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Abstract:	Achondrite meteorites are remnants of the earliest planetary differentiation processes in the Solar System. They have been used to anchor short-lived radiochronometers to absolute ages determined from long-lived radiochronometers. More specifically, when comparing the isotopic systematics of the short-lived 26AI-26Mg chronometer anchored to absolute U-corrected Pb-Pb ages, inferences about the distribution of 26AI (half-life of ~717 000 yr) in the protoplanetary disk can be evaluated. The ungrouped achondrite Erg Chech (EC) 002 has a distinct mineralogy and more evolved elemental composition compared to basaltic achondrites. In situ and solution 26AI-26Mg chronometry and 53Mn-53Cr chronometry suggest that EC 002 formed within ~ 0.7 to 2.2 Ma after the formation of Ca-AI-rich inclusions (CAIs), making it the oldest known sample of igneous crust in the Solar System (Barrat et al., 2021; Anand et al., 2022; Zhu et al., 2022; Fang et al., 2022). Here we present the U-corrected Pb-Pb age and 26AI-26Mg age obtained by MC-ICPMS solution analysis of the same mineral separate samples of EC 002. In addition, six merrillite grains were analyzed by in-situ SIMS to determine their Pb-Pb individual ages. The U isotope composition of EC 002 exhibits internal heterogeneities between leached pyroxene (238U/235U = 137.766 \pm 0.027) and the bulk rock (238U/235U = 137.8190 \pm 0.0074). The Pb isotope composition of progressively leached pyroxenes are characterized by radiogenic 206Pb/204Pb ratios (ranging from 41 to 23487). Using the U isotope composition of the leached pyroxenes, the resulting age of the 207Pb/206Pb-204Pb/206Pb isochron is 4565.87 \pm 0.30 Ma (2 σ). The weighted mean of the Pb-Pb ages of seven SIMS analyses of merrillites are 4564.3 \pm 5.2 Ma (2 σ). These similar ages (within uncertainty) indicate rapid cooling and the absence of significant thermal events after ~ 4559 Ma on the parent body of EC 002. The 26AI- 26Mg isochron through a bulk, pyroxene, fine-grained and four plagioclase fractions defines an ini					

ab ma Pt Th wh the pr sa da	psolute Pb-Pb age of CV3 CAIs (4567.30 ± 0.16 Ma; Connelly et al., 2012), the Al-Mg odel age of EC 002 is 4565.47 ± 0.20 Ma, slightly younger than its U-corrected Pb- o age. The concordance of the Pb-Pb and 26Al-26Mg ages of ungrouped CC achondrites hen anchored to EC 002 suggest that 26Al was homogeneously distributed between the NC and CC reservoirs at the time of their parent body accretion. Furthermore, the esence of internal U isotope heterogeneities found between mineral and whole-rock amples of EC 002 supports the need of U isotope analysis of meteoritic samples ated using the Pb-Pb chronometer.
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1	Al-Mg and U-Pb chronological records of Erg Chech 002 ungrouped
2	achondrite meteorite
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32 Abstract

33 Achondrite meteorites are remnants of the earliest planetary differentiation processes in the Solar 34 System. They have been used to anchor short-lived radiochronometers to absolute ages determined 35 from long-lived radiochronometers. More specifically, when comparing the isotopic systematics of the short-lived ²⁶Al-²⁶Mg chronometer anchored to absolute U-corrected Pb-Pb ages, inferences 36 about the distribution of ²⁶Al (half-life of ~717 000 yr) in the protoplanetary disk can be evaluated. 37 38 The ungrouped achondrite Erg Chech (EC) 002 has a distinct mineralogy and more evolved elemental composition compared to basaltic achondrites. In situ and solution ²⁶Al-²⁶Mg 39 chronometry and 53 Mn- 53 Cr chronometry suggest that EC 002 formed within ~ 0.7 to 2.2 Ma after 40 41 the formation of Ca-Al-rich inclusions (CAIs), making it the oldest known sample of igneous crust 42 in the Solar System (Barrat et al., 2021; Anand et al., 2022; Zhu et al., 2022; Fang et al., 2022). Here we present the U-corrected Pb-Pb age and ²⁶Al-²⁶Mg age obtained by MC-ICPMS solution 43 44 analysis of the same mineral separate samples of EC 002. In addition, six merrillite grains were 45 analyzed by in-situ SIMS to determine their Pb-Pb individual ages.

46 The U isotope composition of EC 002 exhibits internal heterogeneities between leached pyroxene $(^{238}U/^{235}U = 137.766 \pm 0.027)$ and the bulk rock $(^{238}U/^{235}U = 137.8190 \pm 0.0074)$. The Pb isotope 47 composition of progressively leached pyroxenes are characterized by radiogenic ²⁰⁶Pb/²⁰⁴Pb ratios 48 49 (ranging from 41 to 23487). Using the U isotope composition of the leached pyroxenes, the resulting age of the ${}^{207}\text{Pb}/{}^{206}\text{Pb}-{}^{204}\text{Pb}/{}^{206}\text{Pb}$ isochron is 4565.87 ± 0.30 Ma (2 σ). The weighted 50 51 mean of the Pb-Pb ages of seven SIMS analyses of merrillites are 4564.3 ± 5.2 Ma (2 σ). These 52 similar ages (within uncertainty) indicate rapid cooling and the absence of significant thermal events after ~ 4559 Ma on the parent body of EC 002. The 26 Al- 26 Mg isochron through a bulk rock, 53 pyroxene, fine-grained and four plagioclase fractions defines an initial 26 Al/ 27 Al ratio of [8.89 ± 54

55	0.79] × 10 ⁻⁶ corresponding to a formation age of 1.83 ± 0.12 Ma after CAIs ([5.23 ± 0.13] × 10 ⁻⁵ ;
56	Jacobsen et al., 2008). The initial ²⁶ Al abundance is consistent with previous MC-ICP-MS ²⁶ Al-
57	26 Mg reported systematics for EC 002 (Fang et al., 2022), but 0.46 ± 0.13 Myr older than the <i>in</i>
58	situ SIMS ²⁶ Al- ²⁶ Mg age previously reported by Barrat et al. (2021). When anchored to the absolute
59	Pb-Pb age of CV3 CAIs (4567.30 \pm 0.16 Ma; Connelly et al., 2012), the Al-Mg model age of EC
60	002 is 4565.47 ± 0.20 Ma, slightly younger than its U-corrected Pb-Pb age.
61	The concordance of the Pb-Pb and ²⁶ Al- ²⁶ Mg ages of ungrouped CC achondrites when anchored
62	to EC 002 suggest that ²⁶ Al was homogeneously distributed between the NC and CC reservoirs at
63	the time of their parent body accretion. Furthermore, the presence of internal U isotope
64	heterogeneities found between mineral and whole-rock samples of EC 002 supports the need of U
65	isotope analysis of meteoritic samples dated using the Pb-Pb chronometer.

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68 Keywords

69 early Solar System, planetary differentiation, achondrite, Al-Mg chronology, U-Pb chronology

70 <u>1. Introduction</u>

71 The use of radiometric dating has been a cornerstone of unravelling the mysteries surrounding the 72 formation and early evolution of the Solar System. Of the various chronometers, the absolute Pb-Pb chronometer and the short-lived, relative ²⁶Al-²⁶Mg chronometer have been particularly useful 73 in dating extra-terrestrial materials. The ²⁶Al-²⁶Mg chronometer can resolve events that took place 74 75 within ~ 30,000 years, while the U-corrected Pb-Pb chronometer has, among other milestones, 76 established the age of the Solar System between ~ 4567 and 4568 Ma by dating Ca-Al-rich 77 inclusions in CV3 chondrites (CAIs; Amelin et al., 2010; Bouvier and Wadhwa, 2010; Connelly 78 et al., 2012; Sanborn et al., 2019). Despite the merits of both these chronometers, questions remain about their significance. For instance, meaningful applications of the ²⁶Al-²⁶Mg chronometer rely 79 on a homogeneous initial distribution of the parent nuclide ²⁶Al ($T_{1/2} = 0.717$ Ma, NuDat 3.0, 80 81 National Nuclear Data Center) between samples and a chronological reference (e.g., CAIs, 82 achondrites). To determine absolute and accurate U-corrected Pb-Pb ages using the dual long-lived decay chains of ²³⁵U to ²⁰⁷Pb and ²³⁸U to ²⁰⁶Pb, the ²³⁸U/²³⁵U ratio needs to be precisely known. It 83 was assumed that the ²³⁸U/²³⁵U ratio was invariant at 137.88 among early Solar System materials, 84 85 until significant variations of up to 3.5% in different objects were discovered (Stirling et al., 2005; Amelin et al., 2010; Brennecka et al., 2010). The assumption of a homogeneous distribution of 86 87 ²⁶Al in the protoplanetary disk has repeatedly been challenged, without a consensus in the scientific 88 community emerging. Studies involving CAIs, amoeboid olivine aggregates (AOAs), bulk 89 meteorites (Larsen et al., 2011), chondrules (Bollard et al., 2019) and angrites (Schiller et al., 2015) suggested an initial ²⁶Al/²⁷Al ratio in the inner Solar System around 1×10^{-5} , about 80% lower 90 than the canonical value of ~ 5.2×10^{-5} (Jacobsen et al., 2008). Other studies have disagreed with 91 92 these conclusions (e.g., Wasserburg et al., 2012; Kita et al., 2013; Gregory et al., 2020). In

particular, combined U-corrected Pb-Pb and ²⁶Al-²⁶Mg dating of achondrites, e.g., angrites or 93 unique, ungrouped meteorites, have been frequently utilized to evaluate the distribution of ²⁶Al 94 95 within the protoplanetary disk (e.g., Bouvier et al., 2011; Schiller et al., 2015; Wimpenny et al., 2019). The Pb-Pb and ²⁶Al-²⁶Mg ages of some meteorites that formed in the non-carbonaceous 96 97 inner Solar System (NC reservoir; Warren, 2011; Kruijer et al., 2020), such as the angrite 98 D'Orbigny (Amelin, 2008b; Schiller et al., 2015; Tissot et al., 2017), used as an anchor meteorite 99 for short-lived radionuclide chronometers, and the unique achondrite Asuka 881394 (Wadhwa et 100 al., 2009; Hublet et al., 2017; Wimpenny et al., 2019) do not match in model ages when anchored 101 to CAIs from the CV3 chondrites Efremovka and Allende using their reported U-corrected Pb-Pb ages (Connelly et al., 2012) and canonical ${}^{26}Al/{}^{27}Al$ ratio of $[5.23 \pm 0.13] \times 10^{-5}$ (Jacobsen et al., 102 2008). Conversely, the Pb-Pb and ²⁶Al-²⁶Mg systematics of achondrites that formed in the 103 104 carbonaceous chondrite (CC) reservoir of the outer Solar System, such as NWA 6704 (Amelin et 105 al., 2019; Sanborn et al., 2019) and NWA 2976 (Bouvier et al., 2011b), exhibit concordant Ucorrected Pb-Pb and 26 Al- 26 Mg ages when anchored to the absolute age of CAIs of 4567.30 ± 0.16 106 Ma (Connelly et al., 2012), suggesting a homogeneous distribution of ²⁶Al between CAIs and CC 107 meteorites. The discordance between U-corrected Pb-Pb and ²⁶Al-²⁶Mg ages of some NC 108 meteorites has been interpreted by different studies to reflect either heterogeneity of ²⁶Al in the 109 110 Solar System (Schiller et al., 2015), or that the ²⁶Al-²⁶Mg systematics were disturbed through thermal metamorphism or shock heating from impact events (Sanborn et al., 2015; Koefoed et al., 111 112 2016; Sanborn et al., 2019; Wimpenny et al., 2019).

In order to further evaluate the distribution of ²⁶Al in the early Solar System, we have used both the Pb-Pb and ²⁶Al-²⁶Mg chronometers to date the formation of the unique achondrite Erg Chech 002. Erg Chech 002 is a recent meteorite find with an unusual chemistry and mineralogy: (1) the

116 whole-rock composition is comparable to terrestrial andesites in silica and alkaline element 117 concentrations (Barrat et al., 2021) and (2) it contains large (up to 9 cm) orthopyroxene megacrysts 118 (Gattacceca et al., 2021) in a groundmass of sodic plagioclase, pigeonite and silica (Fig. 1). 119 Geochemically, EC 002 exhibits a distinct trace element pattern compared to other andesitic 120 meteorites, with no significant anomalies in alkali and high field-strength elements relative to CI 121 chondrites (Barrat et al., 2021; Nicklas et al., 2022). Highly siderophile elements show 122 fractionation between the compatible and incompatible elements that suggest metal-silicate 123 separation occurred on the parent body of EC 002 (Nicklas et al., 2022).

Mass-independent Δ^{17} O values of EC 002 suggest an affinity with four anomalous eucrites, 124 125 Bunburra Rockhole, EET 92023, Emmaville and Asuka 881394, but these meteorites are 126 mineralogically different from EC 002 (Gattacceca et al., 2021). The O isotope composition, the negative Tm anomaly of the whole-rock (Barrat et al., 2021), as well as the Cr and Nd stable 127 128 isotope anomalies (Anand et al., 2022; Fang et al., 2022; Zhu et al., 2022) indicate accretion of the 129 EC 002 parent body in the NC reservoir. The elemental composition supports formation by partial 130 melting of a chondritic precursor, followed by rapid cooling after cooling to 900°C, likely by 131 excavation or ejection from an impact event (Barrat et al., 2021).

