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# Th/U variability in Allende chondrules

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## Abstract

*Lead isotope compositions were measured on both single and combined chondrules from the CV3 carbonaceous chondrite Allende with the goal of determining the range of Th/U implied by the radiogenic  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  values. All samples were aggressively acid step-leached to separate radiogenic from primordial lead. It is found that apparent Th/U varies both between individual chondrules and between the different leaching fractions of each chondrule or group of chondrules. Specifically, the apparent Th/U ratio deviates from the planetary value (3.876), varying spectacularly from 0.65 to 14.6. Variations between leachates and residues disclose the existence of internal heterogeneities, while inter-chondrule variations reveal the presence of external heterogeneities. Three main explanations for the observed Th-U fractionation that are not mutually exclusive prevail: (1) uranium species, notably UO and UO<sub>2</sub>, coexisted in the nebular gas at high temperature, whereas Th existed exclusively as ThO<sub>2</sub>; (2) chondrules*

26 *interacted with an exotic oxidized vapor; and (3) chondrules represent melt of dust of different*  
27 *origins, a hypothesis dictated by the evidence of internal heterogeneity. The extent to which the*  
28 *measured apparent Th/U variability is due to each of these particular processes is difficult to*  
29 *assess, but the existence of substantial Th/U heterogeneity, especially within, but also among,*  
30 *single (or pooled) chondrules from the same chondrite calls for caution when Pb-Pb linear*  
31 *arrays, or mixing lines, are assigned isochronous significance.*

32

33 **Keywords:** Chondrules; CAIs; Allende; Pb isotopes; Th/U; Solar Nebula

34

## 35 **1. Introduction**

36 In the early protoplanetary disk, at various distances from the nascent Sun, partial condensation  
37 of the hot nebular gas formed nanometer- to micrometer-sized dust particles. The gas itself was  
38 produced by the partial or total evaporation of presolar dust present in the parent molecular  
39 cloud. Recent models (Pignatale et al., 2018) suggest that in the inner region of the disk, very  
40 rapidly, i.e., within less than 100 ka, the dust accreted and was reprocessed at high temperature  
41 to yield the prominent calcium-aluminum-rich inclusions (CAIs) so well-known from meteorites.  
42 Calcium-aluminum-rich inclusions are considered to be the earliest mineral assemblage of the  
43 Solar System because of their highly refractory nature corresponding to the condensation of the  
44 first ~5% of the nebular gas of Solar composition (Davis and Richter, 2014). At lower  
45 temperature, less refractory silicate dust condensed, was accreted with dust pre-existing in the  
46 disk, and partially molten in the nebular gas during brief heating events before finally being  
47 quenched to form chondrules, which are rounded millimeter- to (rare) centimeter-sized objects  
48 (Scott and Krot, 2014). Calcium-aluminum-rich inclusions and chondrules are the two major

49 high-temperature components of primitive chondritic meteorites. Dating these solids is the basis  
50 for establishing the age of the Solar System as well as the chronology of the events that shaped  
51 its earliest times. As such, we discuss both CAIs and chondrules in this paper even though we  
52 present new data only on chondrules.

53 The Pb-Pb system is a derivative of the dual U-Pb dating system, which eliminates the need to  
54 measure U and Pb concentrations. Importantly, the derived Pb-Pb date is dependent on the  
55  $^{238}\text{U}/^{235}\text{U}$  ratio. Early studies assumed a constant  $^{238}\text{U}/^{235}\text{U}$  ratio of 137.88, but Brennecke et  
56 al. (2010) demonstrated that this ratio is actually variable, thereby placing new limitations on the  
57 accuracy and uncertainty of Pb-Pb dates, such as the age of the Solar System and other proposed  
58 absolute, as well as relative, early Solar System ages (e.g., Amelin et al., 2010; Connelly et al.,  
59 2012; 2017). These limitations have since been alleviated by the simultaneous measurement of  
60  $^{238}\text{U}/^{235}\text{U}$  and Pb isotopic compositions leaving only pre-2010 studies affected as these were  
61 based on the assumption that  $^{238}\text{U}/^{235}\text{U}$  was constant. Post-2010 studies have gradually  
62 corrected the issue. The age currently used for the Solar System,  $4567.30 \pm 0.16$  Ma (Connelly et  
63 al., 2012), is derived from internal Pb-Pb isochrons obtained on CAIs from the CV3  
64 carbonaceous chondrite Efremovka. Nevertheless, despite thorough documentation of  $^{238}\text{U}/^{235}\text{U}$   
65 in CAIs and chondrules over the past decade, absolute Pb-Pb and relative Hf-W and Al-Mg ages  
66 of chondrules remain inconsistent: while some chondrules are as old as CAIs according to the  
67 Pb-Pb system (Connelly et al., 2012; Bollard et al., 2017), they are, on average,  $2.2 \pm 0.8$  Ma  
68 younger according to the  $^{182}\text{Hf}$ - $^{182}\text{W}$  system (Budde et al., 2016) and  $\sim 1$ -3 Ma younger according  
69 to the  $^{26}\text{Al}$ - $^{26}\text{Mg}$  system (Villeneuve et al., 2009; Kita and Ushikubo, 2012).  $^{26}\text{Al}$ - $^{26}\text{Mg}$   
70 systematics further indicate that the formation of chondrule precursors started  
71 contemporaneously with the formation of CAIs and lasted a maximum of 1.5 Ma (Luu et al.,

72 2015; Chen et al., 2018). There is at present no robust explanation for the discrepancies between  
73 absolute Pb-Pb and relative  $^{26}\text{Al}$ - $^{26}\text{Mg}$  and  $^{182}\text{Hf}$ - $^{182}\text{W}$  ages other than for the Al-Mg system to  
74 call on  $^{26}\text{Al}$  heterogeneity in the accretionary disk (Bollard et al., 2019), but this in turn is  
75 difficult to reconcile with astrophysical models of disk formation and early evolution (Pignatale  
76 et al., 2019).

