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K, Rb, Ge, and Cu isotopes in Oued Chebeika 002 compared with CI chondrites, Ryugu, and Bennu

D.S. Grewal, N.X. Nie, B. Luais, Z.J. Zhang, Q. Ahmad, A. Vazquez Ochoa, P. Ni

Supplementary Information

The Supplementary Information includes:

- Analytical Methods
- Tables S-1 and S-2
- Supplementary Information References

Analytical Methods

Major and trace elements. ~200 mg of bulk sample of Oued Chebeika 002 was crushed in an agate mortar that had been previously cleaned with diluted HNO_3, rinsed with 18.2 MΩ high-purity water, and dried with acetone under a laminar-flow hood (CRPG- Nancy). Part of the sample powder was analysed for major and trace elemental compositions at the SARM analytical facilities (Service Analytique des Roches et des Minéraux, CRPG-Nancy, France) following routine $LiBO_2$ alkaline fusion dissolution techniques and using a Thermo Fisher ICP-OES iCap Pro for major elements, and a Thermo Fisher ICP-MS iCapQ for trace elements (Table S-1). The Ge concentration in OC002 was determined using the standard addition method, to achieve better accuracy and high-precision measurements. Analytical details and errors on the measurements are given in Carignan *et al.* (2001).

K and Rb isotope measurements. The K and Rb chemical purification and isotopic analyses were carried out at the Cosmochemical Analysis and Testing (CAT) Laboratory at MIT. 45.9 mg of OC002 was ground using a cleaned agate mortar. The powder was digested in double-distilled HNO_3 + HF (2:1 v/v) at 130 °C on a hot plate for 48 hours, followed by repeated treatment with aqua regia (3:1 v/v HCl-HNO_3) until no visible precipitate remained. The sample was then dried, converted, and redissolved in 4 ml 1M HNO_3, ready for chromatographic separation.

The separation of K and Rb followed the "Sr resin method" described in Table 1 of Nie *et al.* (2021), with a minor modification. Specifically, a Ti-removal step was incorporated as the first step using the same column as Column 1 (16 ml AG50W-X8), and Column 2 of the original protocol was removed. This modification simplified the procedure by reusing the 16 ml AG50W-X8 resin without changing resins or columns for Ti removal. In the modified protocol, after cleaning, conditioning, and loading the samples, Column 1 was first eluted with 80 ml of 0.8M HNO_3 + 0.2M HF to remove matrix elements (Na, Fe, Ti, and Al), followed by collection of K and Rb in the subsequent 136 ml of the same acid mixture. The combined K/Rb fraction was dried and redissolved in 4 ml of 0.5M HNO_3, then reloaded onto the same column and eluted with 0.5M HNO_3 (corresponding to Column 1 in Nie *et al.*, 2021), followed by purification through Sr resin columns (Column 3 in Nie *et al.*, 2021). The Rb cut collected from Column 3 was processed repeatedly

when necessary, depending on the matrix-to-Rb ratio (particularly K/Rb), to ensure complete removal of residual matrix elements and obtain a pure Rb solution.

After purification, K and Rb isotopic compositions were measured using a Thermo Fisher Scientific Neoma multi-collector inductively coupled plasma mass spectrometer equipped with a pre-cell mass filter (MC-ICP-MS/MS) and a collision–reaction cell (CRC). Detailed analytical conditions, including cup configurations and tuning parameters, are reported in Zhang *et al.*, 2025). Potassium isotopes were analysed under dry plasma conditions using an APEX Ω desolvating nebulizer at a sample uptake rate of ~150 µL/min, with a standard Ni sampler cone and H-type skimmer cone. Measurements were performed in low-resolution mode with the MS/MS module operated at 10% magnetic field strength. A mixture of He and H_2 was introduced into the CRC to suppress ArH^+ interferences. Under these conditions, we obtained ~22 V for ^{39}K at concentrations of 50 ng/g, corresponding to a sensitivity of 440 V/ppm for ^{39}K.