EC 002 was first dated by in situ ²⁶Al-²⁶Mg analysis using secondary ionization mass spectrometry (SIMS), as well as noble gas geochemistry (Barrat et al., 2021). The Al-Mg systematics result in an initial ²⁶Al/²⁷Al ratio of $[5.72 \pm 0.07] \times 10^{-6}$ and an age of 2.29 ± 0.04 Ma after CAI formation, making it the oldest igneous meteorite found to date. A subsequent study of the ²⁶Al-²⁶Mg chronology by MC-ICP-MS reported a different initial ²⁶Al/²⁷Al ratio of $[8.89 \pm 0.09] \times 10^{-6}$, resulting in an age of 1.83 ± 0.04 Ma after CAI formation (Fang et al., 2022). Additionally, the formation age of EC 002 was modelled at 4565.6 ± 0.6 Ma and 4566.6 ± 0.6 Ma by two separate

studies using the short-lived ⁵³Mn-⁵³Cr chronometer, albeit anchored to the D'Orbigny angrite 139 140 (Anand et al., 2022; Zhu et al., 2022). To get a better constraint on the crystallisation history of 141 EC 002, assess its potential as a new anchor for short-lived radionuclides and to further evaluate the distribution of ²⁶Al in the early Solar System, we analyzed the Mg, Pb and U isotope 142 143 compositions of whole-rock and mineral fractions from the same sample piece by multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to determine the ²⁶Al-²⁶Mg and U-144 145 corrected Pb-Pb ages. We also analysed merrillite Ca-phosphates by *in-situ* secondary ion mass 146 spectrometry (SIMS) Pb-Pb analysis to constrain the crystallization history and thermal records of 147 EC002.

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149 <u>2. Methods</u>

150 2.1 Sample preparation

For U-Pb and Al-Mg studies, a ~ 600 mg section of Erg Chech 002 (from Ben Hoefnagels, Big Bang Meteorites) was rinsed in acetone and water, prior to being crushed in an agate mortar. Roughly 120 mg were taken as a bulk rock fraction. Pyroxene and feldspar minerals were separated by hand-picking under binoculars, with repeated crushing and sieving. Eight feldspar fractions were hand-picked, along with a pyroxene and a fine-grained (<60 μ m) fraction for Mg isotope analysis.

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158 2.2 Characterisation and SIMS Pb-Pb dating of phosphates

A 1-inch polished section mounted in epoxy was prepared from a 0.75g slice of EC 002 (Mirko Graul Meteorite) at the Bayerisches Geoinstitut (BGI). The section was first carbon-coated and analysed to obtain multi-field BSE-EDS element maps (Fig. 1; preselected to be Na, Mg, Al, Si, P, O, Fe, Ca, Ti, Zr, Cr, Ni, S, Cl) using a focused ion beam scanning electron microscopy (FEI
Scios FIB-SEM) at BGI. For this purpose, the electron beam was tuned to 20 kV and 1.6 nA. We
selected six merrillite grains for SIMS analyses.

165 Further petrographic observations were carried out at BGI using a Zeiss Gemini 1530 scanning 166 electron microscope operated at 20 kV under BSE-EDS mode. Mineral compositions were 167 measured using a JEOL JXA 8200 electron microprobe equipped with five spectrometers operated 168 at 15 kV and 15 nA with \sim 1 µm focused electron beam (5 µm for merrillites) and counting time of 169 20s on peak and 10s on background (10s on peak for Na, Cl and F, and 5s on background to reduce 170 the beam induced damage and loss of volatile during analysis). The standards used were: Na and 171 Si (albite), Ca (wollastonite or apatite), K (orthoclase), Mg (enstatite), Fe (Fe metal), Mn and Ti 172 (MnTiO₃), Al (spinel), Ni (Ni metal), Cr (Cr metal), and P (apatite).

173 For SIMS, the carbon coating of the same polished mount of EC 002 was removed. The mount 174 was cleaned with alcohol, dried, and coated with a 50 nm gold film before SIMS analysis. High 175 precision ²⁰⁷Pb-²⁰⁶Pb phosphate dating was performed using a Cameca IMS 1280-HR type 176 secondary ion mass spectrometer (SIMS) at the Heidelberg Ion Probe (HIP), Universität 177 Heidelberg. Duoplasmatron ion source was operated to generate a primary O^{-} ion beam with 23 178 kV impact energy, 20-40 nA current and beam size of 20-30 µm on sample surface. During each 179 analysis, a two-minute pre-sputtering was applied to remove potential surface contamination. Positive secondary ions of ⁴⁰Ca₂³¹P¹⁶O₄⁺, ²⁰⁴Pb⁺, ²⁰⁶Pb⁺, ²⁰⁷Pb⁺, ²³⁸U⁺, ²³⁸U¹⁶O⁺ were extracted, 180 181 mass filtered at a mass resolution (M/ Δ M) of ~4000 before detected sequentially in a low-noise 182 ion-counting electron multipliers for 1s, 20s, 10s, 10s, 10s and 6s, respectively under single 183 collection mode. Thirty cycles per analysis were typically applied for better statistics.

⁴⁰Ca₂³¹P¹⁶O₄⁺ was used for peak centering and ²³⁸U¹⁶O⁺ for calculating U and Pb secondary ion yields.



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Figure 1: Backscattered electron image overlaid with energy dispersive spectroscopy composed as a multi-field phase colored map of Erg Chech 002 (Si in yellow, Na in dark blue, Al in grey, Mg in red, Ca in pink) polished mount used for the SIMS analyses. Large pyroxene megacrysts and rounded olivine crystals are surrounded by groundmass of sodic plagioclase, pigeonite and accessory chromite, merrillite and silica polymorphs.

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194 2.3 Determination of ${}^{27}Al/{}^{24}Mg$ ratios

A bulk rock fraction consisting of roughly 120 mg, one pyroxene and eight feldspar mineral fractions prepared for Mg isotope analysis were dissolved in a 29 M HF- 15 M HNO₃ (5:1) mixture at 120 °C, before being dried down and re-dissolved in 15M HNO₃. The samples were dried down

again and then converted to its chloride form with 6 M HCl. Determination of the ²⁷Al/²⁴Mg ratios 198 199 of the mineral separates was performed using a Thermo Fischer iCAP Qc quadrupole ICP-MS at 200 the University of Western Ontario (UWO). Of the eight feldspar fractions, after an initial analysis, those with similar ²⁷Al/²⁴Mg ratios were combined in order to maximize Mg content, allowing for 201 analysis at higher concentrations, without sacrificing the spread of ²⁷Al/²⁴Mg ratios. This resulted 202 203 in four feldspar fractions, alongside the bulk rock, pyroxene and fine-grained fractions. During analysis, gravimetrically prepared Al-Mg solutions, ranging from ²⁷Al/²⁴Mg ratios of 0.001 to 50, 204 were used to calibrate ²⁷Al/²⁴Mg ratios of the samples. Terrestrial standards BCR-2 and San Carlos 205 206 olivine, and bulk rock CV3 chondrite Allende were analyzed with the samples to verify the 207 accuracy of the analysis and are reported alongside their isotopic compositions in Table 1. Uncertainties associated with ${}^{27}\text{Al}/{}^{24}\text{Mg}$ ratios is $\pm 5\%$, with exception of the bulk rock fraction, 208 which in two separate analyses resulted in distinct ²⁷Al/²⁴Mg ratios. To account for the increased 209 210 uncertainty, the error there is the 2SE of the average of both analyses.

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212 2.4 Magnesium isotope analysis

An aliquot equivalent to 0.6 mg of the bulk rock fraction and corresponding to $\approx 20 \ \mu g$ Mg was set aside for Mg separation, along with the pyroxene, fine-grained and feldspar fractions. We used a two-stage ion-exchange chromatography protocol, following a modified version of the protocol described by Wombacher et al. (2009).

The protocol uses about 1.2 ml of AG50W-X8 (200-400 mesh) resin deposited within HCl-cleaned BioRad® plastic columns. For the first stage, the columns and resin are cleaned again together with ca. 20 ml of 6 M HCl. The resin is then conditioned with 3.6 ml of 10 M HCl. The sample is taken up in 0.3 ml 10 M HCl and then loaded onto the columns, before Mg and other matrix

221 elements (such as Al, Cr and Ni) are eluted by 3.2 ml of 10 M HCl. Subsequent Ca and Fe elution 222 are accomplished by adding 15 ml of 8 M HCl and 20 ml of 4 M HCl, respectively, to the columns. 223 To ensure sufficient recovery of Mg, the first 0.8 ml of the Ca elution step are collected separately 224 and dried down. The same procedure is repeated a second time with the separate cut which is then 225 collected and combined with the 3.2 ml from the previous run. Magnesium is then further separated 226 from the remaining matrix elements by a third stage, using the same columns and resin as the 227 previous stages. The resin is first conditioned with 3.6 ml 0.4 M HCl before the sample is loaded 228 onto the column in 0.3 ml of 0.4 M HCl. Remaining matrix elements are eluted by adding 33.6 ml 229 of 0.4 M HCl and then 7.2 ml of 0.15 M HF. For Mg elution, 1 ml of 1 M HCl is added before an 230 additional 20 ml are added (Table 2). This method results in a total yield of > 99.6 % of Mg. We 231 used dissolved homogenized powders of the San Carlos olivine and the Allende CV3 meteorite as 232 inter-laboratory secondary standards, that underwent the full protocol with each set of columns. 233 To evaluate that the column chemistry did not introduce any fractionation on Mg isotopes, a pure 234 Mg standard solution was analyzed without column processing, with column processing, and after 235 the solution being added to the Mg-free matrices of terrestrial standards BCR-2 and BIR-1. 236 Between these analyses, no resolvable differences in Mg isotope compositions were found (Table 237 1).

Magnesium isotope compositions of EC 002 fractions were analyzed by a Thermo Fisher Neptune Plus MC-ICP-MS at the Friedrich-Alexander-Universität (FAU) in Erlangen. The ²⁴Mg, ²⁵Mg and ²⁶Mg ion beams were measured simultaneously on the L4, Center and H4 Faraday cups, respectively, with a 10^{10} amplifier on the L4 cup, and run in medium resolution mode with a Jet sample cone and H skimmer cone interface. The sample and standard solutions were diluted to approximately 300 ppb (\approx 90 V on ²⁴Mg), where Mg amounts allowed, in 2% HNO₃ and matched

244 to within 5% or less of their concentrations. Solutions were introduced using a Cetac Aridus II 245 desolvating nebulizer system. Standard-sample bracketing with the DSM-3 standard was used to 246 correct for mass fractionation and instrumental drift. Generally, analyses consisted of four sample 247 measurements bracketed by five standard measurements, with each measurement consisting of a 248 peak center, 20 cycles at 8.4 s of integration time followed by 150 s of wash time. The instrumental 249 background was measured prior to each sample and standard analysis. Total procedural blanks 250 were less than 5 ng, a negligible amount relative to the amount of Mg in the samples ($\approx 75 \ \mu g$). 251 We report our Mg isotope data in δ -notation (in per mil), the relative differences of ${}^{x}Mg/{}^{24}Mg$ 252 ratios of the sample to the bracketing standard, where x = 25 or 26: $\delta^{x}Mg = ([{}^{x}Mg/{}^{24}Mg]_{sample}/[{}^{x}Mg/{}^{24}Mg]_{standard} - 1) \times 1000$ 253 (Eq. 1) Mass-independent variations in ²⁶Mg due to ²⁶Al decay (δ^{26} Mg*) were determined by internally 254 normalizing the measured ${}^{26}Mg/{}^{24}Mg$ ratio to ${}^{25}Mg/{}^{24}Mg = 0.12663$ (Catanzaro et al., 1966) using 255 256 the exponential law with fractionation factor $\beta = 0.511$: $\delta^{26}Mg^* = (\delta^{26}Mg - (1 + \delta^{25}Mg/1000)^{(1/\beta)} - 1) \times 1000$ 257 (Eq. 2) 258

Table 1: Al-Mg data for Mg solution standard Cambridge-1, terrestrial rock standard San Carlos olivine, and bulk rock CV3 chondrite Allende, as well as unprocessed and processed standard solution isotope compositions to verify the absence of fractionation effects during column chemistry. n.r.: not reported.

Standards	$^{27}\text{Al}/^{24}\text{Mg}$	±	$\delta^{25}Mg$ [‰]	2SE	$\delta^{26}Mg^{*}$ [‰]	2SE	n
Cambridge-1			-1.374	0.020	-0.005	0.006	22
literature ^a			-1.343	0.036	n.r.	n.r.	49
literature ^b			-1.335	0.032	n.r.	n.r.	
San Carlos olivine	0.0021	0.0009	-0.162	0.009	-0.005	0.005	9
literature ^c	0.0031	0.0004	-0.16	0.07	0.00	0.05	36

Allende	0.1300	0.0039	-0.174	0.026	0.013	0.009	4
literature ^c	0.1294	0.0007	-0.16	0.03	0.03	0.05	
BCR-2	3.796	0.052					
literature ^c	3.76	0.04					
UWO ICP Std ^d			-0.329	0.027	0.018	0.022	12
UWO ICP Std ^e			-0.296	0.027	-0.013	0.031	8
UWO ICP Std $^{\rm f}$			-0.323	0.020	0.006	0.041	8
UWO ICP Std ^g			-0.309	0.023	-0.003	0.033	16
UWO ICP Std ^h			-0.318	0.018	0.006	0.021	28

^a From An and Huang (2014). ^b From Vogl et al. (2020). ^c From Bouvier et al. (2013). ^d Unprocessed. ^e

Column processed. ^f Added to Mg-free matrices of terrestrial standards BCR-2 and BIR-1, column processed. ^g All column-processed combined (b+c). ^h All standard solution measurements combined (a+b+c).