77 In contrast to CAIs, most chondrules have  $^{238}\text{U}/^{235}\text{U}$  close to the terrestrial ratio (Connelly et al.,  
78 2017). Nevertheless, the long-standing fundamental question in U-Pb and Pb-Pb chronology of  
79 whether alignments in  $^{207}\text{Pb}$ - $^{206}\text{Pb}$ - $^{204}\text{Pb}$  space represent true isochrons or are instead merely  
80 mixing lines is still open. Of course, any isochron can formally be considered a mixture of an  
81 initial component and a pure radiogenic component. Radiogenic ingrowth, however, preserves all  
82 alignments in isochron plots through time, and there is no feature intrinsic to the data  
83 guaranteeing that at the time the radiogenic system closes, it was isotopically homogeneous. If  
84 different chondrules, or CAIs, appear to form an alignment in the  $^{207}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot,  
85 whereas they do not align in the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot, it is therefore legitimate to  
86 inquire whether original Pb was homogeneous or rather a mixture of genetically unrelated Pb  
87 components.

88 The combination of the U-Pb with the Th-Pb system sheds light on this problem. Even though  
89 the apparent  $^{232}\text{Th}/^{238}\text{U}$  ratio derived from radiogenic  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  (where \* refers to  
90 ‘radiogenic’) is a geochemical and cosmochemical tracer of unique strength that has been known  
91 for decades, it has been under-utilized, even though the data necessary for its calculation are  
92 obtained as a by-product of every U-Pb and Pb-Pb isotope chronology study, all of which focus  
93 primarily on uraniumogenic Pb. Some Pb chronology papers (e.g., Amelin, 2005; Wimpenny et al.,  
94 2019) omit the  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  data, precluding calculation of  $\kappa$ . The unique virtue of

95  $\kappa$  as a tracer is that, unlike the elemental ratios calculated from direct measurements of  
96 concentrations,  $\kappa$  can "see through" acid leaching and be accurate despite incongruent partial  
97 dissolution, as long as it is calculated from Pb isotopic ratios that are sufficiently radiogenic to  
98 make the uncertainty on the initial Pb isotopic composition insignificant. Lack of alignment in a  
99 Pb isotope plot that involves two radioactive progenitors, most typically U and Th in the  
100  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{208}\text{Pb}/^{206}\text{Pb}$  plot, requires that more than one phase is accountable for the ingrowth  
101 of radiogenic Pb and should raise concern as to whether the isochron assumption (a unique initial  
102 isotopic composition and closed system evolution) is satisfied.

103 The isochron issue is particularly delicate for chondrules and CAIs, which likely formed in a  
104 range of different positions in the Solar Nebula, and therefore were not in isotopic equilibrium at  
105 the time the U-Th-Pb chronometers started. In addition, the isochron option requires reasonably  
106 robust evidence that the initial Pb of individual samples (here chondrules or CAIs) defining a  
107 given isochron was homogeneous. In order to assess the mixing line alternative to isochrons, we  
108 measured the Pb isotope abundances in 14 single Allende chondrules and six samples of  
109 multiple, or pooled, Allende chondrules. Given that high-precision Pb isotope data on Allende  
110 chondrules with extremely small blanks have been published previously (Amelin et al., 2010;  
111 Connelly et al., 2012; 2017; Bollard et al., 2017), the purpose and design of the present study  
112 from its outset never were to propose a new high-precision, low-blank  $^{207}\text{Pb}/^{206}\text{Pb}$  isochron age,  
113 but rather to focus on the  $^{208}\text{Pb}$ - $^{206}\text{Pb}$ - $^{204}\text{Pb}$  systematics of Allende chondrules to assess whether  
114 they comply with the assumption that they host Pb that can be accounted for by a binary  
115 combination of a single primordial, Canyon Diablo-type, component and a single radiogenic  
116 component, which is the basic underlying assumption for any alignment to qualify as an  
117 isochron. Since on Earth low-temperature processes and extremely small degrees of melting are

118 the only processes that affect the Th/U ratio, we expect that Th/U variability in chondrites, which  
 119 is already known to a first order from chemical techniques (Rocholl and Jochum, 1993) to scatter  
 120 well beyond the narrow  $\pm 15\%$  range around the planetary value of 3.876 (Blichert-Toft et al.,  
 121 2010a) we are used to from terrestrial igneous samples, will provide new insights into very high-  
 122 temperature processes in the nebular gas. To put apparent Th/U data as inferred from measured  
 123 radiogenic  $^{208}\text{Pb}/^{206}\text{Pb}$  in context, we review the relevant literature data on Allende chondrules  
 124 and CAIs. Additionally, the Th/U variability documented here in Allende chondrules is assessed  
 125 in the light of uranium speciation in the nebular vapor at high temperatures, which in turn is used  
 126 to evaluate whether Th/U variations in chondrules and CAIs reflect changing thermodynamic  
 127 conditions in the nebular gas or admixtures of exotic nucleosynthetic components.

## 128 2. The power of the $^{232}\text{Th}$ - $^{208}\text{Pb}$ system

129 The single-stage equations of this system are well known:

$$130 \quad x = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_{T_0} + \mu(e^{-\lambda_{238\text{U}}T_0} - 1) = x_{T_0} + \left(\frac{^{206}\text{Pb}^*}{^{204}\text{Pb}}\right)_0 \quad (1a)$$

$$131 \quad z = \left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}}\right)_0 = \left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}}\right)_{T_0} + \mu\kappa(e^{-\lambda_{232\text{Th}}T_0} - 1) = z_{T_0} + \left(\frac{^{208}\text{Pb}^*}{^{204}\text{Pb}}\right)_0 \quad (1b)$$

132 where  $T_0$  is the age of the system,  $\mu$  and  $\kappa$  are the  $^{238}\text{U}/^{204}\text{Pb}$  and  $^{238}\text{U}/^{232}\text{Th}$  ratios at  $T=0$ ,  
 133 respectively, and \* denotes radiogenic Pb. In an  $x, z$  plot, growth curves are defined with the  
 134 equation  $x=x(T)$  and  $z=z(T)$ , while isochrons are straight-lines  $z=ax+b$  defined by a unique initial  
 135 composition  $(x_{T_0}, z_{T_0})$  and a unique slope  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ . Unfortunately,  $x$  and  $z$  are normalized  
 136 to the small  $^{204}\text{Pb}$ , and this induces strong and misleading correlations between the data  
 137 (Albarède et al., 2004). This led most geochemists to use the ‘inverse’ plot  $z/x = a+b/x$  or  
 138  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$ . An isochron in this plot is as a straight-line, whose slope is an

139 expression not relevant at this stage, and whose intercept is  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ . Given that  $\lambda_{232\text{Th}}T_0$   
140  $< \lambda_{238\text{U}}T_0 < 1$ , Eqn. 1a and 2b can be expanded and divided by one another:

141 
$$\left(\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*}\right)_0 \approx \kappa \frac{\lambda_{232\text{Th}}}{\lambda_{238\text{U}}} \left(1 - \frac{\lambda_{238\text{U}}T}{2}\right) \quad (2)$$

142 (Bouvier et al., 2009). For ~4.5 Ga samples, the expression  $\kappa \approx 4.1$   $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  is a good  
143 approximation. In this plot, isochrons form a bundle of straight-lines intersecting at the point  
144 representing initial Pb's intersection with the ordinate axis ( $^{204}\text{Pb} \equiv 0$ ) at  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  (Fig. 1). A  
145 remarkable property of the inverse plot is that, due to the slow decay of the parent isotopes, the  
146 curvature of the growth curves is small, which makes  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  rather insensitive to the  
147 actual history of radiogenic ingrowth. In the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot, the Th/U ratio  
148 associated with Pb in each sample is derived from the intercept of the line joining the points  
149 representing the sample and initial Pb, typically Canyon Diablo (see discussion in Blichert-Toft  
150 et al., 2010). The apparent Th/U of the samples calculated from the Pb isotope relationships  
151 therefore are much more robust than directly measured Th/U values which, in particular, are  
152 readily affected by alteration and definitely affected by the mandatory leaching procedures used  
153 prior to Pb purification and isotopic analysis in order to separate radiogenic from primordial Pb  
154 (Amelin et al., 2010).

155 In addition, the bundle of isochrons in the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot allows the nature of a  
156 common non-radiogenic Pb component to be identified: when the samples have been  
157 substantially contaminated by terrestrial Pb, the  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{204}\text{Pb}/^{206}\text{Pb}$  values at the  
158 intersection should be significantly different from primordial Pb (see below).

159 When the system contains multiple Th carriers with variable Th/U, the  $^{207}\text{Pb}/^{206}\text{Pb}$  and  
160  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  are decoupled. This property may hint at potentially foreign

161 components, which is a feature of the data that their interpretation must account for. The  
162 relationships of the uranogenic and thorogenic Pb components are illustrated schematically in  
163 **Fig. 2**.

### 164 **3. Material and Methods**

165 The Allende chondrules analyzed here were separated at the Institut de Physique du Globe de  
166 Paris under clean laboratory conditions. The Allende meteorite fragment containing the  
167 chondrules was first crushed with a trimmer (hydraulic press) until the size of the fragments was  
168 reduced to ~1.5 cm. Subsequent gentle crushing in a sapphire mortar and sieving with nylon  
169 sieves allowed elimination of the finest powder to collect free chondrules in the sieved fraction  
170 and, with tweezers under a binocular microscope, separate those chondrules that were still  
171 partially enclosed within the matrix. Because no selection of chondrules were made based on  
172 optical observation or other criteria, the present set of 14 single chondrules and six multiple  
173 chondrule pools most likely consists predominantly of type I porphyritic chondrules since this  
174 type constitutes the vast majority of Allende chondrules (>95% are type I and ~94% are  
175 porphyritic; Scott, 2007). Enclosing or residual matrix was gently rubbed off the chondrules  
176 prior to leaching and we surmise that the radiogenic character of Pb itself is one of the most  
177 realistic means of assessment of the efficiency of the chondrule separation and cleaning process.

178 The separated chondrules were processed for Pb isotopic analysis under clean laboratory  
179 conditions at the Ecole Normale Supérieure in Lyon (ENS Lyon). Because aggressive acid step  
180 leaching is known to achieve efficient separation of radiogenic and initial Pb (Frei and Kamber,  
181 1995), after weighing each individual chondrule, or pool of multiple chondrules, into new, pre-  
182 cleaned Savillex beakers, they were leached successively in double-distilled hot 1M HBr, hot 6M  
183 HCl, and hot concentrated HNO<sub>3</sub>, each acid a single leach for 1 hour at 120°C interspersed with

184 ultrasonication steps and clean ( $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ ) water rinses, then dissolved in a 3:1:0.5 mixture  
185 of double-distilled concentrated HF:HNO<sub>3</sub>:HClO<sub>4</sub>. All residue and leachate fractions were taken  
186 individually through 0.25 ml anion-exchange chromatographic columns to separate Pb (collected  
187 with double-distilled 6M HCl after elution of the sample matrix with double-distilled 1M HBr),  
188 which was analyzed for its isotopic composition by MC-ICP-MS, also at ENS Lyon. Total  
189 analytical blanks were processed in the same way as samples (see below).

190 Lead isotopic analyses were carried out on a Neptune Plus HR MC-ICP-MS (Thermo Scientific)  
191 using an Aridus II desolvating nebulizer system (Teledyne CETAC Technologies). Samples were  
192 dissolved in distilled 0.05M HNO<sub>3</sub> + 1 ppb Tl; the added Tl was used to correct the unknowns  
193 (samples and standards) for instrumental mass bias using an exponential law (Maréchal et al.,  
194 1999). Sample-standard bracketing was done by measuring, respectively, 5 ppb solutions of the  
195 Pb isotopic Standard Reference Material 981 from the National Institute of Standards and  
196 Technology (NIST) every two samples throughout the run sessions and normalizing to the values  
197 of Eisele et al. (2003) for NIST 981. The external reproducibility, estimated from repeat standard  
198 measurements of NIST 981, was better than 100-200 ppm (or 0.01-0.02%) for Pb isotope ratios  
199 based on  $^{204}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$  and better than 50 ppm (or 0.005%) for  
200  $^{207}\text{Pb}/^{208}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ , and  $^{207}\text{Pb}/^{208}\text{Pb}$ .

201 The signal of the samples is estimated to vary within  $\pm 10\%$  and the signal of the blanks is  
202 estimated to be known within a factor of  $\sim 3$ , which constrains the range of the sample/blank ratio  
203 to within an order of magnitude. The total procedural Pb blank was 20 pg or less (Table 1) and  
204 its isotopic composition, also reported in Table 1, is known to within 2%. The signal of the blank  
205 was subtracted from those of the samples on each isotope and error was propagated using 2000  
206 Monte Carlo cycles using the equations in Bouvier et al. (2007). Subtracting the blank from the

207 samples left 41 samples (residues and leachates) with >150 pg Pb, the lower cut-off value set for  
208 including the data in isochron regressions, as opposed to 48 samples prior to blank correction  
209 (Table 1).