Rubidium isotope measurements were conducted on the same instrument under dry plasma conditions using an APEX Ω desolvating nebulizer equipped with a standard Ni sampler cone and an X-type skimmer cone. Analyses were performed in low-resolution mode with the MS/MS module operated at 20 % magnetic field strength. Solutions were analysed at concentrations of 3-30 ng/g depending on Rb content in digested aliquots. We obtained ~4 V for ^{85}Rb at concentrations of 3 ng/g, corresponding to a sensitivity of 1333 V/ppm for ^{85}Rb.

Isotopic compositions are reported in per mil (‰) notation relative to SRM 999c for K and SRM 984 for Rb:

$$\delta^{41/39}K\ (‰) = [(^{41}K/^{39}K)_{sample} / (^{41}K/^{39}K)_{SRM\ 999c} - 1] \times 1000$$
$$\delta\ ^{87/85}Rb\ (‰) = [(^{87}Rb/^{85}Rb)_{sample} / (^{87}Rb/^{85}Rb)_{SRM\ 984} - 1] \times 1000$$

Uncertainties for individual samples are reported as 95 % confidence intervals and are based on repeated measurements (n = 3-12) of each sample solution, assuming a Student's t-distribution. Two geostandards (BCR-2 and AGV-2) were processed alongside the meteorite samples through the same chromatographic columns and analysed under identical conditions. For BCR-2, the measured isotope compositions are $\delta^{41/39}K = -0.446 \pm 0.040$ ‰ (n = 8) and $\delta^{87/85}Rb = -0.210 \pm 0.030$ ‰ (n = 10), which agree within uncertainty with literature values ($\delta^{41/39}K = -0.49$ ‰; Wang *et al.*, 2021; $\delta^{87/85}Rb = -0.16$ ‰; Nie *et al.*, 2021). For AGV-2, the measured values are $\delta^{41/39}K = -0.452 \pm 0.083$ ‰ (n = 6) and $\delta^{87/85}Rb = -0.160 \pm 0.034$ ‰ (n = 12), also consistent with published values ($\delta^{41/39}K = -0.45$ ‰; Wang *et al.*, 2021; $\delta^{87/85}Rb = -0.15$ ‰; Nie *et al.*, 2021).

Ge isotopic measurements. The Ge chemistry and isotopic measurements were performed on an aliquot of the same OC002 sample powder used for the major and trace element analyses. The protocol for sample digestion and matrix separation is specific to Ge chemistry and follows the methods described in Ahmad *et al.* (2026); Luais (2007, 2012); and Luais and Florin (2025). All chemical reagents used were high-purity HF and HNO_3 acids from SeaStar™ and 18.2 MΩ deionised water. All steps of chemistry were carried out in the ISO-6 IRISS clean-lab facilities at CRPG-Nancy (France).

We analysed the OC002 sample along with the previously characterised CV-type Allende chondrite and the BIR-1 geostandard (Icelandic basalt) to assess analytical accuracy and reproducibility. Because of the high carbon contents (at the percent level) in CI-type and carbonaceous chondrites, we performed a pre-digestion heating of the chondrite samples at 600 °C in a furnace in platinum crucibles for carbon combustion (Luais and Florin, 2025). The chondrite and BIR-1 sample powders were then digested in 3:1 mixtures of concentrated HF and HNO_3 acids in screw-top Teflon vials on a hot plate at 65 °C to avoid any loss of volatile Ge. Alternating ultrasonic and hot plate steps were applied over several days until a whitish, cloudy solution free of any visible particles was obtained, resulting from the formation of Al-Mg-Ca-fluorides that do not incorporate Ge (Luais, 2012). A final centrifugation step ensured complete recovery of Ge in the supernatant solution.

After evaporation to dryness, the residue was dissolved in 1M HF for subsequent germanium isolation using a combined double-stack resin-exchange chromatography column (Luais, 2012; Ahmad *et al.*, 2026). This technique enables collection of a pure Ge fraction in a single chromatographic sequence. The procedure consists of loading the 1M HF sample solution onto an AG 1-X8 anion exchange resin, followed by additional 1M HF to elute the matrix. After placing an AG 50W-X8 cation-exchange resin column beneath the anionic column, 5 ml of 0.2M HNO_3 is passed through both columns to elute germanium. After removing the AG 1-X8 anion exchange column, an additional 2 ml of

0.5M HNO_3 is passed through the AG 50W-X8 cation-exchange resin to ensure complete Ge purification and recovery.