Stage 1 + 2			Stage 3			
	Resin: 1.	2 ml of AG5	0W-X8 (200-400 mesh)			
Step	Acid	Volume Step [ml]		Acid	Volume [ml]	
Resin cleaning	4 M HCl	ca. 20	Resin conditioning	0.4 M HCl	3.6	
Resin conditioning	10 M HCl	3.6	Load sample	0.4 M HCl	0.3	
Load sample	10 M HCl	0.3	Matrix elution	0.4 M HCl	33.6	
Mg + matrix elution	10 M HCl	3.2	Be, Ti, Al elution	0.15 M HF	7.2	
Post-Mg step	8 M HCl	0.8	Pre-Mg step	1 M HCl	1	
Ca elution	8 M HCl	14.2	Mg elution	1 M HCl	20	
Fe elution	4 M HCl	10	Wash out	6 M HCl	5	
Wash out	4 M HCl	10				

268 **Table 2:** Three-stage Mg separation scheme modified from Wombacher et al. (2009)

269

270

271 *2.5 Lead isotope analysis*

272 Pervasive terrestrial Pb contamination (Pb_c) of meteoritic samples is a major concern. Meaningful 273 207 Pb- 206 Pb isochrons are linear arrays of a two-component system made up of radiogenic Pb (Pb_r), 274 produced by the decay of 235 U and 238 U, and, in most cases, initial Pb (Pb_i). Adding a third 275 component, Pb_c, to this system can pull data points off the Pb_r + Pb_i line towards the Pb_c isotope

276 composition, affecting the linearity of the isochron. This requires effective removal of all Pb_c from 277 samples (e.g., Connelly et al., 2017). Alternatively, Pb-Pb ages can also be accurately calculated 278 from linear arrays made of Pb_r and Pb_c , if the sample contains no initial Pb (Pb_i). This is achieved 279 through a step-wise dissolution procedure where crushed samples were leached first by weak acids 280 to remove surface contamination before increasingly strong acids were used to dissolve minerals 281 (Connelly and Bizzarro, 2009). The pyroxene fraction, totalling ~ 61 mg, underwent such a 282 procedure as described in Bouvier et al. (2011). The sample was ultrasonicated in 0.5 M HBr, then 283 Milli-Q water and twice in 0.5 M HNO₃ for 15 minutes each. Subsequent steps involved a hot-284 plate fluxing in 6 M HCl and 7 M HNO₃ (twice) at 120°C for an hour, ultrasonication in 1 M HF 285 for an hour and 12-hour-long hot-plate fluxing at 90°C in 1 M HF (Table 3). Since the first three 286 steps are designed to remove terrestrial Pb and are unlikely to have any chronological meaning 287 (e.g., Merle et al., 2020), these were collected all together in one beaker. Steps 5 and 6 (both 7 M 288 HNO₃) were also mixed, as the amount of Pb (0.13 ng total) would have been insufficient for a 289 precise determination of the Pb isotope ratios if these two leaching steps had been analyzed 290 separately.

The collected washes from each step were then dried down before being dissolved in a conc. HF-HNO₃ mixture for ~48 hrs. After ultrasonication for an hour and subsequent drying down, the samples are re-fluxed in conc. HNO₃, before being ultrasonicated once again and taken up in 6 M HCl to convert the samples to their chloride form. Prior to Pb separation, the fractions were analyzed for their U and Pb concentrations using Thermo Fischer iCAP Qc quadrupole ICP-MS at the University of Western Ontario (UWO).

297

Table 3: Leaching protocol for samples prepared for Pb isotopic analysis.

Step	Acid	Processing	Duration	Repeat	Repeat Collected as.	
1	0.5 M HBr	Ultrasonication washing	15 min	once	Wash-1 (W1)	
2	Water	Ultrasonication washing	15 min	once	Wash-2 (W2)	Combined as W1-3
3	0.5 M HNO ₃	Ultrasonication washing	15 min	twice	Wash-3 (W3)	
4	6 M HCl	Hot plate fluxing at 120°C	1 hr	once	Wash-4 (W4)	
5	7 M HNO ₃	Hot plate fluxing at 120°C	1 hr	once	Wash-5 (W5)	Combined as
6	7 M HNO3	Hot plate fluxing at 120°C	1 hr	once	Wash-6 (W6)	W5+6
7	1 M HF	Ultrasonication washing	1 hr	once	Wash-7 (W7)	
8	1 M HF	Hot plate fluxing at 90°C	12 hrs	once	Wash-8 (W8)	

299

For Pb separation, PTFE columns with 100 µl of AG1-X8 (200-400 mesh) anion-exchange resin are used following the procedure described in Bouvier et al. (2007), which was based on Marsh et al. (1978). Before loading, the samples are dried down and taken up in 1.5 M HBr and centrifuged to separate any remaining undissolved materials. Matrix elements are first eluted using 1.5 M HBr after the sample load. Lead is finally eluted using 0.5 M HNO₃. This procedure is repeated a second time to guarantee sufficient purification of Pb from matrix elements. The eluted matrix elements were collected together for U isotope analysis. 307 Lead isotope compositions were determined using a Thermo Fisher Neptune Plus MC-ICP-MS 308 equipped with a Cetac Aridus II desolvating nebulizer at Université Clermont-Auvergne (UCA) 309 and followed the protocols of Ancellin et al. (2019). The total Pb masses in the various leachates 310 range from 0.13 ng to 3 ng and were taken up in 0.5 to 1.5 ml of 0.05M HNO₃, depending on their 311 Pb concentration. Sample and standard solutions were both doped with the NBS 997 Tl standard 312 to a concentration of 1 ppb and bracketed with the NBS 981 Pb standard (Abouchami et al., 2000) 313 to correct internally and externally for instrumental mass fractionation. In addition, the radiogenic 314 NBS 983 Pb standard was included in the analytical sessions as a secondary standard. Before every 315 standard and sample measurement, a background measurement with baseline analysis was taken, 316 which was subtracted from the standards or samples during data reduction. Peak center and 317 baseline analysis were performed on all standard measurements but only on samples diluted in 1.5 318 ml of 0.05M HNO₃, to ensure sufficient material for was available for the isotopic analysis. Two 319 samples, where enough ²⁰⁴Pb was present, were analyzed in a Faraday cup (FC) setup (EC W1-3 320 and ECW4). The other samples were analyzed with a secondary electron multiplier (SEM) on 321 ²⁰⁴Pb, as the intensity in a FC setup would be below 0.3 mV. This setup has the disadvantage that 322 ²⁰⁸Pb cannot be measured on H4 due to the fixed spacing imposed by the pin attaching H3 and H4 323 (Table 4). Sample analyses consisted of 60 cycles with 8.4 s integration time in the FC setup, 324 whereas the analyses in the SEM setup consisted of only 25 cycles, with no peak center or baseline 325 analysis.

The measured Pb isotopic data were reduced offline in Excel and R, and "inverse" isochrons were calculated using IsoplotR (Vermeesch, 2018) and Isoplot 4.15 in Excel (Ludwig, 2008). Total procedural blanks ranged from 0.3 to 1.8 pg, resulting in sample/blank ratios from 131 to 3808, and compositions were corrected accordingly, following the equations provided in the Appendix

330	of Bouvier et al. (2007). Errors on ²⁰⁴ Pb/ ²⁰⁶ Pb and ²⁰⁷ Pb/ ²⁰⁶ Pb ratios for isochron regression were
331	either the correlated errors or the daily external reproducibility of the NBS 981 or NBS 983
332	standards (depending on which standard is more representative of the sample ratios), whichever is
333	larger.
334	The full session Pb isotope data averages are reported in Table 5.

335

Table 4: Overview of cup configurations used for Pb isotope analysis with all Faraday cups (FC)or with central Secondary Electron Multiplier (SEM).

Cup	L3	L2	L1	C (or SEM)	H1	H2	H3
Pb (FC)	²⁰² Hg	²⁰³ Tl	²⁰⁴ Pb	²⁰⁵ Tl	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb
Pb (SEM)		²⁰² Hg	²⁰³ Tl	²⁰⁴ Pb	²⁰⁵ Tl	²⁰⁶ Pb	²⁰⁷ Pb

- 338
- 339

340 2.6 Uranium isotope analysis

341 Analysis of the U isotope composition of a bulk rock sample and leached pyroxenes (included 342 W5+6, W7, W8 and R) of EC 002 were performed with a Neptune MC-ICP-MS at the Leibniz 343 Universität Hannover, following the protocols of Roebbert et al. (2021). The collected matrix 344 elements of two aliquots of the terrestrial standard BCR-2, equal to ~ 5 ng and ~ 20 ng of U that 345 underwent prior Pb separation (as for EC 002), were analyzed along with the meteorite samples to 346 ensure that no U isotope fractionation occurred during the separation of Pb (Table 6). The ²³⁶U-347 ²³³U double-spike solution IRMM 3636 was used to correct for instrumental mass-bias (Richter et 348 al., 2010). Each sample was analyzed twice, bracketed by the CRM-112a standard, over 60 cycles 349 at 4 s integration time. Concentrations between standards and samples were individually matched and intensities on ²³⁸U were 2.5 V and 12 V for the leached pyroxene and the bulk rock fraction, 350

respectively. Because of the relatively low ion beams, all U isotopes, including 238 U, were measured using amplifiers with 10⁻¹¹ Ohm resistors. The standard IRMM 184 was analyzed along with the samples and its results are reported in Table 6.

354

355 <u>3. Results</u>

356 3.1 Al-Mg systematics

Magnesium isotope compositions and ²⁷Al/²⁴Mg ratios of the analyzed mineral fractions of EC 357 002 are summarized in Table 7. The 27 Al/ 24 Mg ratios span a range from 0.98 for the Px fraction to 358 34.4 in feldspars. Excesses in ²⁶Mg are not resolved from the terrestrial fractionation line for the 359 bulk rock and Px fractions at δ^{26} Mg* = 0.013 ± 0.020‰ and 0.010 ± 0.010‰, respectively. In the 360 361 feldspar fractions and fines fraction, radiogenic ²⁶Mg excesses are resolved and range from 0.132 362 $\pm 0.010\%$ to 2.058 ± 0.015 ‰. A regression line through the data is obtained with Isoplot 4.15 (Ludwig, 2008), with a slope corresponding to the ²⁶Al/²⁷Al at the time of crystallization of [8.89 363 364 ± 0.79] $\times 10^{-6}$ and an y-intercept δ^{26} Mg*₀ of -0.058 ± 0.026 % (both 2 σ), representing the initial Mg isotope composition at time of crystallization (MSWD = 4.6). This ${}^{26}\text{Al}/{}^{27}\text{Al}_0$ corresponds to 365 a crystallization age of 1.83 ± 0.12 Ma after CAI formation (Fig. 2a). This corresponds to an 366 367 absolute age of 4565.47 \pm 0.20 Ma when anchored to the canonical ²⁶Al/²⁷Al value of [5.23 \pm 0.13] 368 $\times 10^{-5}$ (Jacobsen et al., 2008) and the absolute age of CAIs at 4567.30 \pm 0.16 Ma (Connelly et al., 369 2012). When anchored to the D'Orbigny angrite (Pb-Pb age: 4563.51 ± 0.29 (Amelin, 2008b; 370 Tissot et al., 2017), initial 26 Al/ 27 Al: $[3.98 \pm 0.15] \times 10^{-7}$ (Schiller et al, 2015), $[5.06 \pm 0.15] \times 10^{-7}$ 371 ⁷ (Spivak-Birndorf et al., 2009)), the ²⁶Al-²⁶Mg formation age of EC 002 is 4566.72 \pm 0.32 Ma and 4566.47 \pm 0.40 Ma, calculated from the initial ²⁶Al/²⁷Al ratios of Schiller et al. (2015) and Spivak-372

- 373 Birndorf et al. (2009), respectively. These ages are 1.26 ± 0.38 Myr and 1.01 ± 0.45 Myr, 374 respectively, older than when anchored to CAIs.
- Regressing the subset of feldspar fractions results in an initial ${}^{26}\text{Al}/{}^{27}\text{Al}$ of $[8.36 \pm 0.49] \times 10^{-6}$ and
- a $\delta^{26}Mg_{0}^{*}$ of -0.010 ± 0.032‰ (MSWD = 0.0017), equal within the stated uncertainties of the regression through the complete dataset (Fig. 2b).
- 378 The δ^{25} Mg values of EC 002 fractions lie between -0.729 ± 0.012‰ and -1.104 ± 0.013‰, which 379 are distinctly lighter than the compositions of the terrestrial San Carlos olivine and the CV3 380 chondrite Allende.
- 381
- 382 *3.2 Uranium isotope composition*

The results for the ²³⁸U/²³⁵U ratios in both the bulk rock and the re-combined W5-R leachates and residue of EC 002 are summarized in Table 6. Both samples were measured twice, with their weighted average ²³⁸U/²³⁵U ratios being 137.819 \pm 0.010 for the bulk rock, and 137.766 \pm 0.027 for the leachates (both 2 σ). The uncertainty associated with the analyses, particularly on the leachates, is mainly due to the low U concentration of this sample (2.5 V on ²³⁸U from \approx 5 ng U). **Table 5**: Mass, Pb and U elemental data, and Pb isotope data for EC 002 and full session Pb isotope data for standards NBS 981 and

- 390 NBS 983. Nantan model ages are calculated from the primordial Pb isotope composition, represented by the Nantan troilite (Blichert-
- 391 Toft et al., 2010). SK model ages are calculated from the modern terrestrial Pb composition as given by Stacey and Kramers (1975).