210 Actual Th and U concentrations were not measured on any fraction on the grounds that leaching  
211 is highly likely to fractionate elemental ratios (e.g., Amelin et al., 2010). We consider in contrast  
212 that leaching does not fractionate  $^{208}\text{Pb}$  from  $^{206}\text{Pb}$  to an extent that would significantly modify  
213  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ , and, therefore, the apparent Th/U ratios derived from  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  (Fujii et al.,  
214 2011; Yang and Liu, 2015).

215 The measured Pb isotopic compositions are listed in Table 1 and the blank-corrected values in  
216 **Table 2** together with other calculated parameters including error propagation and apparent Th/U  
217 ratios.

218 Isochrons were calculated by minimizing the weighted chi-squared function 2 of York (1969)  
219 using Matlab ® optimization software with internal errors, while ages were obtained using the  
220 following values:  $^{238}\text{U}/^{235}\text{U}=137.79$ ,  $\lambda_{238\text{U}}=0.155125 \text{ Ga}^{-1}$ ,  
221  $\lambda_{235\text{U}}=0.98485 \text{ Ga}^{-1}$ ,  $\lambda_{232\text{Th}}=0.049475 \text{ Ga}^{-1}$ . The Monte Carlo method with log-normal errors was  
222 preferred to the other conventional models. Widely used algorithms such as Isoplot software  
223 (Ludwig, 2012) are most often used with a normal error distribution, which occasionally leads to  
224 error ellipses extending into the forbidden quadrant of negative coordinates (e.g., Amelin et al.,  
225 2019, Fig. 1 and 3; Wimpenny et al., 2019, Fig. 1 and 5) and therefore invalidates the error  
226 assessment. Errors were propagated using 2000 Monte Carlo cycles. The contribution of each  
227 point to the chi-squared was used to identify outliers. Statistics, in particular the commonly used  
228 Mean Squared Weighted Deviation (MSWD), may help assess whether linear arrays are true

229 alignments and consistent with the basic isochron assumptions (unique initial isotopic  
230 composition and closed system evolution). Unfortunately, it is well established that for old  
231 samples, and this is particularly relevant to chondrules and CAIs, radiogenic ingrowth  
232 progressively accounts for virtually all the isotopic variation at the expense of initial  
233 heterogeneities (Juteau et al., 1984; Vidal et al., 1984; Kalsbeek, 1992). In other words, the  
234 MSWD of a potential isochron array diminishes with radiogenic ingrowth and is not age-  
235 invariant. The expression ‘isochron age’ is used in the following to refer to the apparent age of  
236 the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  (where, as for  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ , \* refers to ‘radiogenic’) intercept of the least-  
237 square alignment in the  $^{207}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot even when the associated MSWD  
238 indicates that the linear array in question, from a statistical point of view, is not an isochron but  
239 an errorchron.

240 Analytical precision and blank levels are not critical to determining  $^{232}\text{Th}/^{238}\text{U}$  ( $\sim\text{Th}/\text{U}$ ) ratios,  
241 which are the main focus of the present work. The blank was determined by running full  
242 chemical separations, including leaching, without sample added. The blank level is consistent  
243 between dedicated blank runs (14-20 pg) and the smallest amounts of Pb present in leachates 1-  
244 4Lc and 2-1Lc (7-14 pg) (Table 1). Once corrected for the blank, typical 95 percent confidence  
245 errors on  $^{204}\text{Pb}/^{206}\text{Pb}$  are 0.5 to 6% (typically 1-2%) and those on  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$   
246 0.01-0.02%.

#### 247 **4. Results**

248 The 41 samples containing more than 150 pg Pb, including leachates and residues, give an  
249 apparent age of  $4561.2 \pm 0.6$  Ma (2 sigma; MSWD=71) (Fig. 3a). The isochron age obtained by  
250 pooling 11 of the 14 individual single-chondrule residues is  $4564.0 \pm 0.9$  Ma (2 sigma;

251 MSWD=4.6) (Fig. 3b) with the most radiogenic samples being reasonably consistent with the  
252 range of ages published so far (e.g., Amelin and Krot, 2007). Three samples were discarded on  
253 the basis of a higher contribution to the chi-squared. Caution should be used when making a  
254 direct comparison with published ages, notably those of Connelly et al. (2012), since these pool  
255 leachate fractions, likely more susceptible to collect terrestrial Pb than residues, from isolated  
256 chondrules and not residues as in the present work. That being set aside, ages for different  
257 chondrules generally can be directly compared as most chondrules have  $^{238}\text{U}/^{235}\text{U}$  close to the  
258 terrestrial ratio (Connelly et al., 2017). The combination of multiple chondrule residues (i.e.,  
259 representing external as opposed to internal isochron statistics) and the small amount of Pb (of  
260 the order of pg, which meant running sample solutions of the order of ppt) left after the severe  
261 leaching protocol that was applied in the present work likely accounts for the rather large error of  
262 almost 1 Ma (about twice or three times the errors on other ages on similar material in the  
263 published literature; e.g., Connelly et al., 2012; 2017) on the 11-point residue isochron and the  
264 large MSWD. The MSWD of 18.4 on the single-chondrule residue age (Fig. 3b) shows that the  
265 data points scatter beyond analytical error and that the best-fit line should not be considered as a  
266 statistically significant isochron. The same of course is true for the even larger MSWD of 71 on  
267 the all-sample residue-leachate age (Fig. 3a). The single-chondrule residue age, however, despite  
268 its larger error compared to other ages in the literature, is similar to that reported for the CR  
269 chondrite Acfer 059 ( $4564.7 \pm 0.7$  Ma; Amelin et al., 2002) and only marginally younger than  
270 previous ages obtained on Allende chondrules, which range from  $4567.3 \pm 0.4$  to  $4564.7 \pm 0.3$  Ma  
271 (Connelly et al., 2012; 2017). Importantly, the residues plot on a line that does not go through the  
272 currently best estimate of initial, or primordial, Pb (Blichert-Toft et al., 2010a) in  $^{207}\text{Pb}/^{206}\text{Pb}$ –  
273  $^{204}\text{Pb}/^{206}\text{Pb}$  space (Fig. 3b). As previously observed by Connelly et al. (2017), the expected

274 isotopic value of terrestrial contamination also plots off the isochron, which simply confirms  
275 decade-long observations that common Pb plots to the right of the geochron. We therefore  
276 consider that Pb in each residue fraction is a mixture of variable proportions of initial Pb and  
277 radiogenic Pb with little terrestrial contamination.