Ge isotopic measurements were conducted at CRPG using a Neptune Plus MC-ICP-MS coupled with a Cetac HGX-200 hydride generator introduction system (HGIS) with an uptake rate of ~200 µl·min^{-1} (Rouxel and Luais, 2017; Florin *et al.*, 2020). This technique eliminates isobaric interferences from elements that do not form hydrides (*e.g.*, Zn, Fe, Ni), thereby avoiding matrix effects. It provides a gain in signal sensitivity of at least a factor of 30, enabling measurement of very low quantities of Ge at the tens-of-ppb level with the high precision required for routine isotopic measurements of 10-20 ng Ge. At the beginning of each analytical session, gas flow rates, torch parameters, and ion lenses were optimised using a solution of the NIST SRM 3120a Ge standard (Luais, 2012). Gain calibration between the Faraday cups was performed prior to optimising peak shapes and centering the peaks. Analyses were carried out on diluted 10 ppb samples and standard solutions, with beam intensities matching to within 7% between samples and standards, giving an average ^{74}Ge beam intensity of 2 V during the course of this study. Typical acquisition sequences consisted of alternating measurements of the NIST SRM 3120a Ge standard and samples, with a washout time of 200 s in 0.5M HNO_3 between standard and samples. Data acquisition consisted of 40 integration cycles measured during 8.4 s, yielding an internal precision better than 5 ppm/amu (2SE).

This configuration allows calculation of Ge isotope ratios using the standard-bracketing method, expressed in delta notation relative to the NIST SRM 3120a Ge standard measured before and after each sample:

$$\delta^{74/70}\text{Ge (‰)} = [(^{74}\text{Ge}/^{70}\text{Ge})_{\text{sample}} / (^{74}\text{Ge}/^{70}\text{Ge})_{\text{NIST 3120a}} - 1] \times 1000$$

The total Ge procedural blanks, including chemistry and MC-ICP-MS measurements, were <0.2 ng, representing 0.04% of chemically processed Ge; therefore, no blank correction was applied.

The JMC and Aldrich Ge standards, as well as the BIR-1 geostandard (Luais, 2012) were used as secondary standards to evaluate the long-term stability, accuracy, and precision of isotopic measurements (Table S-2). Average values for the JMC and Aldrich Ge standard solutions yielded $\delta^{74/70}$Ge = −0.299 ± 0.093 ‰ (n = 13) and $\delta^{74/70}$Ge = −1.968 ± 0.119 ‰ (n = 16), respectively (2σ SD). The BIR-1 basalt yielded $\delta^{74/70}$Ge = 0.65 ± 0.12‰ (n = 5), while the CV-type Allende meteorite and its reference material gave $\delta^{74/70}$Ge = 0.093 ± 0.073 ‰ (n =6), and 0.08 ± 0.100 ‰ (n=6), respectively (Table S-1). All results are consistent within 2 standard deviations with published reference values (Luais, 2012; Luais and Florin, 2025; Ahmad *et al.*, 2026). At least five replicates were required to achieve external reproducibility of ~0.1 ‰ (2σ SD).

Cu isotopic measurements. ~4 mg of the OC002 aliquot was dissolved overnight on a hot plate in a 2:1 mixture of concentrated HF and HNO_3 for Cu isotope analysis. The dissolved solution was dried down and converted to chloride form, then dissolved in 8M HCl for Cu column purification. Copper separation was conducted using BioRad quartz glass columns with a diameter of 0.5 cm. Each column was filled with approximately 5 cm of BioRad AG1-X8 (200-400 mesh) resin. Matrix elements were eluted using 6.5 ml of 8M HCl, and the Cu fraction was subsequently eluted in another 9.5 ml of 8M HCl. The purification process was repeated once to further purify Cu. The final products were converted to nitric form and dissolved in 2% nitric acid for mass spectrometer analysis.