Sample	mass [mg]	Pb [ng]	U [ng]	Sample/ Blank	²⁰⁶ Pb/ ²⁰⁴ Pb raw	²⁰⁴ Pb/ ²⁰⁶ Pb	2SE [%]	²⁰⁷ Pb/ ²⁰⁶ Pb	2SE [%]	Nantan model age [Ma]	±	SK model age [Ma]	±
EC-W1-3 *	1.6	3.2	2.2	3808	41.5	0.024092	0.015	0.72121	0.0024	4529.73	0.10	4571.38	1.54
EC-W4 *	1.0	1.3	6.5	1549	42.5	0.023515	0.035	0.71755	0.0054	4526.72	0.16	4565.57	1.49
EC-W5+6*	0.3	0.1	0.2	131	343.9	0.00268	3.42	0.6370	0.045	4568.19	1.07	4571.84	1.00
EC-W7 ^{&}	4.1	0.6	0.3	302	10902.7	—	—	0.6250	0.021	4566.15	0.30	4566.14	0.30
EC-W8 &	44.2	0.8	0.8	1331	6953.1	0.000122	7.25	0.62538	0.0085	4565.63	0.14	4565.78	0.14
EC-R &	42.9	1.2	1.0	1366	16604.9	0.000039	21.3	0.62513	0.0085	4565.91	0.14	4565.96	0.14
Standards NBS 983						²⁰⁶ Pb/ ²⁰⁴ Pb corr	2SD [%]	²⁰⁷ Pb/ ²⁰⁶ Pb corr	2SD [%]		n		
- SEM setup 0	.25 ppb					2762.5	1.29	0.071186	0.25		5		
- FC setup 1 p	pb					2721.75	7.85	0.07124	0.60		10		
- literature ^a						2695.4	5.4	0.07120	0.06				
NBS 981													
- SEM setup 0	.5 ppb					16.9437	0.26	0.91466	0.06		10		
- FC setup 1 p	pb					16.9412	0.26	0.91475	0.06		14		
- literature ^b						16.9405	0.01	0.91475	-				

^a Catanzaro et al. (1968). ^b Abouchami et al. (2000). * measured using Faraday cup setup. [&] measured using SEM setup.

Sample	Mass [mg]	U [ng]	²³⁸ U/ ²³⁵ U	2σ	n	²³⁸ U intensity [V]
EC 002 Bulk rock	~120	15	137.819	0.007	2	12
EC 002 Px leachates	~160	5	137.766	0.027	2	2.5
BCR-2 a	11.8	20	137.797	0.017	2	15
BCR-2 b	2.9	5	137.815	0.046	2	4
IRMM 184			137.668	0.008	8	2.5 - 15

Table 6: Weighted average U isotope compositions of EC 002 bulk rock and pyroxene samples and of BCR-2 terrestrial basalt standard,
 as well as repeat analyses of the IRMM 184 U isotope standard (Richter et al., 2010).

396

Table 7: Al-Mg data for EC 002 fractions.

Sample	²⁷ Al/ ²⁴ Mg	±	δ ²⁵ Mg [‰]	2SE	$\delta^{26}Mg^{*}$ [‰]	2SE	n
EC Px	0.98	0.05	-0.825	0.014	0.010	0.010	4
EC Bulk rock	1.05	0.18	-0.736	0.037	0.013	0.020	7
EC fines	3.45	0.17	-0.840	0.054	0.139	0.006	8
EC fsp2-4	6.33	0.32	-0.729	0.012	0.370	0.004	4
EC fsp1+8	9.03	0.45	-1.104	0.013	0.532	0.005	4
EC fsp7	10.7	0.54	-0.957	0.010	0.636	0.016	4
EC fsp6	34.4	1.72	-0.956	0.015	2.058	0.015	4

Merrillites	²⁰⁷ Pb/ ²⁰⁴ Pb	±1s.e.	²⁰⁶ Pb/ ²⁰⁴ Pb	±1s.e.	²⁰⁷ Pb/ ²⁰⁶ Pb	±1s.e.	²⁰⁷ Pb/ ²⁰⁶ Pb corr [Ma] ^a	±1s.e.	²⁰⁷ Pb/ ²⁰⁶ Pb age [Ma] ^b	±1s.e.
M1	2368	352	3799	565	0.6245	0.0036	0.6226	0.0037	4561.0	8.6
M4	1738	191	2773	306	0.6243	0.0033	0.6226	0.0032	4560.9	7.5
M5	24360	8636	38710	13750	0.6271	0.0023	0.6268	0.0023	4570.7	5.2
M8-1	5252	889	8429	1426	0.6233	0.0027	0.6228	0.0025	4561.4	5.8
M8-2	8178	1597	13080	2554	0.6254	0.0032	0.6249	0.0032	4566.5	7.4
M12	5315	1474	8442	2342	0.6244	0.0048	0.6223	0.0044	4560.4	10.2
M14	2620	429	4164	682	0.6243	0.0038	0.6225	0.0036	4560.8	8.4
Weighed mean age \pm 95% confidence interval (Ma)									4564.3 ±	5.2
									-	

Table 8: Pb isotope data and corresponding Pb-Pb ages of merrillites analyzed by SIMS

400 a^{207} Pb- 206 Pb corr. compositions are corrected from primordial Pb contribution. b^{207} Pb- 206 Pb ages are calculated using the 238 U/ 235 U=137.82 ± 0.01 of the measured

401 whole-rock composition of EC 002 and correlated errors between Pb and U isotopic measurements.

402 3.3 MC-ICP-MS Pb isotopic analysis

403 Lead isotope data for leachates and residue of a pyroxene fraction are presented in Table 5. Leachates W7 and W8, as well as the residue, are highly radiogenic, with raw ²⁰⁶Pb/²⁰⁴Pb ratios 404 ranging from 6953 to 16604. The first leachates (W1-3 to W5+6) have ²⁰⁶Pb/²⁰⁴Pb ratios in the 405 406 range of 41 to 344, with a low sample-to-blank ratio of 131 for W5+6. The sample-to-blank ratios 407 of the remaining leachates range from and 1549 to 3808, with the exception of W7 at 302. In an "inverse" ²⁰⁴Pb/²⁰⁶Pb-²⁰⁷Pb/²⁰⁶Pb space, the leachates and residues are significantly overdispersed 408 409 (MSWD = 391). Nevertheless, they plot along a line projecting towards the point of terrestrial Pb 410 as defined by the model of Stacey and Kramers (1975), indicating that the pyroxene in the sample 411 is free of initial, primordial Pb (Fig. 3) and that the Pb isotope compositions of the leachates and residues are a mixture of only radiogenic Pb (204 Pb = 0) and terrestrial Pb. This has been previously 412 413 observed in the angrites Sahara 99555 (Amelin, 2008a; Connelly et al., 2008) and NWA 1670 414 (Schiller et al., 2015), as well as some chondrules (Bollard et al., 2017).

A statistically meaningful isochron (probability of fit > 0.05) can be calculated using leachates W4, W7, W8 and the residue R, however, W7 is omitted due to its negative 204 Pb/ 206 Pb ratio after background- and blank-correction, despite it still plotting along the isochron. This leaves three fractions defining the isochron (MSWD = 3.3), resulting in an age of 4565.87 ± 0.30 Ma (2 σ) (Fig. 4), calculated with the 238 U/ 235 U ratio 137.766 ± 0.027, determined from the pyroxene fraction. All ages given include error propagation on the U isotope composition, except for individual 207 Pb*/ 206 Pb* model ages of the leachates and residue.

The ²⁰⁷Pb*/²⁰⁶Pb* model ages (Table 5), calculated from both initial Pb as represented by the
Nantan troilite (Blichert-Toft et al., 2010) and the Stacey & Kramers (SK) point representing
terrestrial Pb, show no age difference for a given highly radiogenic leachate or the residue, as they

425 plot close enough to the y-axis to not make any significant difference in y-intercept $(= {}^{207}\text{Pb}*/{}^{206}\text{Pb}*)$. The agreement between those leachates and the residue also demonstrates that 426 no fractionation occurred due to the use of HF in the leaching procedure. For the less radiogenic 427 428 leachate W4, the Nantan and SK model ages differ significantly, the SK model ages being in line 429 with the other leachates and residue of its respective fraction, indicating once again that there likely 430 was no primordial Pb present in the sample. The weighted average of the SK model ages for W4, 431 W8 and R results in an Pb-Pb age of 4565.87 ± 0.40 Ma (MSWD = 2.1). Adding the SK model age for W7, where only its ²⁰⁷Pb/²⁰⁶Pb ratio is considered, to the weighted average gives an age of 432 433 4565.90 ± 0.36 Ma (MSWD = 1.7).



435

436 **Figure 2**: Internal ²⁶Al-²⁶Mg isochrons defined by **a**) pyroxene, bulk rock, fine-grained and 437 plagioclase fractions, corresponding to a ²⁶Al/²⁷Al ratio of $(8.89 \pm 0.79) \times 10^{-6}$ and a formation age 438 of 1.83 ± 0.12 Ma after CAI formation, based on the canonical ²⁶Al/²⁷Al abundance (Jacobsen et

439 al., 2008); and **b**) only plagioclase fractions, corresponding $(8.36 \pm 0.49) \times 10^{-6}$ and a formation 440 age of 1.90 ± 0.09 Ma after CAI formation. Uncertainties are 2SE errors on δ^{26} Mg* measurements 441 and $\pm 5\%$ on 27 Al/²⁴Mg ratios.



Figure 3: Regression line through the analyzed Pb fractions. Leachate W7 is omitted due to its negative blank-corrected ²⁰⁴Pb/²⁰⁶Pb ratio. Also plotted are data points for the Nantan troilite, representing the primordial Pb composition of the Solar System (Blichert-Toft et al., 2010), and the Stacey and Kramers (1975) data point representing the terrestrial Pb composition. Symbols of data points have been enlarged for clarity, larger than their uncertainties.



450 Figure 4: Inverse Pb-Pb isochron diagram for Erg Chech 002. The uncertainty on W4 is smaller
451 than the ellipse, as it is enlarged for clarity. The inset shows the highly radiogenic leachate W8
452 and residue. Leachate W7 would plot along the regression line in negative ²⁰⁴Pb/²⁰⁶Pb vs.
453 ²⁰⁷Pb/²⁰⁶Pb space.

454

455 *3.4 Pb-Pb merrillite ages by SIMS*

Merrilites have a homogeneous and H-free composition of Ca_{8.5}Na_{0.8}Mg_{0.7}Fe_{0.3}(PO₄)₇ (n=4). Raw
Pb isotopic data were reduced and calibrated against measurements of standard Madagascar apatite
(485 Myr, Thomson et al., 2012) using in-house-developed software (ZIPS version 3.1.1, by
Christopher Coath). Common lead correction was made using the composition and model of
Stacey and Kramers (1975) and primordial Pb isotopic composition reported for Canyon diablo

461 troilite by Tatsumoto et al. (1973). In the absence of suitable merrillite standard, U and Pb 462 secondary ion yields were not known precisely, as such, U/Pb systematics cannot be measured 463 with satisfactorily precision. But if the analysed points were used as hypothetical standard, all 464 results plotted tightly into a concordant cluster, strongly suggesting that the observed discrepancy 465 derived chiefly from matrix effect (i.e., using apatite as standards for merrillite samples). Due to 466 the extremely high radiogenic Pb isotopic ratios measured for merrillites in Erg Chech 002 (common lead $^{204}Pb < 0.1$ cps, and $^{204}Pb/^{206}Pb$ ratio on the order of $10^{-4}-10^{-5}$), the choice of the 467 468 apatite standard (comparably aged apatite or merrillite standards are not available) as well as 469 primordial Pb isotopic ratio did not affect the calculated Pb-Pb merrillite ages.

The seven ²⁰⁷Pb-²⁰⁶Pb ages of individual analysis (Table 8) were calculated from radiogenic ²⁰⁷Pb^{*}-²⁰⁶Pb^{*} ratio using the U decay constants from Steiger and Jäger (1977), with uncertainties of 0.2-0.4% ($\pm 2\sigma$), and a ²³⁸U/²³⁵U ratio of 137.82 \pm 0.01 (from our whole-rock measurement). In the end, the ²⁰⁷Pb-²⁰⁶Pb merrillite age for EC 002 was reported with a weighted mean of 4564.3 \pm 5.2 Ma (2 σ), as seen in Fig. 5.

475



478 Figure 5: Weighted mean age in Ma with 1σ and 95% confidence interval for 7 spot analyses of
479 6 individual merrillite grains of EC 002 (Table 8).

480

477

481 <u>4.Discussion</u>

482 *4.1 Lead isotope systematics*

Even though only three fractions make up our 207 Pb- 206 Pb isochron, with a rather non-radiogenic leachate and a highly radiogenic leachate and residue, it is statistically meaningful (Pb-Pb age = 4565.87 ± 0.09 Ma, MSWD = 3.3, probability of fit = 0.068). Three-point isochrons are generally considered to be unreliable, as the regression may be subject to increased bias by outlying data points and data filtering. These concerns are valid, however, in this case, the highly radiogenic leachates used in the regression argue for the reliability of our age determined from the isochron:

Pb-Pb ages are determined by the intercept of the regression line with the y-axis in an "inverse" 489 490 Pb-Pb diagram (²⁰⁷Pb*/²⁰⁶Pb*). In the case of EC 002, the later leachates and residue are highly 491 radiogenic, defining a precise intercept, making any scatter of the less radiogenic leachates less 492 influential on the Pb-Pb age. This is visible when including leachates that were not used in the final isochron and in the ²⁰⁷Pb*/²⁰⁶Pb* model ages. For example, including W5+6 instead of, or in 493 494 addition to, W4 results in overdispersed errorchrons with an absolute age of 4565.78 ± 0.31 Ma 495 (MSWD = 8.3) or 4565.91 ± 0.50 (MSWD = 27), respectively. In addition to this example, the weighted average of the 207 Pb*/ 206 Pb* SK model ages of the W4, W8 and R fractions (4565.87 ± 496 497 0.36 Ma, MSWD = 2.1) is consistent with the isochron age, as is the weighted average of the model 498 ages when including the W7 leachate (4565.90 ± 0.40 Ma, MSWD = 1.7). Hence, we interpret the 499 absolute age of 4565.87 \pm 0.30 Ma as defined by the isochron as the crystallization age of EC 002 500 (Fig. 4).