278 The large range in apparent Th/U values deduced from the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot (Fig. 4)  
279 is a novel observation. The range of apparent Th/U variations within individual chondrules  
280 (Fig. 5) is smaller than the range among chondrules (Fig. 4), although variations of up to 30% are  
281 significant compared with terrestrial rocks (Blichert-Toft et al., 2016; Elliott et al., 1999). Most  
282 residues of individual chondrules have apparent Th/U ranging from 3.0 to 5.2 (Figs. 4 and 5),  
283 consistent with the chondritic Th/U value of  $3.9 \pm 0.2$  (Rocholl and Jochum, 1993) and the more  
284 recent and more precise planetary value of  $3.876 \pm 0.016$  (Blichert-Toft et al., 2010a), but with  
285 extreme outliers at 0.65 (10R) and 14.6 (16R) (Figs. 4 and 5; sample 16R is off scale in Fig. 5).  
286 Likewise, the apparent Th/U of the six combined chondrule fractions (combined because each of  
287 the chondrules in these pooled samples was too small to be analyzed individually), de-  
288 emphasized here because of their rather unradiogenic Pb, varies between 2.9 and 5.1 (Table 2).  
289 There is no correlation between  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  and  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ( $r=-0.075$ ), i.e. no correlation  
290 between the model Th/U and Pb-Pb ages calculated by subtracting primordial Pb from the  
291 sample, which discounts simple binary mixing.

## 292 **5. Discussion**

### 293 *5.1 Isochrons vs mixing lines*

294 Let us first address whether using the  $^{232}\text{Th}$ - $^{208}\text{Pb}$  system helps validating isochrons vs mixing  
295 lines in the U-Pb system. First, the long-standing issue of the nature of the non-radiogenic end-  
296 member can be addressed by observing that the points representing the leachates and the residues

297 form a bundle of arrays. In contrast to the  $^{207}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot, this bundle is open in  
298 the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot and even more so because the Th/U range is large. Only if  
299 terrestrial Pb is part of the non-radiogenic component this bundle should have a common  
300 intersection different from CD primordial Pb. For such a bundle with equations made of  
301 leachate-residue pairs or triplets in the form  $z/x = a_i + b_i/x$  (where  $i$  refers to the  $i$ -th sample), the  
302 intersection  $(1/x_0, z_0/x_0)$  can be simply obtained from the slope and intercept of the  $a_i$  vs  $b_i$  array  
303 rewritten as  $a_i = -b_i/x_0 + z_0/x_0$ . With the present samples having presumably gone through  
304 different histories, we did not attempt to run a full least-squares calculation with error handling.  
305 A simple regression on residue-leachate pairs gives quite a good fit ( $r^2=0.994$ ) confirming that  
306 the non-radiogenic end-member is very similar for all the chondrules. The coordinates of the  
307 intersection,  $(^{206}\text{Pb}/^{204}\text{Pb})_0 = 9.33$  and  $(^{208}\text{Pb}/^{204}\text{Pb})_0 = 29.4$ , compare well with the Nantan-CD  
308 values of 9.305 and 29.53 of Blichert-Toft et al. (2010). This demonstrates that the terrestrial  
309 contamination of the Allende fragment used for the present study is surprisingly small.

310 The inverse  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$  plot displays strong variability of  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ , and  
311 therefore of apparent Th/U, between chondrules (Fig. 4) and, to a lesser extent, also within  
312 chondrules (Fig. 5). The same is observed for literature data (Fig. 6), even more markedly so for  
313 CAIs than chondrules (Fig. 6), showing that phases with very different Th/U coexist in the same  
314 inclusion. An alternative approach to deducing the number of U, Th, and Pb carriers is to plot the  
315 fractions of initial Pb ( $^{204}\text{Pb}$ ) and radiogenic isotopes ( $^{206}\text{Pb}^*$ ,  $^{207}\text{Pb}^*$ , and  $^{208}\text{Pb}^*$ ) removed at  
316 each leaching stage vs the fraction of total Pb (Fig. 7). The number of leaching steps in the  
317 present study being too small, we instead plotted the results for two chondrules from NWA 5697,  
318 C1 and C3, and one Efremovka CAI (22E) analyzed by Connelly et al. (2012, 2017). For the two  
319 chondrules, the extraction efficiency is different for initial and radiogenic Pb, which shows that

320 U and Th have one carrier and initial Pb another. For these two samples, there is no evidence of  
321 separate carriers and the isochron claim holds. For CAI 22E, in contrast, even if initial Pb and  
322 radiogenic Pb components remain separated, there is evidence of separate carriers for U and Th.  
323 The Th carrier being much more soluble in HBr, HCl, and HNO<sub>3</sub>, it is most likely associated  
324 with phosphate. The U carrier being preferentially liberated by HF has to be either silicates,  
325 oxides, or other titano-aluminates. Whether these minerals are genetically related is unclear.

### 326 *5.2 The origin of Th/U variations*

327 Th/U variations in chondrules and CAIs may result from a number of processes. Large isotopic  
328 heterogeneities exist both within and among different meteorite classes in general and among  
329 chondrules in particular. Early observations of clear correlations between neutron-rich isotopic  
330 anomalies (<sup>54</sup>Cr, <sup>50</sup>Ti), (s/r nuclide abundances), stable nuclide abundances (Zn, Cu), and  $\Delta^{17}\text{O}$   
331 (Dauphas et al., 2002; Luck et al., 2003; 2005; Trinquier et al., 2007; 2009; Moynier et al., 2010)  
332 led Warren (2011) to describe the Solar Nebula as a mixture of different components that were  
333 not thoroughly homogenized in the accretion disk. Most chondrules formed from dust aggregates  
334 derived from pre-solar cloud material and condensates of the nebular gas, including the carriers  
335 of these heterogeneities (e.g., Krot et al., 2009). Precursors of variable origin (refractory grains,  
336 CAI fragments, olivine, Fe metal) were variously thermally processed during chondrule melting  
337 events. Relict Mg-rich olivine crystals can be present in chondrules as shown by their <sup>16</sup>O-  
338 enriched isotopic compositions relative to the glassy mesostasis and the main silicate phases  
339 (e.g., Weinbruch et al., 1993; Jones et al., 2004; Pack et al., 2004; Chaussidon et al., 2008;  
340 Rudraswami et al., 2011; Tenner et al., 2013; Marrocchi et al., 2019). This implies that olivine  
341 crystals did not completely evaporate or melt during chondrule formation. Precursor refractory  
342 dust (either CAI fragments or refractory condensates) would have behaved similarly. Exchanges

