.41	0.56 ± 0.52
Dauphas <i>et al.</i> (2002)	2.57 ± 0.78	1.80 ± 0.46	1.78 ± 0.21	1.10 ± 0.53	1.67 ± 0.34
Burkhadt <i>et al.</i> (2011)	3.35 ± 0.36	2.44 ± 0.25	1.68 ± 0.09	0.82 ± 0.16	1.10 ± 0.14
Budde <i>et al.</i> (2016)	1.41 ± 0.27	0.97 ± 0.19	0.81 ± 0.05	0.40 ± 0.08	0.44 ± 0.12
Render <i>et al.</i> (2017)	1.43 ± 0.08	0.98 ± 0.05	0.84 ± 0.05	0.43 ± 0.05	0.49 ± 0.10
Orgueil (CI)					
Dauphas <i>et al.</i> (2002)	0.53 ± 0.57	0.13 ± 0.49	0.72 ± 0.25	0.39 ± 0.30	-0.47 ± 0.35
Burkhardt <i>et al.</i> (2011)	1.12 ± 0.59	0.79 ± 0.41	0.69 ± 0.23	0.26 ± 0.19	0.44 ± 0.34
Murchison (CM)					
Burkhardt <i>et al.</i> (2011)	6.44 ± 0.39	4.82 ± 0.2	3.17 ± 0.16	1.66 ± 0.14	2.28 ± 0.22
NWA 6604, DaG 412 (CK)					
Yokoyama <i>et al.</i> (2019)	2.4 ± 0.86	1.69 ± 0.23	1.36 ± 0.14	0.64 ± 0.05	0.76 ± 0.24
Yokoyama <i>et al.</i> (2019)	8.37 ± 0.86	6.38 ± 0.24	3.89 ± 0.14	1.95 ± 0.05	2.73 ± 0.24

The uncertainties shown are calculated at the 95 % confidence interval or the 2SD.



Table S-2 Recovery yield of Molybdenum (%) during the SOM extraction experiment using 43.73 mg of powdered Tagish Lake.

	Mo (%)
Hexane	0.06
DCM	0.10
MeOH	0.04

Table S-3 Organic reagents and procedural blank results.

	Mo (ng)
Blank in organic reagents	
Hexane	0
Dichloromethane	0
Methanol	0.01
Procedural blank	
<i>Chemistries at Tokyo Tech</i>	
Round-1	TAB-1 2.5
	TAB-2 2.3
Round-2	TAB-3 0.5
	TAB-4 0.4
<i>Chemistries at UMd</i>	
	0.4*

*Estimated from blank values of similar experiments.



Table S-4 Molybdenum isotopic composition for the Highland Valley terrestrial molybdenum sample.

	$\epsilon^{92}\text{Mo}$	$\epsilon^{94}\text{Mo}$	$\epsilon^{95}\text{Mo}$	$\epsilon^{97}\text{Mo}$
	0.35 ± 0.29	0.29 ± 0.20	0.15 ± 0.14	0.00 ± 0.11
	0.28 ± 0.29	0.16 ± 0.18	0.14 ± 0.14	-0.08 ± 0.12
	-0.30 ± 0.33	0.00 ± 0.23	-0.16 ± 0.17	-0.17 ± 0.13
	0.50 ± 0.27	0.12 ± 0.18	0.09 ± 0.13	-0.06 ± 0.10
	0.36 ± 0.29	0.04 ± 0.18	0.03 ± 0.15	-0.04 ± 0.11
	-0.06 ± 0.22	-0.15 ± 0.19	-0.20 ± 0.12	-0.18 ± 0.11
n	6	6	6	6
AVG	0.19	0.08	0.01	-0.09
2SD	0.61	0.30	0.31	0.14
95% conf.	0.32	0.16	0.16	0.07
TIMS data* (n = 2)	0.41 ± 0.76	0.17 ± 0.27	0.03 ± 0.15	-0.05 ± 0.06

Mo isotope ratios are normalized to $^{98}\text{Mo}/^{96}\text{Mo} = 1.453173$.

Uncertainties are reported as the 2SE run statistics of individual analyses.

*From Bermingham *et al.* (2018). Errors are 2SD of repeat analyses of the Mo standard solution.



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