501 Seven SIMS measurements of merrillites are consistent within errors and provide a weighted mean 502 age of 4564.3 \pm 5.2 Ma (2 σ). While relatively much less precise than the age determination by 503 solution analyses, this Ca-phosphate formation age is similar within uncertainty to the pyroxene 504 Pb-Pb age. This reinforces the conclusions made by Barrat et al. (2021) suggesting a rapid cooling 505 of the parent body. The diffusion rate of Pb in Ca-phosphate is faster than in pyroxene and therefore 506 the closure temperature of the U-Pb system in phosphate is protracted toward lower temperatures 507 (Cherniak, 2001) and more prone to resetting temperatures such as those sustained during impact 508 events. This additional thermochronological information supports that EC 002 cooled rapidly after 509 crystallization and was neither subjected to substantial impact events nor extensively thermally 510 metamorphosed after ~4559 Ma. Detailed thermochronological records can be used to constrain 511 EC 002's parent body accretion history and size, and burial depth.

512

513 4.2 Uranium-corrected Pb-Pb age of Erg Chech 002

The ${}^{238}\text{U}/{}^{235}\text{U}$ ratio of bulk rock EC 002 is 137.819 ± 0.010, distinct from the combined leachates 514 515 (W5 to R) of the Px fractions at 137.766 \pm 0.027 by 0.38 \pm 0.21 ‰. The resulting U-corrected Pb-516 Pb ages are 4566.43 ± 0.14 Ma and 4565.87 ± 0.30 Ma, respectively, a difference of 0.56 ± 0.28 Myr. With that in mind, the choice of ${}^{238}U/{}^{235}U$ ratio for calculating the Pb-Pb age is an important 517 518 consideration, as the interpretation of the result may change depending on which value is used. 519 Since the Pb isotope systematics of EC 002 were determined on a pyroxene fraction of EC 002, we use the ²³⁸U/²³⁵U ratio of the same mineral fraction to calculate the U-corrected Pb-Pb age. The 520 521 Pb-Pb ages in achondrites are usually determined from leachates and residues of pyroxene, which 522 incorporate more U (e.g., Amelin, 2008b; Bouvier et al., 2011). The U isotope compositions of the 523 same meteorites are however determined on unleached whole-rocks, sometimes from different 524 laboratories (Brennecka and Wadhwa, 2012; Tissot et al., 2017). If U contamination in secondary 525 minerals formed during desert weathering (e.g. carbonates, sulfates) or U isotope heterogeneity 526 between pyroxenes and bulk rock samples exist in dated samples, U-corrected Pb-Pb ages would 527 require further correction. Ideally, whenever Pb-Pb ages are determined from mineral fractions, so should the ²³⁸U/²³⁵U ratio. In practice, however, this is most often hampered by the large sample 528 529 amounts necessary (> 100 mg) to ensure sufficient U to obtain a precise analysis. Analyzing the 530 same mineral fractions for U and Pb isotopic compositions ensures consistency and avoids the 531 assumption that there are no U isotope variations between pyroxene and bulk rock fractions of the 532 sample or contribution from terrestrial U contamination or secondary minerals (e.g., carbonates) 533 in whole-rock composition, which is a great concern for desert find meteorites.

The difference in ²³⁸U/²³⁵U ratio between the bulk rock and pyroxene fractions requires an explanation and could reasonably have originated through i) internal heterogeneities between minerals and the bulk rock sample; ii) fractionation during the acid-leaching procedure; or iii) fractionation during column chemistry and/or isotopic analysis.

The third possibility can be ruled out, as two BCR-2 aliquots underwent the same chromatographic and analytical procedures with comparable amounts of U as the two EC 002 samples without producing any evidence of fractionation within their statistical uncertainties (Table 6). These results also rule out any significant interference on mass 235 during analysis of small U amounts, as suggested by Connelly et al. (2019) to explain an outlier 238 U/ 235 U ratio in a troilite nodule of IVA meteorite Muonionalusta (Blichert-Toft et al., 2010).

Previously, Brennecka and Wadhwa (2012) reported a slightly lighter U isotope composition (by 0.30 \pm 0.25 ‰) of the leachate fraction compared to the residue of the angrite NWA 6291, for which they invoked the removal of terrestrial components during leaching. Tissot et al. (2017), however, pointed out that the leachate contained ~ 64% of total U of the sample and that such an amount was unlikely to be exclusively of terrestrial origin, and instead argued for U isotope variability between pyroxene and phosphate, caused by magmatic differentiation, to explain different ²³⁸U/²³⁵U ratios between plutonic and volcanic angrites.

In the case of EC 002, the early leachates (W1 to W4) contain almost 80% of total U of the sample. Following the argumentation of Tissot et al. (2017), this suggests that the origin of the distinct $^{238}U/^{235}U$ ratios is isotopic heterogeneity between pyroxene and any remaining minerals. The acidleaching procedure should not have affected the U isotope composition of the pyroxene, as the acids used in the early leaching steps (0.5 M HBr, water, 0.5 M HNO₃ and 6 M HCl; Table 3), whose leachates were not included in the analyzed fraction, do not dissolve pyroxene. Rather, they dissolve feldspar, phosphates, troilite, as well as any potential secondary terrestrial components, that may have remained attached to pyroxene grains after hand-picking (Bouvier et al., 2005; Ito et al., 2019). Therefore, the U isotope composition of the "re-combined residue" consisting of leachates W5-8 and the residue from the leaching procedure should represent the true $^{238}U/^{235}U$ ratio of the EC 002 pyroxene megacrysts, free of other mineral or terrestrial contamination.

Based on this, a mass balance calculation estimates a 238 U/ 235 U ratio of ~137.83 for the removed components (re-combined W1 to W4 leachates), a difference of up to ~ 0.45 ‰. This is larger than observed in NWA 6291 (Brennecka and Wadhwa, 2012), but comparable to results reported in a conference abstract by Huyskens et al. (2020) between merrillite and the bulk rock fraction in the plutonic angrite Angra dos Reis.

These results show that the bulk rock U isotope composition may not be wholly representative for age correcting pyroxene fractions using Pb-Pb chronometry. Age corrections may be necessary to account for potential isotopic heterogeneities between pyroxene and bulk rock fractions of certain achondrites. This discussion re-emphasizes the need for more detailed and systematic investigations into the U isotope compositions of achondrites and their minerals, but also the effect that acid leaching potentially has on them.

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576 $4.3^{26}Al^{-26}Mg$ systematics

577 Regressing the ²⁶Al-²⁶Mg data from seven fractions of EC 002 results in an isochron with excess 578 scatter (MSWD = 4.6) and a crystallization age of 1.83 ± 0.12 Ma after CAI formation (Fig. 2a). 579 The four plagioclase fractions of our dataset define an isochron with an age of 1.90 ± 0.09 Ma after

580 CAI formation, identical within the stated uncertainties but with no excess scatter (MSWD = 581 0.002; Fig. 2b). When anchored to the absolute age of CAIs (4567.30 \pm 0.16; Connelly et al., 582 2012), they result in absolute ages of 4565.47 \pm 0.20 Ma and 4565.40 \pm 0.18 Ma, respectively. The 583 excess scatter of the regression through all fractions is likely the result of the presence of accessory 584 phases in the fines fraction, and/or xenolithic material in the bulk rock and pyroxene fractions (e.g., 585 Barrat et al., 2021, Nicklas et al, 2022). The plagioclase-only isochron is less likely to be affected 586 by xenolithic material, which could explain the low MSWD. The difference is not resolvable at 587 this level of precision, therefore for chronological purposes we conservatively use the isochron 588 that includes all fractions $(1.83 \pm 0.12 \text{ Ma after CAI formation})$ going forward.

589 The crystallization age of 1.83 ± 0.12 Ma after CAI formation is consistent with, albeit less precise 590 than the age of 1.83 ± 0.04 Ma determined by Fang et al. (2022). Both these ages are respectively 0.46 ± 0.13 and 0.46 ± 0.05 Myr older than the 26 Al- 26 Mg age of 2.29 ± 0.04 Ma after CAI 591 formation (both re-calculated with a ²⁶Al half-life of 0.717 Myr) reported by Barrat et al. (2021), 592 593 which was determined by SIMS (Fig. 6). Our age is strengthened by the analysis of different plagioclase fractions with a good spread in ²⁷Al/²⁴Mg ratios, and with that subset of our data in 594 595 agreement with our overall isochron. The differences of these results to those of Barrat et al. (2021) 596 have also been discussed by both Fang et al. (2022) and Zhu et al. (2022). Potentially, when 597 analyzing sample spots with very low amounts of Mg by SIMS, such as those with ²⁷Al/²⁴Mg ratios 598 between 2000 and 5000, matrix effects have to be strongly considered when using in-situ analytical 599 methods and counting statistics errors could become a factor, where background corrections could 600 hypothetically overcorrect the amount of Mg isotopes, leading to spuriously low ²⁶Mg excesses. Furthermore, the calibrating standard used, Miyake-Jima plagioclase, has a ²⁷Al/²⁴Mg ratio of 601

602 396.3, an order of magnitude lower than the plagioclase analyzed in their sample of EC 002, which 603 could lead to miscalibration for the measurements with higher ${}^{27}Al/{}^{24}Mg$ ratios (Zhu et al., 2022). 604 An alternative interpretation is that the isochron determined by Barrat et al. (2021) represents the time of closure of pure plagioclase ($^{27}Al/^{24}Mg > 1500$), whereas our isochron with fractions that 605 606 contain at least some proportion of other minerals represents the time of closure of a mineral 607 mixture with a higher closure temperature for Mg diffusion. Closure temperatures of pyroxene and 608 anorthite have been estimated at 900°C to 1000°C and 700°C to 800°C, respectively (Wadhwa et 609 al., 2009). With the age difference of 0.46 ± 0.13 Myr between isochrons, based on those closure 610 temperatures as an upper limit, the cooling rate would be 465°C/Myr, several orders of magnitude 611 slower than what Barrat et al. (2021) estimated from the petrology of EC 002 (5°C/yr from 1200 612 °C to 1000°C, and >0.1 to 1°C/day below 900°C). Such a large difference cannot be explained by 613 the isochrons representing different times of closure of minerals and still satisfy the petrological 614 constraints established on the cooling rate of EC 002. Fang et al. (2022) argued similarly that the 615 plagioclase cores analyzed by the SIMS ion probe were not a closed system for Mg diffusion. The younger SIMS ²⁶Al-²⁶Mg age (Barrat et al., 2021) may be the result of the resumption of Mg 616 617 diffusion due to a re-heating event above the closure temperature in plagioclase.

In addition, the δ^{26} Mg*₀ values (initial ²⁶Mg/²⁴Mg ratio) between our study, Barrat et al. (2021) and Fang et al. (2022) are distinct (Fig. 7). Barrat et al. (2021) first reported the δ^{26} Mg*₀ of 0.065 ± 0.085 ‰, followed by the -0.009 ± 0.005 ‰ of Fang et al. (2022). The δ^{26} Mg*₀ for our regression through all fractions is -0.058 ± 0.026 ‰, distinctly lower than both previous studies. The δ^{26} Mg*₀ of the regression through the plagioclase fractions only is -0.010 ± 0.032 ‰, which is similar to the initial value of Fang et al. (2022). Our two initial values are less precise than the one reported by Fang et al. (2022) due to the absence of data points with ²⁷Al/²⁴Mg ratios < 0.9, but more precise

from the higher value reported by Barrat et al. (2021). The difference between the all-fraction and 625 626 plagioclase-only isochron may be attributed to earlier-formed xenolithic material affecting the bulk rock and pyroxene fractions. The $\delta^{26}Mg_0^*$ of -0.058 ± 0.026 ‰, while within uncertainty of the 627 628 "canonical" initial Solar System value (-0.034 %; Jacobsen et al., 2008; Schiller et al., 2010), 629 would require crystallization coeval with the formation of CAIs, which is inconsistent with all reported ²⁶Al-²⁶Mg ages. Some studies have reported "sub-canonical" initial δ^{26} Mg*₀ values up to 630 631 -0.128 ‰ in otherwise "canonical" CAIs (Wasserburg et al., 2012; MacPherson et al., 2017), arguing for δ^{26} Mg*₀ heterogeneity in the early Solar System. While this could explain the low 632 633 δ^{26} Mg*₀ of -0.058 ± 0.026 ‰, there is no evidence for this in other Al-Mg studies of chondrites 634 and achondrites. Part of this discrepancy in δ^{26} Mg*₀ values reported so far is that both Barrat et al. (2021) and Fang et al. (2022) calculated the mass-independent $\delta^{26}Mg^*$ values using the 635 636 equilibrium fractionation factor ($\beta = 0.521$). For EC 002, which is a rapidly cooled sample, we 637 argue that kinetic mass fractionation ($\beta = 0.511$) more appropriately models Mg isotope 638 fractionation, as equilibrium mass fractionation is negligible under these conditions (Teng et al., 639 2007). This is further supported by the mass-dependent fractionation of our rock standard data of 640 the San Carlos olivine and CV3 chondrite Allende (Figs. S1 and S2). As Fang et al. (2022) did not publish the stable Mg isotope compositions of their mineral fractions, their δ^{26} Mg* values cannot 641 642 be re-calculated with the kinetic fractionation factor to estimate the effect of fractionation factor. 643 Re-calculating the data from Barrat et al. (2021) with the kinetic fractionation factor results in a 644 δ^{26} Mg*₀ value of 0.024 ± 0.055 ‰. This is closer to the value of Fang et al. (2022) and our plagioclase-only isochron, indicating a likely better approximation of the true $\delta^{26}Mg_0^*$ value of 645 646 EC 002. For completeness, using the equilibrium fractionation factor instead shifts the $\delta^{26}Mg^{*}_{0}$

values of our isochrons even lower to -0.086 ± 0.035 ‰ and -0.037 ± 0.032 ‰ for the full and plagioclase-only isochron, respectively.



Figure 6: Comparison of initial ²⁶Al/²⁷Al ratios between this study, Fang et al. (2022) and Barrat
et al. (2021). Error envelopes of isochrons have been omitted for clarity.