343 between chondrule melts and the ambient gas are restricted to elements with moderate to low  
344 volatility such as Na (Alexander et al., 2008), K (Humayun and Clayton, 1995; Yu et al., 2003),  
345 Fe (Ebel et al., 2018), Mg (Galy et al., 2000), and Si (Libourel et al., 2006), all having 50%  
346 condensation temperatures ( $T_c$ ) below 1400 K (Lodders, 2003). Thorium and U both being  
347 highly refractory, like Al, with a 50%  $T_c > 1600$  K (Lodders, 2003) are expected to behave in a  
348 conservative manner during chondrule formation.

349 External Th/U heterogeneity among individual chondrules is unlikely to be due to fractional  
350 crystallization. The Th/U ratio varies with the fraction of melt crystallized  $F$  as

$$\frac{d \ln(\text{Th}/\text{U})}{d \ln[U]} = \frac{D_{\text{Th}} - D_{\text{U}}}{D_{\text{U}} - 1}$$

351 (Albarède, 1995, p. 37), which for Th and U is a very small number. Both Th and U are  
352 incompatible elements and the exponent  $D_{\text{Th}}-D_{\text{U}}$  is in the range of  $10^{-3}$  to  $10^{-2}$  (Blundy and  
353 Wood, 2003). Closed-system magmatic fractionation of Th relative to U during chondrule  
354 crystallization does not change bulk Th/U values among liquid chondrules, which suggests that  
355 accessory mineral phases with extreme Th/U, such as hibonite, are trapped from the dust.  
356 Variations of the Th/U ratio within chondrules (internal heterogeneity) may reflect their  
357 formation from a variable mix of precursors. They may also reflect the presence of late-stage  
358 accessory phases, which the leaching procedures may preferentially dissolve without adding  
359 useful information on the crystallization process. As discussed previously, however, internal  
360 heterogeneities are subdued relative to external heterogeneities. The Th/U variations among  
361 different chondrules inferred from  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  ratios therefore remain the strongest and most  
362 informative evidence that different material with a complex history coexist in the Allende  
363 meteorite.

364 In contrast, fractionation of U relative to Th is expected to take place during the formation of  
365 chondrule precursors, which include CAIs, because of condensation/evaporation processes and  
366 interactions between solids and vapor over a large range of temperatures and oxygen fugacities.  
367 In contrast to troilite, which seems to have recorded a rather uniform planetary Th/U ratio of  
368 ~3.9 (Blichert-Toft et al., 2010a), Pb in samples from the IVA asteroid, which appear to have  
369 formed exceptionally early after CAIs (Blichert-Toft et al., 2010b), has recorded very low Th/U  
370 (0.3 for Muonionalusta; Blichert-Toft et al., 2010b; 1.1 for Steinbach; Connelly et al., 2019).  
371 Th/U ratios are known to be heterogeneous both within a given CAI (Connelly et al., 2012;  
372 Bollard et al., 2017) and among CAIs (ranging from 2.1 to 70; Brennecka et al., 2010; Tissot et  
373 al., 2016) (Fig. 6). Apatite and merrillite are phosphatic phases that only appear upon  
374 metamorphism by exsolution of phosphorus from the metal in re-equilibrated mineral  
375 assemblages or by aqueous alteration at rather low temperature (Krot et al., 1995). In addition,  
376 whenever they appear, like in H4-H6 and L5-L6 ordinary chondrites, they do so with planetary  
377  $\kappa$  values (Göpel et al., 1994) or lack  $^{208}\text{Pb}/^{204}\text{Pb}$  data (e.g., Amelin, 2005). The most important  
378 high-temperature phases in CAIs that could effectively enrich Th over U are hibonite and  
379 melilite (Brennecka et al., 2010; Kennedy et al., 1994). The Th/U variations can therefore be  
380 ascribed to the difference in condensation temperature between U and Th (50%  $T_c$  of 1610 and  
381 1659 K, respectively; Lodders, 2003), which in turn is controlled by the condensation  
382 temperature of Al (1653 K; Lodders, 2003) in the form of hibonite. Most CAIs have had a  
383 complex high-temperature condensation/evaporation history as demonstrated by their petrology  
384 and isotopic compositions. Type B CAIs were partially molten in the range of 1500-1670 K and  
385 underwent partial evaporation at higher temperatures (Stolper and Paque, 1986; Richter et al.,

386 2002). The valences of Ti and V in CAIs show that this took place under highly reducing oxygen  
387 fugacities corresponding to a gas of Solar composition (Simon et al., 2007).

388 The major fraction of precursor silicate dust condensed at lower temperatures, possibly under  
389 various oxygen fugacities. This would control the U-Th speciation in the nebular gas and thus the  
390 Th/U ratio in chondrule melts at equilibrium. Variations of oxygen fugacity in the chondrule-  
391 forming region can result from transport and vaporization of H<sub>2</sub>O ice (Cuzzi and Zahnle, 2004)  
392 and from partial evaporation of precursor silicate dust (Ebel and Grossman, 2000). Available  
393 oxygen can combine with carbon and silicon to form CO and SiO. A series of equations can be  
394 written such as



397 The equivalence point of the first equation, defined by  $P_{\text{Si}} = P_{\text{SiO}}$ , defines the oxygen partial  
398 pressure  $P_{\text{O}_2}$  as

$$399 \quad \ln P_{\text{O}_2} = -\Delta G^\circ / RT$$

400 where  $\Delta G^\circ$  is the change in Gibbs free energy of the first reaction. These values can be found in  
401 JANAF tables (Chase et al., 1998) and the variation of the equivalence point with temperature  
402 calculated in a T-log  $P_{\text{O}_2}$  plot as shown in Fig. 8. It is well established that, at high temperatures,  
403 uranium vapor can be oxidized as UO, UO<sub>2</sub>, and UO<sub>3</sub> as  $P_{\text{O}_2}$  increases. Likewise, Th may be  
404 oxidized as ThO and ThO<sub>2</sub>. Under strongly oxidizing conditions, U can also be hydrated as  
405 UO<sub>2</sub>(OH)<sub>2</sub> (Olander, 1999; Alexander, 2005). The thermodynamic data for U, Th, and their  
406 oxides can be found in Green (1980), Cox et al. (1989), Guillaumont and Mompean (2003), and  
407 Konings et al. (2014). At low  $P_{\text{O}_2}$ , in a vapor dominated by Si, CO, and H<sub>2</sub>, U tends to be in the  
408 UO<sub>2</sub> form. These conditions would be suitable for Allende inclusions (Grossman et al., 2012).