Copper isotope analysis was performed under high-energy mode on a Nu Sapphire collision-cell multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at UCLA. Sample aliquots were diluted to 50 ppb and introduced into the mass spectrometer in wet plasma mode. The sensitivity was approximately 30 V/ppm at a sample introduction rate of 60 µL/min. Standard-sample bracketing using the ERM-AE633 standard was used to correct for instrumental mass bias. Each sample was measured 6 times, with each measurement consisting of 30 cycles with 4 seconds of integration. Variations in Cu ratios are reported relative to the international standard SRM976 after correcting for a −0.01‰ difference between SRM976 and ERM-AE633 (Moeller *et al.*, 2012).

$$\delta^{65/63}\text{Cu (‰)} = [(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}} / (^{65}\text{Cu}/^{63}\text{Cu})_{\text{SRM 976}} - 1] \times 1000$$

A geological standard, AGV-2, was analysed along with OC002 to verify the external precision of the session. A $\delta^{65/63}$Cu value of 0.036 ± 0.024‰ (2SE, n = 6) was obtained for AGV-2, consistent with the recommended value of 0.04 ± 0.04 ‰ (Moynier *et al.*, 2017).

Supplementary Tables

Table S-1 Bulk element abundances in Oued Chebeika 002 (in wt. % for major elements and Ni, and in µg/g for the other elements).

Oued Chebeika 002			
SiO_2	25.11	**Pb**	2.46
Al_2O_3	1.56	**Rb**	2.34
Fe_2O_3 Total	28.20	**Sb**	0.438
MnO	0.319	**Sc**	6.12
MgO	17.50	**Sn**	1.55
CaO	1.89	**Sr**	9.72
Na_2O	0.75	**Ta**	0.017
K_2O	0.063	**Th**	0.029
TiO_2	0.079	**U**	0.010
P_2O_5	0.15	**V**	49.8
LOI	n.d.	**W**	0.328
		Y	1.15
As	1.63	**Zn**	341
Ba	< L.D.	**Zr**	5.5
Be	< L.D.	**La**	0.232
Bi	0.118	**Ce**	0.606
Cd	0.71	**Pr**	0.084
Co	516	**Nd**	0.423
Cr	2737	**Sm**	0.135
Cs	0.172	**Eu**	0.050
Cu	*216* *	**Gd**	0.170
Ga	11.2	**Tb**	0.032
Ge	36.5	**Dy**	0.209
Hf	0.142	**Ho**	0.049
In	0.099	**Er**	0.129
Mo	1.24	**Tm**	0.021
Nb	0.269	**Yb**	0.131
Ni %	1.04	**Lu**	0.020

n.d. : not determined

< L.D. : under the detection limit

* The measured Cu concentration (216 ppm) is well above the 107 ppm obtained by isotope dilution and exceeds the range of other CI chondrites, Ryugu, and Bennu (~108-156 ppm). We currently have no explanation for this discrepancy. We use the isotope-dilution value of 107 ppm in all figures.

Table S-2 Germanium isotopic compositions of Oued Chebeika 002, and Allende (CV), BIR-1 samples, secondary Ge standard solutions analysed during the course of this study.

	Reference	n	$\delta^{72/70}$Ge	±2σ SD	$\delta^{73/70}$Ge	±2σ SD	$\delta^{74/70}$Ge	±2σ SD	***	$\delta^{74/70}$Ge	±2σ SD
Oued Chebeika 002 (CI)		5	0.513	0.015	0.727	0.072	0.980	0.067	Orgueil (CI)	0.901 [1]	0.057
Allende (CV) *	MNHN02811	6	0.058	0.034	0.069	0.070	0.093	0.073	Allende	0.096 [1]	0.120
Allende (CV) RM**	USNM 3529	6	0.045	0.057	0.056	0.089	0.080	0.100			
BIR-1 geostandard		5	0.362	0.104	0.504	0.112	0.65	0.125	BIR-1	0.612 [1] 0.61 [2]	0.095 0.09
Secondary std solutions											
JMC Ge Standard		13	-0.140	0.044	-0.183	0.039	-0.299	0.093	n= 67	-0.309	0.095
Aldrich Ge Standard		16	-1.014	0.059	-1.515	0.095	-1.968	0.119	n =68	-1.967	0.090

* Muséum National d'Histoire Naturelle Paris

** Smithsonian Institution of Washington, Reference material, split15, position 24

*** [1] Luais and Florin (2025); [2] Ahmad *et al*. (2026)

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