The δ^{25} Mg mass-dependent values of the analyzed mineral fractions are isotopically light compared to terrestrial rocks, bulk chondrites and other achondrites (e.g., Sedaghatpour and Teng, 2016). Due to the absence of reported mass-dependent Mg isotope data by Fang et al. (2022), we cannot compare our data to this other study of EC 002. Standards that underwent analysis and the same Mg separation procedure as the one employed for samples are consistent with their reported compositions (Table 1). Any process to fractionate Mg isotopes would therefore have had to occur

between crystallization and dissolution of the samples. Terrestrial alteration may be a possibility. EC 002 shows signs of oxidation and secondary weathering products (Gattaccecca et al., 2021), but terrestrial weathering should cause an enrichment in heavier Mg isotopes, not a depletion (Teng et al., 2010). While the exact provenance of these light δ^{25} Mg values is unknown, the good agreement of the initial ²⁶Al/²⁷Al ratio with Fang et al. (2022) suggests that the responsible process, be it natural or analytical, did not affect the mass-independent values nor the ²⁶Al-²⁶Mg chronometry.



Figure 7: Presentation of the different $\delta^{26}Mg_{0}^{*}$ values of Barrat et al. (2021), Fang et al. (2022), as well as our isochron containing all fractions and the isochron containing only plagioclase fractions. Plotted alongside are the $\delta^{26}Mg^{*}$ evolution lines assuming canonical and sub-canonical $^{26}Al^{27}Al$ ratios and $\delta^{26}Mg_{0}^{*}$ values (5.23 × 10⁻⁵, -0.034 ‰: Jacobsen et al., 2008; 1.6 × 10⁻⁵, -0.016 ‰: Larsen et al., 2011).

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673 4.4 Combined short-lived chronology and U-corrected Pb-Pb ages

674 Time anchors are used to calculate absolute model ages of samples that were dated by short-lived

675 chronometers. To anchor relative ²⁶Al-²⁶Mg to absolute ages, analyzed samples are most-

676 commonly anchored to the absolute age of CAIs (4567.30 ± 0.16 Ma; Connelly et al., 2012).

677 Some achondrites have also been proposed and used as anchors, such as the angrite D'Orbigny,

678 particularly for the ⁵³Mn-⁵³Cr chronometer due to the lack of Mn in CAIs (e.g., Glavin et al.,

679 2004; Wadhwa et al., 2009; Sanborn et al., 2019).

680 The distribution and abundance of the parent nuclide at time of formation between individual

681 meteorites as well as meteorite formation reservoirs can be then made. For example, previous

682 studies of angrites has suggested that the initial ²⁶Al/²⁷Al of the inner Solar System (NC

reservoir) was ~ 1×10^{-5} , significantly lower than the accepted "canonical" value (~ 5×10^{-5})

determined from CAIs (Schiller et al., 2015). This was based on a discrepancy of ~ 1 to 2 Myr

between Pb-Pb ages and ²⁶Al-²⁶Mg ages of the angrites when anchored to CAIs. They posit that

the inner Solar System (NC reservoir) was depleted in ²⁶Al through thermal processing due to it

being closer to the proto-Sun (Schiller et al., 2018), before CI-like, ²⁶Al-enriched dust was

admixed to that formation reservoir (Bollard et al., 2019). To further investigate this hypothesis,

689 we anchor 26 Al- 26 Mg ages of different NC and CC achondrites to the absolute age of EC 002 as

690 determined by our U-corrected Pb-Pb chronology. The early formation, rapid cooling history and

undisturbed history of EC 002 (Barrat et al., 2021) make it a suitable candidate as an anchor

692 meteorite.

The recent reporting of the Cr isotope systematics of EC 002 (negative bulk ε^{54} Cr values; Anand et al., 2022; Zhu et al., 2022) combined with O isotope data (Anand et al., 2022; Gattaccecca et al., 2021) and negative Tm* anomaly (Barrat et al., 2021) indicate that EC 002 formed in the NC

696 reservoir, near the angrites, brachinites and HEDs. Therefore, its parent body should have formed 697 with the same ²⁶Al abundance as the angrite parent body. This can be easily examined by anchoring the ²⁶Al-²⁶Mg ages of three angrites (D'Orbigny, Sahara 99555 and NWA 1670) to EC 002. These 698 three angrites also have published Pb-Pb ages, though the ${}^{238}U/{}^{235}U$ ratio of NWA 1670 has not 699 700 been analyzed (Schiller et al., 2015), so that any potential discrepancies between the ²⁶Al-²⁶Mg and U-corrected Pb-Pb chronometers can be examined. The resulting ²⁶Al-²⁶Mg ages are visualized 701 702 in Fig. 8 and listed in Table S3. To summarize, the U-corrected Pb-Pb age of D'Orbigny, Sahara 703 99555 and NWA 1670 are systematically older by ~ 0.5 to 1.5 Myr than their 26 Al- 26 Mg ages anchored to EC 002. This suggests that ²⁶Al heterogeneity is not the underlying cause of these age 704 705 discrepancies, but rather that there is some chronological disturbance in the angrites. This has been 706 previously discussed based on apparent isotopic disturbances of Sm-Nd systematics in D'Orbigny 707 (Sanborn et al., 2015). Furthermore, Sahara 99555 exhibits evidence of terrestrial alteration (e.g., 708 Floss et al., 2003) and potential re-distribution of Pb on the mineral grain scale (Amelin, 2008a), 709 and NWA 1670 may have been shocked (Keil, 2012 and references therein), all of which could 710 have affected the accuracy of the radiometric systems. Evidence for post-crystallization Mg 711 isotope re-equilibration in plagioclase has also been observed in the NC ungrouped achondrite 712 Asuka 881394 (Nyquist et al., 2003; Wadhwa et al., 2009; Hublet et al., 2017; Wimpenny et al., 713 2019), which shares a similar age discrepancy when anchored to EC 002 (Fig. 8, Table S3). In contrast to the angrites and Asuka 881394, the ²⁶Al-²⁶Mg ages (anchored to EC 002) of the 714 715 two ungrouped carbonaceous achondrites NWA 2976 and NWA 6704 are concordant to their U-716 corrected Pb-Pb ages (Fig. 8, Table S3: Schiller et al., 2010a; Bouvier et al., 2011b). This implies that, within the resolution of the chronometers, there were no significant variations of the ²⁶Al 717 718 abundance between the NC (EC 002) and CC reservoir (NWA 2976 and NWA 6704).

719 In addition, it is important to note that using the U-corrected Pb-Pb age with the bulk rock 720 238 U/ 235 U ratio of 137.819 ± 0.010 and the corresponding older age of 4566.43 ± 0.14 Ma does not significantly alter the interpretation of these findings. Of the three angrites, the ²⁶Al-²⁶Mg age 721 722 of D'Orbigny (when anchored to EC 002) becomes concordant with its U-corrected Pb-Pb age. Those of NWA 1670 and also Sahara 99555, when using the more precise ²⁶Al-²⁶Mg data of 723 724 Schiller et al. (2015), still are over 0.5 Myr younger than their U-corrected Pb-Pb ages. Crucially, both the ²⁶Al-²⁶Mg ages of the two ungrouped carbonaceous achondrites NWA 2976 and NWA 725 726 6704 remain concordant with their U-corrected Pb-Pb ages (Table S3). All these pieces of evidence do not suggest that ²⁶Al was distinctly different between the NC and CC reservoirs, and 727 that ²⁶Al heterogeneities are not the cause of discordant ages between the ²⁶Al-²⁶Mg and U-728 729 corrected Pb-Pb chronometers.

One remaining issue between the ²⁶Al-²⁶Mg and U-corrected Pb-Pb ages of EC 002 is their 730 731 own discordance when anchored to the absolute age of CAIs. The age difference between the U-732 corrected Pb-Pb age and the 26 Al- 26 Mg age of EC 002 is 0.40 ± 0.36 Myr (our data) or 0.40 ± 0.34 Myr (Fang et al., 2022). This results in ²⁶Al/²⁷Al ratios at the time of CAI formation of [3.54 ^{+1.82}/-733 1.22×10^{-5} and $[3.54^{+1.43}/_{-1.03}] \times 10^{-5}$, respectively. These values appear lower than the "canonical" 734 ²⁶Al/²⁷Al ratio, though both are within uncertainty of at least some internal isochrons of CAIs that 735 736 also have old Pb-Pb ages (e.g., Jacobsen et al., 2008; Bouvier and Wadhwa, 2010). Both values, 737 however, are clearly higher than the suggested ²⁶Al/²⁷Al ratio of the angrite parent body (APB) at time of CAI formation ($[1.33^{+0.21}/.0.18] \times 10^{-5}$; Schiller et al., 2015). These age differences could 738 739 be resolved by invoking earlier formation of CAIs at ~ 4567.7 Ma. The timing and duration of CAI 740 formation has been discussed largely by previous workers (Bouvier and Wadhwa, 2010; Bouvier 741 et al., 2011a; Sanborn et al., 2019; Wimpenny et al., 2019) and is beyond the scope of this study.

The most recent U-corrected absolute Pb-Pb age of CAIs (4567.30 \pm 0.16 Ma; Connelly et al., 2012) is based on a weighted mean of four CAIs from the CV3 chondrites Efremovka and Allende (Amelin 2010, Connelly et al., 2012), both of which underwent aqueous alteration that may have re-distributed isotopes and disturbed the Pb-Pb systematics (e.g., Bouvier and Wadhwa, 2010; Krot et al., 2021). The initial ²⁶Al/²⁷Al ratios of those four CAIs have also not been determined *in situ* by SIMS, thereby not confirming if they actually formed with a "canonical" ²⁶Al/²⁷Al ratio.

748 Furthermore, there have been reports of older U/Th or U-corrected Pb-Pb ages of two CAIs, 749 2364-B1 from the CV3 chondrite NWA 2364 (Bouvier and Wadhwa, 2010) and 6991-B4 from the 750 CV3 chondrite NWA 6991 (although not peer-reviewed, Bouvier et al., 2011a), with absolute Pb-Pb ages of 4568.2 ($^{+0.2}$ / $_{-0.4}$) Ma and 4567.94 ± 0.31 Ma, respectively. Both D'Orbigny and NWA 751 752 6704 are concordant when anchored to the 2364-B1 CAI age, in contrast to the Efremovka + 753 Allende CAIs (Sanborn et al., 2019). The U isotope composition of CAI 2364-B1 was not 754 measured but estimated using the low measured Th/U ratio of the sample. Bouvier and Wadhwa (2010) used the correlation found between U/Th with 238 U/ 235 U (Brennecka et al., 2010) to propose 755 756 an adjustment of up to -0.3 Myr to the internal mineral separate Pb-Pb age of the 2364-B1 CAI. 757 The 2364-B1 U/Th-corrected Pb-Pb age is therefore consistent with the U-corrected 6991-B4 Pb-758 Pb age. The correlation between U/Th ratios and U isotopic compositions in CAIs was confirmed 759 by Tissot et al. (2016) as produced by the decay of short-lived ²⁴⁷Cm. The CAIs measured by two 760 other studies did not fall on this correlation (Amelin et al., 2010; Connelly et al., 2012). Therefore, 761 those samples did not support this proxy for correcting Pb-Pb ages of CAIs. The process 762 responsible for such U isotopic variations in CAIs (beside from ²⁴⁷Cm decay) is unknown.

The U and Al-Mg isotope compositions of NWA 6991 compact type A CAI (called B4) were measured (Bouvier et al., 2011a), but these data have not been published in a peer-reviewed

765 journal and remain available only in an abstract form. A protracted formation interval of CAIs of 766 up to 0.4 Myr, as suggested by Kawasaki et al. (2019, 2020), based on *in situ* ²⁶Al-²⁶Mg dating, 767 could potentially resolve the differences in absolute ages. This would, however, still require 768 investigation into the absolute timing of such CAIs, and not necessarily impact the age of the oldest CAIs that define the initial ²⁶Al/²⁷Al ratio in the Solar System. As it currently stands, the age of 769 770 4567.30 ± 0.16 Ma (Connelly et al., 2012) remains the most robust U-corrected Pb-Pb age for a 771 CAI. Nevertheless, renewed attention to U-corrected Pb-Pb ages combined with Al-Mg 772 systematics of CAIs from more pristine chondrites may be warranted.

Two recent studies aimed to determine the initial ⁵³Mn/⁵⁵Mn ratio of EC 002 to calculate its 773 formation age using the ⁵³Mn-⁵³Cr chronometer (Zhu et al., 2022; Anand et al., 2022). Notably, 774 775 the results of the two studies do not agree with each other (Fig. 9, Table S3). Zhu et al. (2022) determined an initial 53 Mn/ 55 Mn ratio of $[5.85 \pm 0.45] \times 10^{-6}$ from an isochron based on various 776 777 mineral fractions, resulting in an absolute age of 4566.66 ± 0.56 Ma when anchored to D'Orbigny. Conversely, the initial ⁵³Mn/⁵⁵Mn ratio of $[4.76 \pm 0.39] \times 10^{-6}$, determined by Anand et al. (2022) 778 779 from leachates as well as a whole-rock, silicate and chromite fractions, results in an absolute age 780 of 4565.56 \pm 0.59 Ma, therefore younger by 1.10 \pm 0.95 Myr than the study by Zhu et al. (2022). 781 Anand et al. (2022) argue that the older age of Zhu et al. (2022) stems from higher fractions of 782 xenolithic material within their sample set, as evidenced by larger ε^{54} Cr variations in them. While 783 a sample like EC 002 is susceptible to heterogeneities between samples due to the presence of 784 large megacrysts, it is questionable that this would result in an age difference as large as ~ 1 Myr. 785 We note that Zhu et al. (2022) excluded xenolithic fractions (based on their ε^{54} Cr values) from 786 their isochron. Certainly, these incongruent results warrant further measurements.