409 With increasing  $P_{O_2}$ , the vapor is dominated by SiO, CO, and H<sub>2</sub>, and the dominant U form  
410 becomes UO<sub>3</sub>, which is believed to represent the environment of chondrules. The form  
411 UO<sub>2</sub>(OH)<sub>2</sub> is only stable under unrealistic values of  $P_{O_2}$ . In contrast, Th remains in its ThO<sub>2</sub>  
412 form. In strongly depolymerized melt and under the reducing conditions of the Solar Nebula,  
413 both U and Th are tetravalent and in 6-fold coordination (Farges, 1991; Farges et al., 1992).  
414 Since gaseous Th is entirely in the ThO<sub>2</sub> form, Th/U fractionation essentially reflects the  
415 UO<sub>2</sub>/(UO<sub>2</sub> + UO<sub>3</sub>) ratio, and more generally U speciation in the vapor. There is simply not  
416 enough Al with respect to oxygen for hibonite condensation to affect  $P_{O_2}$  significantly. Variable  
417 Th/U ratios may, therefore, reflect the oxygen fugacity of the parent gas interacting with  
418 chondrules and other solid materials and be the signature of very early nebular processes such as  
419 the loss of hydrogen.

420 The internal variation of apparent Th/U within individual chondrules suggests that, in addition to  
421 fractionation taking place in the protoplanetary disk under various temperatures and  $P_{O_2}$ , part of  
422 the Th/U variability in chondrules is likely to be inherited from pre-solar phases carrying  
423 chemical and isotopic heterogeneities or, as attested to by the wealth of modern measurements  
424 and observations (Dauphas et al., 2002; Luck et al., 2003; 2005; Trinquier et al., 2007; 2009;  
425 Moynier et al., 2010; Warren, 2011), from an isotopically heterogeneous nebular gas. These two  
426 interpretations are not mutually exclusive since the dominance curves in gas (equivalence lines)  
427 in Fig. 8 are nearly parallel, and a probable cause of  $T$  and  $P_{O_2}$  variations is mixing of hot gas  
428 with colder material with  $P_{O_2}$  modified by dust condensation at lower temperatures. The  
429 relatively poor alignments defined when whole Pb isotope data sets on chondrules are taken into  
430 consideration and the lack of alignment of Pb-Pb isochrons with initial, or primordial, Pb hint at

431 initial Pb isotope heterogeneity or at a complex evolution of the U-Pb system (Amelin et al.,  
432 2002; Connelly et al., 2012; 2017; this work) (Figs. 2 and 5).

433 Understanding Th/U variations among chondrules can benefit from CAI evidence. The  
434 correlation between  $^{235}\text{U}/^{238}\text{U}$  and both Th/U and Nd/U in CAIs (Brennecka et al., 2010; Tissot  
435 et al., 2016) was interpreted to reflect the decay of  $^{247}\text{Cm}$  although Amelin et al. (2010) had  
436 argued against this interpretation by comparing Allende whole-rock and CAI values of  $^{235}\text{U}/^{238}\text{U}$   
437 and Nd/U. If this correlation were of universal relevance, the Th/U ratios  $<3.876$  identified in the  
438 present Allende chondrules (Fig. 4) and the CAIs analyzed by Connelly et al. (2012) (Fig. 6)  
439 would be difficult to account for by excess  $^{247}\text{Cm}$ . Excess  $^{236}\text{U}$  produced by neutron capture is an  
440 alternative possibility. However, although nuclear excesses due to neutron capture are well  
441 documented in Allende by Sm isotopic measurements (Carlson et al., 2007; Bouvier and Boyet,  
442 2016), the cross-section of  $^{235}\text{U}(n)^{236}\text{U}$  for thermal neutron capture is too small to result in a  
443 measurable effect on  $^{232}\text{Th}$  via alpha decay. Preferential recoil of  $^{238}\text{U}$  during decay from  
444 nanophases and low-temperature alteration are possible alternative interpretations but difficult to  
445 test. A conservative conclusion is that chondrules and CAIs formed at different times during the  
446 thermal evolution of their parent vapor and dust in different regions of the Solar Nebula with  
447 variable nucleosynthetic heritages. Mineralogical and geochemical observations, notably those  
448 on Th/U in chondrules, demonstrate the extent of interaction between these different nebular  
449 reservoirs.

450 Regardless of the final interpretation of the origin of apparent Th/U variations in CAIs and  
451 chondrules, the consequences of their undisputable existence for the age of the Solar System and  
452 the age(s) of CAIs and chondrules are significant. Even if CAIs likely have been maintained  
453 within a narrow time window at temperatures high enough to cause full Pb isotope evaporation

454 (Thrane et al., 2006; Jacobsen et al., 2008; Kita et al., 2013), this is not necessarily the case for  
455 chondrules, which may still contain Pb (Bland et al., 2005). The Pb-Pb alignments so far  
456 considered to be isochrons may contain an undetermined contribution of mixing, which may  
457 include both primordial and terrestrial Pb. This is also valid for the single-chondrule Pb-Pb age  
458 of  $4564.0 \pm 0.9$  Ma presented here. Hence, the assessment of an absolute age not only to date the  
459 Solar System but also to ‘anchor’ chronologies based on extinct radioactivities needs more work  
460 and further clarification, in particular Pb-Pb ages on single chondrules. The similarity of Th/U in  
461 chondrites (Rocholl and Jochum, 1993; Blichert-Toft et al., 2010a) and chondrules, as discussed  
462 in the present work, with the planetary value suggests that the inner Solar System has an average  
463  $\kappa$  value of 3.9. Focusing Pb-Pb chronology on material with apparent Th/U ratios consistent with  
464 planetary values increases the chances of dating early Solar System events rather than objects  
465 with a complex inheritance.