787 Regardless of the cause of these different ages, the chronological repercussions of the 1 Myr gap 788 are substantial: the younger age obtained by Anand et al. (2022) is consistent with the U-corrected Pb-Pb age of EC 002, and with the ²⁶Al-²⁶Mg ages anchored to CAIs (this study; Fang et al., 2022). 789 Furthermore, the ⁵³Mn-⁵³Cr ages of the three angrites D'Orbigny, NWA 1670 and Sahara 99555 790 791 (Glavin et al., 2004; Sugiura et al., 2005), NC achondrite Asuka 881394 (Wimpenny et al., 2019) 792 and CC achondrite NWA 6704 (Sanborn et al., 2019), when anchored to the U-corrected Pb-Pb 793 age of EC 002 are all concordant within the resolution of the chronometers. This result contrasts 794 with the older ⁵³Mn-⁵³Cr age by Zhu et al. (2022), to which none of the above achondrites are concordant (Fig. 10, Table S3). Given this context, it would seem that the initial ⁵³Mn/⁵⁵Mn ratio 795 of $[4.76 \pm 0.39] \times 10^{-6}$ (Anand et al., 2022) may be more representative of EC 002. The 796 concordance between ⁵³Mn-⁵³Cr ages and U-corrected Pb-Pb ages when anchored to EC 002 with 797 that particular value furthermore suggests that the ⁵³Mn-⁵³Cr chronometer was not disturbed in 798 799 Asuka 881394 and the angrites, in comparison with the ²⁶Al-²⁶Mg chronometer. This would imply 800 that the cause of chronological disturbance in those samples is due to Mg diffusion in plagioclase 801 through later thermal events, rather than a more general re-setting of the chronometers. For ²⁶Al-²⁶Mg chronometry, D'Orbigny should be avoided as an anchor based on these findings. 802

In summary, the age gap between U-corrected Pb-Pb and 26 Al- 26 Mg ages (when anchored to CAIs) in some angrites and Asuka 881394 is most likely to be attributed to later re-setting of the 26 Al- 26 Mg chronometer. Alternatively, U-corrected Pb-Pb ages of CAIs from the Efremovka and Allende meteorites that may have been affected by secondary alteration, resulting in spuriously young Pb-Pb ages. Heterogeneous 238 U/ 235 U ratios in bulk meteorites, as evidenced in pyroxene separates of EC 002, may contribute to age shifts of up to ~ 0.5 Myr, but are unlikely the main cause of age discordances of up to 2 Myr. Further advances in the analytical precision of both U and Pb isotope measurements could potentially reveal more and/or larger differences in ages between the ²⁶Al-²⁶Mg and Pb-Pb chronometers, indicating smaller scale chronological disturbances or secondary processes in meteorite parent bodies.

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Figure 8: Age comparison between U-corrected Pb-Pb ages and ²⁶Al-²⁶Mg ages anchored to EC 815 816 002 (4565.87 \pm 0.30 Ma: this study), D'Orbigny (4563.51 \pm 0.29 Ma: Amelin, 2008a; Tissot et 817 al., 2017) and CAIs (4567.30 \pm 0.30: Connelly et al., 2012) of various achondrites. Data and 818 their sources are presented in Table S3. For clarity, the plotted U-corrected Pb-Pb age of Sahara 819 99555 is the weighted mean of Amelin (2008a) and Connelly et al. (2008), corrected by Tissot et al. (2017). For Asuka 881394 and NWA 2976, the ²⁶Al-²⁶Mg ages plotted are those reported by 820 821 the same studies that reported their U-corrected Pb-Pb ages (Bouvier et al., 2011b; Wimpenny et 822 al., 2019).





Figure 9: Age comparison between U-corrected Pb-Pb ages and 53 Mn- 53 Cr ages anchored to EC 002 (4565.87 ± 0.30 Ma: this study) and D'Orbigny (4563.51 ± 0.29 Ma: Amelin, 2008a; Tissot et al., 2017) of different achondrites, highlighting the 53 Mn- 53 Cr age differences between of Anand et al. (2022) (dark grey colouring) and Zhu et al. (2022) (light grey colouring). Data and their sources are presented in Table S3. For clarity, the U-corrected Pb-Pb age of Sahara 99555 plotted is the weighted mean of Amelin (2008a) and Connelly et al. (2008), corrected by Tissot et al. (2017).



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Figure 10: Age comparison between U-corrected Pb-Pb ages, and ²⁶Al-²⁶Mg ages anchored to 834 CAIs (4567.30 \pm 0.30: Connelly et al., 2012), and both ²⁶Al-²⁶Mg and ⁵³Mn-⁵³Cr ages anchored 835 836 to EC 002 (4565.87 \pm 0.30 Ma: this study) of various achondrites. Data and their sources are presented in Table S3. The initial ⁵³Mn/⁵⁵Mn ratio reported by Anand et al. (2022) is used to 837 838 calculate ⁵³Mn-⁵³Cr ages in this diagram. For clarity, the U-corrected Pb-Pb age of Sahara 99555 839 plotted is the weighted mean of Amelin (2008a) and Connelly et al. (2008), corrected by Tissot et al. (2017), and for Asuka 881394 and NWA 2976, the ²⁶Al-²⁶Mg ages plotted are those 840 841 reported by the same studies that reported their U-corrected Pb-Pb ages (Bouvier et al., 2011b; 842 Wimpenny et al., 2019).

844 <u>5. Conclusions</u>

The ungrouped achondrite Erg Chech 002 was dated by U-corrected Pb-Pb and ²⁶Al-²⁶Mg 845 846 chronology in mineral and bulk rock fractions, as well as *in situ* U-Pb chronology of Ca-phosphates by SIMS. Compared to previous studies that dated EC 002 by in situ ²⁶Al-²⁶Mg analysis (Barrat et 847 848 al., 2021), the ²⁶Al-²⁶Mg age was determined by MC-ICP-MS analysis of seven mineral fraction 849 and results in an age that is 0.43 ± 0.11 Myr older, at 1.83 ± 0.12 Ma after CAI formation and an 850 absolute age of 4565.47 \pm 0.20 Ma when anchored to the absolute age of CAIs. This age is consistent with the reported ²⁶Al-²⁶Mg age by Fang et al. (2022). The U-corrected Pb-Pb age of 851 852 EC 002 is 4565.87 ± 0.30 Ma, determined by pyroxene residue and leachates, and makes EC 002 853 the oldest dated achondrite so far. The U isotope composition was determined for both a bulk rock 854 and a leached pyroxene fraction, resulting in a notable difference between them that is likely caused by internal heterogeneities between mineral phases. For the calculation of the Pb-Pb age, 855 the ${}^{238}\text{U}/{}^{235}\text{U}$ ratio of the (re-combined) leached pyroxenes was used. 856

The U-Pb age determined by *in situ* analysis of merrillites by SIMS is 4564.3 ± 5.2 Ma, equal within uncertainty to the U-corrected Pb-Pb age determined on leached pyroxenes. This indicates that the parent body of EC 002 was not exposed to thermal metamorphism or any substantial impact events after ~ 4559 Ma and underwent rapid cooling.

The good agreement between ²⁶Al-²⁶Mg and U-corrected Pb-Pb ages of CC achondrites when anchored to EC 002, indicates that ²⁶Al was distributed homogeneously between the NC and CC reservoirs, in contrast to previous interpretations suggesting the opposite (e.g., Schiller et al., 2015). The age differences between ²⁶Al-²⁶Mg and U-corrected Pb-Pb ages of angrites and NC achondrite Asuka 881394 when anchored to EC 002 and CAIs are most likely to have been caused by diffusion of Mg isotopes in plagioclase during re-heating episodes or later thermal events. The 867 concordance between ⁵³Mn-⁵³Cr ages and U-corrected Pb-Pb ages of those same achondrites 868 suggest that the ⁵³Mn-⁵³Cr chronometer was not disturbed. Given its old age, precise ²⁶Al-²⁶Mg 869 and U-corrected Pb-Pb ages and straightforward thermal history, EC 002 shows promise to be used 870 as an anchor to date other objects with short-lived chronometers.

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880

881 Appendix A. Supplementary Material

- Table S1: EPMA elemental compositions of merrillites in EC 002.
- Table S2: ²⁶Mg isotopic anomalies (δ^{26} Mg*) of EC 002 mineral fractions calculated with different fractionation (kinetic vs. equilibrium) factors.
- Table S3: compilation of published U-corrected Pb-Pb ages, ²⁶Al-²⁶Mg ages and ⁵³Mn-⁵³Cr ages
 of EC 002 and other achondrites.
- Figures S1 and S2: linearized three-isotope plots of Mg of individual analyses of rock standards

888 San Carlos olivine and CV3 chondrite Allende, respectively.

890 **References**

- Abouchami W., Galer S. J. G. and Hofmann A. W. (2000) High precision lead isotope systematics
 of lavas from the Hawaiian Scientific Drilling Project. *Chem. Geol.* 169, 187–209.
- Amelin Y. (2008a) The U-Pb systematics of angrite Sahara 99555. *Geochim. Cosmochim. Acta*72, 4874–4885.
- Amelin Y. (2008b) U-Pb ages of angrites. *Geochim. Cosmochim. Acta* 72, 221–232.
- Amelin Y., Kaltenbach A., Iizuka T., Stirling C. H., Ireland T. R., Petaev M. and Jacobsen S. B.
- 897 (2010) U-Pb chronology of the Solar System's oldest solids with variable ²³⁸U/²³⁵U. *Earth*898 *Planet. Sci. Lett.* **300**, 343–350.
- Amelin Y., Koefoed P., Iizuka T., Fernandes V. A., Huyskens M. H., Yin Q. and Irving A. J.
- 900 (2019) U-Pb, Rb-Sr and Ar-Ar systematics of the ungrouped achondrites Northwest Africa
 901 6704 and Northwest Africa 6693. *Geochim. Cosmochim. Acta* 245, 628–642.
- An Y. and Huang F. (2014) A review of Mg isotope analytical methods by MC-ICP-MS. *J. Earth Sci.* 25, 822–840.
- 904 Anand A., Kruttasch P. M. and Mezger K. (2022) 53 Mn- 53 Cr chronology and ϵ^{54} Cr- Δ^{17} O genealogy 905 of Erg Chech 002: the oldest andesite in the Solar System. *Meteorit Planet Sci.*
- 906 Ancellin M. A., Vlastélic I., Samaniego P., Nauret F., Gannoun A. and Hidalgo S. (2019) Up to
- 907 1% Pb isotope disequilibrium between minerals hosted in dacites from the Guagua Pichincha
- 908 volcano, Ecuador: Implication for tracing the source and crustal history of continental arc
 909 magmas. *Chem. Geol.* 525, 177–189.
- 910 Barrat J., Chaussidon M., Yamaguchi A., Beck P., Villeneuve J., Byrne D. J., Broadley M. W. and
- 911 Marty B. (2021) A 4,565-My-old andesite from an extinct chondritic protoplanet. *Proc. Natl.*
- 912 *Acad. Sci.* **118**, e2026129118.

- Blichert-Toft J., Zanda B., Ebel D. S. and Albarède F. (2010) The Solar System primordial lead. *Earth Planet. Sci. Lett.* 300, 152–163.
- 915 Bollard J., Connelly J. N., Whitehouse M. J., Pringle E. A., Bonal L., Jørgensen J. K., Nordlund
- 916 Å., Moynier F. and Bizzarro M. (2017) Early formation of planetary building blocks inferred
- 917 from Pb isotopic ages of chondrules. *Sci. Adv.* **3**.
- 918 Bollard J., Kawasaki N., Sakamoto N., Olsen M., Itoh S., Larsen K., Wielandt D., Schiller M.,
- 919 Connelly J. N., Yurimoto H. and Bizzarro M. (2019) Combined U-corrected Pb-Pb dating
- 920 and ²⁶Al-²⁶Mg systematics of individual chondrules Evidence for a reduced initial
- 921 abundance of ²⁶Al amongst inner Solar System chondrules. *Geochim. Cosmochim. Acta* **260**,
- 922 62–83.
- Bouvier A., Blichert-Toft J., Moynier F., Vervoort J. D. and Albarède F. (2007) Pb-Pb dating
 constraints on the accretion and cooling history of chondrites. *Geochim. Cosmochim. Acta* **71**, 1583–1604.
- Bouvier A., Blichert-Toft J., Vervoort J. D. and Albarède F. (2005) The age of SNC meteorites
 and the antiquity of the Martian surface. *Earth Planet. Sci. Lett.* 240, 221–233.
- Bouvier A., Brennecka G. A. and Wadhwa M. (2011a) Absolute chronology of the first solids in
 the Solar System. In *Formation of the First Solids in the Solar System* p. 9054.
- 930 Bouvier A., Spivak-Birndorf L. J., Brennecka G. A. and Wadhwa M. (2011b) New constraints on
- early Solar System chronology from Al-Mg and U-Pb isotope systematics in the unique
 basaltic achondrite Northwest Africa 2976. *Geochim. Cosmochim. Acta* 75, 5310–5323.
- Bouvier A. and Wadhwa M. (2010) The age of the Solar System redefined by the oldest Pb Pb
 age of a meteoritic inclusion. *Nat. Geosci.* 3, 637–641.
- 935 Bouvier A., Wadhwa M., Simon S. B. and Grossman L. (2013) Magnesium isotopic fractionation

- 936 in chondrules from the Murchison and Murray CM2 carbonaceous chondrites. *Meteorit*.
 937 *Planet. Sci.* 48, 339–353.
- Brennecka G. A. and Wadhwa M. (2012) Uranium isotope compositions of the basaltic angrite
 meteorites and the chronological implications for the early Solar System. *Proc. Natl. Acad.*
- 940 Sci. U. S. A. **109**, 9299–9303.
- Brennecka G. A., Weyer S., Wadhwa M., Janney P. E., Zipfel J. and Anbar A. D. (2010) ²³⁸U/²³⁵U
 variations in meteorites: Extant ²⁴⁷Cm and implications for Pb-Pb Dating. *Science (80-.).*327, 449–451.
- Catanzaro E. J., Murphy T. J., Garner E. L. and Shields W. R. (1966) Absolute Isotopic Abundance
 Ratios and Atomic Weight of Magnesium. *J. Res. Natl. Bur. Stand. Sect. A, Phys. Chem.* 70A,
 453–458.
- Catanzaro E. J., Murphy T. J., Shields W. R. and Garner E. L. (1968) Absolute isotopic abundance
 ratios of common, equal-atom, and radiogenic lead isotopic standards. *J. Res. Natl. Bur. Stand. A Phys. Chem.* 72A, 261.
- 950 Cherniak D. J. (2001) Pb diffusion in Cr diopside, augite, and enstatite, and consideration of the
 951 dependence of cation diffusion in pyroxene on oxygen fugacity. *Chem. Geol.* 177, 381–397.
- 952 Connelly J. N. and Bizzarro M. (2009) Pb-Pb dating of chondrules from CV chondrites by
 953 progressive dissolution. *Chem. Geol.* 259, 143–151.
- Connelly J. N., Bizzarro M., Krot A. N., Nordlund Å., Wielandt D. and Ivanova M. A. (2012) The
 absolute chronology and thermal processing of solids in the solar protoplanetary disk. *Science*338, 651–655.
- 957 Connelly J. N., Bizzarro M., Thrane K. and Baker J. A. (2008) The Pb-Pb age of Angrite
 958 SAH99555 revisited. *Geochim. Cosmochim. Acta* 72, 4813–4824.

- Connelly J. N., Bollard J. and Bizzarro M. (2017) Pb–Pb chronometry and the early Solar System. *Geochim. Cosmochim. Acta* 201, 345–363.
- 961 Connelly J. N., Schiller M. and Bizzarro M. (2019) Pb isotope evidence for rapid accretion and
 962 differentiation of planetary embryos. *Earth Planet. Sci. Lett.* 525, 115722.
- 963 Fang L., Frossard P., Boyet M., Bouvier A., Barrat J.-A., Chaussidon M. and Moynier F. (2022)
- Half-life and initial Solar System abundance of ¹⁴⁶Sm determined from the oldest andesitic
 meteorite. *Proc. Natl. Acad. Sci.* 119.
- Floss C., Crozaz G., McKay G., Mikouchi T. and Killgore M. (2003) Petrogenesis of angrites. *Geochim. Cosmochim. Acta* 67, 4775–4789.
- 968 Gattacceca J., McCubbin F. M., Grossman J., Bouvier A., Bullock E., Chennaoui Aoudjehane H.,
- Debaille V., D'Orazio M., Komatsu M., Miao B. and Schrader D. L. (2021) The Meteoritical
 Bulletin, No. 109. *Meteorit. Planet. Sci.* 56, 1626–1630.
- Glavin D. P., Kubny A., Jagoutz E. and Lugmair G. W. (2004) Mn-Cr isotope systematics of the
 D'Orbigny angrite. *Meteorit. Planet. Sci.* 39, 693–700.
- 973 Gregory T., Luu T.-H., Coath C. D., Russell S. S. and Elliott T. (2020) Primordial formation of
- 974 major silicates in a protoplanetary disc with homogeneous ${}^{26}Al/{}^{27}Al$. *Sci. Adv.* **6**, eaay9626.
- 975 Hublet G., Debaille V., Wimpenny J. and Yin Q. Z. (2017) Differentiation and magmatic activity
- 976 in Vesta evidenced by ²⁶Al-²⁶Mg dating in eucrites and diogenites. *Geochim. Cosmochim.*977 *Acta* 218, 73–97.
- Huyskens M. H., Amelin Y. and Yin Q.-Z. (2020) Uranium Isotopic Composition of Angrites. In
 Lunar and Planetary Science Conference p. 1781.
- 980 Ito K., Hibiya Y., Homma Y., Mikouchi T. and Iizuka T. (2019) The promise and potential pitfalls
- 981 of acid leaching for Pb-Pb chronology. *Chem. Geol.* **525**, 343–355.

- Jacobsen B., Yin Q. zhu, Moynier F., Amelin Y., Krot A. N., Nagashima K., Hutcheon I. D. and
 Palme H. (2008) ²⁶Al-²⁶Mg and ²⁰⁷Pb-²⁰⁶Pb systematics of Allende CAIs: Canonical solar
- 984 initial ²⁶Al/²⁷Al ratio reinstated. *Earth Planet. Sci. Lett.* **272**, 353–364.
- 985 Kawasaki N., Park C., Sakamoto N., Young S., Na H., Kuroda M. and Yurimoto H. (2019)
- Variations in initial ²⁶Al/²⁷Al ratios among fluffy Type A Ca–Al-rich inclusions from reduced
 CV chondrites. *Earth Planet. Sci. Lett.* 511, 25–35.
- Kawasaki N., Wada S., Park C., Sakamoto N. and Yurimoto H. (2020) Variations in initial
 ²⁶Al/²⁷Al ratios among fine-grained Ca-Al-rich inclusions from reduced CV chondrites.
 Geochim. Cosmochim. Acta 279, 1–15.
- Keil K. (2012) Angrites, a small but diverse suite of ancient, silica-undersaturated volcanicplutonic mafic meteorites, and the history of their parent asteroid. *Chemie der Erde* 72, 191–
 218.
- 994 Kita N. T., Yin Q. Z., Macpherson G. J., Ushikubo T., Jacobsen B., Nagashima K., Kurahashi E.,
- Krot A. N. and Jacobsen S. B. (2013) ²⁶Al-²⁶Mg isotope systematics of the first solids in the
 early solar system. *Meteorit. Planet. Sci.* 48, 1383–1400.
- 997 Koefoed P., Amelin Y., Yin Q. Z., Wimpenny J., Sanborn M. E., Iizuka T. and Irving A. J. (2016)
- 998 U-Pb and Al-Mg systematics of the ungrouped achondrite Northwest Africa 7325. *Geochim.*
- 999 *Cosmochim. Acta* **183**, 31–45.
- 1000 Krot A. N., Petaev M. I. and Nagashima K. (2021) Infiltration metasomatism of the Allende 1001 coarse-grained calcium-aluminum-rich inclusions. *Prog. Earth Planet. Sci.* **8**, 61.
- 1002 Kruijer T. S., Kleine T. and Borg L. E. (2020) The great isotopic dichotomy of the early Solar
 1003 System. *Nat. Astron.* 4, 32–40.
- 1004 Larsen K. K., Trinquier A., Paton C., Schiller M., Wielandt D., Ivanova M. A., Connelly J. N.,

1005	Nordlund Å., Krot A. N. and Bizzarro M. (2011) Evidence for Magnesium Isotope
1006	Heterogeneity in the Solar Protoplanetary Disk. Astrophys. J. 735, L37.
1007	Ludwig K. R. (2008) Isoplot version 4.15: a geochronological toolkit for microsoft Excel. Berkeley
1008	Geochronol. Center, Spec. Publ., 247–270.
1009	MacPherson G. J., Bullock E. S., Tenner T. J., Nakashima D., Kita N. T., Ivanova M. A., Krot A.
1010	N., Petaev M. I. and Jacobsen S. B. (2017) High precision Al-Mg systematics of forsterite-
1011	bearing Type B CAIs from CV3 chondrites. Geochim. Cosmochim. Acta 201, 65-82.
1012	Marsh S. F., Alarid J. E., Hammond C. F., McLeod M. J., Roensch F. R. and Rein J. E. (1978)
1013	Anion exchange of 58 elements in hydrobromic acid and in hydriodic acid., Los Alamos, NM.
1014	Merle R., Amelin Y., Yin QZ., Huyskens M. H., Sanborn M. E., Nagashima K., Yamashita K.,
1015	Ireland T. R., Krot A. N. and Sieber M. J. (2020) Exploring the efficiency of stepwise
1016	dissolution in removal of stubborn non-radiogenic Pb in chondrule U-Pb dating. Geochim.
1017	<i>Cosmochim. Acta</i> 277 , 1–20.
1018	Nicklas R. W., Day J. M. D., Gardner-Vandy K. G. and Udry A. (2022) Early silicic magmatism
1019	on a differentiated asteroid. Nat. Geosci., 15(9), 696-699.

- 1020 Nyquist L. E., Reese Y., Wiesmann H., Shih C. Y. and Takeda H. (2003) Fossil ²⁶Al and ⁵³Mn in
- the Asuka 881394 eucrite: Evidence of the earliest crust on asteroid 4 Vesta. *Earth Planet*. *Sci. Lett.* 214, 11–25.
- Richter S., Eykens R., Kühn H., Aregbe Y., Verbruggen A. and Weyer S. (2010) New average
 values for the n(²³⁸U)/n(²³⁵U) isotope ratios of natural uranium standards. *Int. J. Mass Spectrom.* 295, 94–97.
- 1026 Roebbert Y., Rosendahl C. D., Brown A., Schippers A., Bernier-Latmani R. and Weyer S. (2021)
- 1027 Uranium isotope fractionation during the anoxic mobilization of noncrystalline U(IV) by

- 1028 ligand complexation. *Environ. Sci. Technol.* **55**, 7959–7969.
- 1029 Sanborn M. E., Carlson R. W. and Wadhwa M. (2015)¹⁴⁷,¹⁴⁶Sm-¹⁴³,¹⁴²Nd, ¹⁷⁶Lu-¹⁷⁶Hf, and ⁸⁷Rb-
- ⁸⁷Sr systematics in the angrites: Implications for chronology and processes on the angrite
- 1031 parent body. *Geochim. Cosmochim. Acta* **171**, 80–99.
- 1032 Sanborn M. E., Wimpenny J., Williams C. D., Yamakawa A., Amelin Y., Irving A. J. and Yin Q.
- 1033 (2019) Carbonaceous achondrites Northwest Africa 6704/6693: Milestones for early Solar
- 1034 System chronology and genealogy. *Geochim. Cosmochim. Acta* **245**, 577–596.
- 1035 Schiller M., Baker J. A. and Bizzarro M. (2010a) ²⁶Al-²⁶Mg dating of asteroidal magmatism in the
- 1036 young Solar System. *Geochim. Cosmochim. Acta* **74**, 4844–4864.
- Schiller M., Bizzarro M. and Fernandes V. A. (2018) Isotopic evolution of the protoplanetary disk
 and the building blocks of Earth and the Moon. *Nature* 555, 507–510.
- 1039 Schiller M., Connelly J. N., Glad A. C., Mikouchi T. and Bizzarro M. (2015) Early accretion of 1040 protoplanets inferred from a reduced inner solar system ²⁶Al inventory. *Earth Planet. Sci.*
- 1041 *Lett.* **420**, 45–54.
- 1042 Schiller M., Handler M. R. and Baker J. A. (2010b) High-precision Mg isotopic systematics of
- 1043
 bulk chondrites. Earth Planet. Sci. Lett.
 297, 165–173.
 Available at:

 1044
 http://dx.doi.org/10.1016/j.epsl.2010.06.017.
- Sedaghatpour F. and Teng F. Z. (2016) Magnesium isotopic composition of achondrites. *Geochim. Cosmochim. Acta* 174, 167–179.
- 1047 Spivak-Birndorf L., Wadhwa M. and Janney P. (2009) ²⁶Al-²⁶Mg systematics in D'Orbigny and
- 1048 Sahara 99555 angrites: Implications for high-resolution chronology using extinct 1049 chronometers. *Geochim. Cosmochim. Acta* **73**, 5202–5211.
- 1050 Stacey J. S. and Kramers J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-

- Steiger R. H. and Jäger E. (1977) Subcommission on geochronology: convention on the use of
 decay constants in geo-and cosmochronology. *Earth Planet. Sci. Lett.* 36, 359–362.
- Stirling C. H., Halliday A. N. and Porcelli D. (2005) In search of live ²⁴⁷Cm in the early solar
 system. *Geochim. Cosmochim. Acta* 69, 1059–1071.
- Sugiura N., Miyazaki A. and Yanai K. (2005) Widespread magmatic activities on the angrite
 parent body at 4562 Ma ago. *Earth, Planets Sp.* 57, 13–16.
- Tatsumoto M., Knight R. J. and Allegre C. J. (1973) Time Differences in the Formation of
 Meteorites as Determined from the Ratio of Lead-207 to Lead-206. *Science (80-.).* 180,
 1279–1283.
- Teng F.-Z., Wadhwa M. and Helz R. T. (2007) Investigation of magnesium isotope fractionation
 during basalt differentiation: Implications for a chondritic composition of the terrestrial
 mantle. *Earth Planet. Sci. Lett.* 261, 84–92.
- Teng F. Z., Li W. Y., Ke S., Marty B., Dauphas N., Huang S., Wu F. Y. and Pourmand A. (2010)
 Magnesium isotopic composition of the Earth and chondrites. *Geochim. Cosmochim. Acta* **74**, 4150–4166.
- 1067 Thomson S. N., Gehrels G. E., Ruiz J. and Buchwaldt R. (2012) Routine low-damage apatite U-
- 1068 Pb dating using laser ablation-multicollector- ICPMS. *Geochemistry, Geophys. Geosystems*1069 13, 1–23.
- 1070 Tissot F. L. H., Dauphas N. and Grossman L. (2016) Origin of uranium isotope variations in early
 1071 solar nebula condensates. *Sci. Adv.* 2, 1–8.
- 1072 Tissot F. L. H., Dauphas N. and Grove T. L. (2017) Distinct ²³⁸U/²³⁵U ratios and REE patterns in
 1073 plutonic and volcanic angrites: Geochronologic implications and evidence for U isotope

¹⁰⁵¹ stage model. *Earth Planet. Sci. Lett.* **26**, 207–221.