## 466 **6. Conclusions**

467 Large variations of Th/U values inferred from radiogenic  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  ratios of chondrules  
468 require that processes other than fractional crystallization of silicate melts were active during  
469 chondrule formation. The most likely interpretation is that chondrules carry Th and U from  
470 different precursors with a different nebular or pre-nebular history. In this study we identified  
471 spectacular Th/U variations in single and pooled chondrules from Allende, as well as in  
472 chondrule and CAI data sets from the published literature, the latter of which have so far been  
473 considered to provide chronologically valid and geologically meaningful uranium ages. The  
474 large observed Th/U variations characterizing these data, however, beg the question of whether  
475 the Pb-Pb ages derived from them can in fact be taken as valid crystallization dates? The large  
476 Th/U heterogeneities documented here suggest that interpreting linear Pb-Pb arrays as isochrons

477 rather than mixing lines requires caution. A planetary, or “normal”, Th/U ratio is a minimum  
478 condition for proceeding further with Pb-Pb dating of any given chondrule or CAI.  
479 Th/U variability can result from the presence of components with a different early nebular or  
480 pre-nebular history. Redox-dependent U speciation in the gas, loss of hydrogen, and/or  
481 introduction of foreign nucleosynthetic components are all possible non-exclusive explanations  
482 for the presence of large Th/U variations in chondrules and their refractory precursors. Pb-Pb  
483 ages of chondrules and CAIs may date the formation of their precursor materials rather than the  
484 formation of the chondrules and the CAIs themselves.

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722

723 **Figure captions**

724 **Figure 1.** Plot showing that the history of radiogenic ingrowth has little incidence on the Th/U  
725 ratio derived from the  $^{204}\text{Pb}/^{206}\text{Pb}$ – $^{208}\text{Pb}/^{206}\text{Pb}$  plot. CD (for Canyon Diablo) stands for primitive  
726 Pb. Isochrons, here drawn in red for  $T = 1.5, 3.0, 4.5,$  and  $4.6$  Ga for three different values of  $\kappa$ ,  
727 can be seen as a binary mixture between a primordial and a radiogenic component  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$   
728 (at  $^{204}\text{Pb}=0$ ). The growth curves, shown here in black for three values of  $\kappa = ^{232}\text{Th}/^{238}\text{U}$ , have  
729 rather small curvatures. The uncertainty on the Th/U ratio of a given sample inferred from this  
730 plot depends much more on its  $\kappa$  than on its history.

731 **Figure 2.** Schematic inverse isochron plots for the U-Pb ( $^{204}\text{Pb}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ , bottom panels)  
732 and U-Th-Pb ( $^{204}\text{Pb}/^{206}\text{Pb}$ – $^{208}\text{Pb}/^{206}\text{Pb}$ , top panels) systems. For a binary mixture (black circles)  
733 of initial (Nantan, the new “Canyon Diablo”, see also caption to Fig. 3) and radiogenic Pb having  
734 evolved in a closed system, the intercept  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ( $^{204}\text{Pb}=0$ ) gives the age of the system,  
735 while the intercept  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  gives the Th/U ratio of the sample. When the  $^{204}\text{Pb}/^{206}\text{Pb}$ –  
736  $^{208}\text{Pb}/^{206}\text{Pb}$  plot reveals a ternary mixture (red circles), such as initial, contaminant, and  
737 radiogenic Pb, or an even more complex situation, alignments in  $^{204}\text{Pb}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$  space  
738 (bottom right-hand-side panel) may be suspected of not representing an isochron but a mixing  
739 line and, hence, the age of the intercept  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  may no longer be a valid chronometer.

740 **Figure 3.** Inverse isochron ( $^{207}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$ ) plots of Pb from leachates and residues  
741 for 14 single chondrules. Only fractions with  $>150$  pg Pb after blank correction have been  
742 plotted. Solid (blue) circles: residues. Open (white) circles: leachates. The best-fit line for the 41  
743 samples with  $>150$  pg Pb, including leachates and residues, defines an age of  $4561.2 \pm 0.6$  Ma (2  
744 sigma; MSWD=71) (panel a). The isochron age in the best-fit sense of 11 of the 14 analyzed

745 individual single-chondrule residues (blue circles) is  $4564.0 \pm 0.9$  Ma (2 sigma; MSWD=18.4)  
746 (panel b). The large MSWD on both ages show that the points scatter beyond analytical  
747 uncertainties. None of the best-fit lines are statistically significant isochrons (hence the choice of  
748 the word best-fit line instead of isochron). The red curves define the error envelope propagated  
749 from internal errors, while the blue curves define the error envelope when errors are multiplied  
750 by the square root of the MSWD (calculated errors). The green star labeled CD for Canyon  
751 Diablo represents the isotopic composition of the currently best estimate of the most primitive Pb  
752 in the Solar System, measured in troilite from the iron meteorite Nantan (Blichert-Toft et al.,  
753 2010a) which supersedes the older Canyon Diablo values. The red star labeled SK represents  
754 “common lead” from Stacey and Kramers (1975).

755 **Figure 4.** Inverse isochron ( $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{204}\text{Pb}/^{206}\text{Pb}$ ) plot for the leaching residues of 14  
756 individual chondrules from Allende. Left-hand scale in red:  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ; right-hand scale:  
757 calculated Th/U. Green star labeled CD = Nantan initial Pb (Blichert-Toft et al., 2010a; see also  
758 caption to Fig. 3). Blue circles: measured Pb isotopic compositions. Red circles:  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$   
759 calculated by extrapolation from initial Pb. Note that the Th/U axis applies to intercepts of  
760 trends at  $^{204}\text{Pb}/^{206}\text{Pb}=0$ . The large spread in Th/U may be indicative of (1) high-temperature  
761 fractionation in the nebular gas; (2) interaction between nebular gas and chondrules at high  
762 temperatures; and/or (3) heterogeneities in the Solar Nebula. Th/U fractionation taking place  
763 within the same chondrule requires that different nucleosynthetic components must coexist on a  
764 very small scale. Inset: Correlation between the slopes and intercepts of the 14 straight-lines  
765 defined by the residue-leachate pairs (see text and Fig. 1). The coordinates of the point common  
766 to all the lines, labeled ‘Intersection’ (open star) shows where they cross. The near superposition

767 of this point on CD (green star) shows that the present Allende chondrules were not significantly  
768 contaminated by modern terrestrial Pb.

769 **Figure 5.** Leachates A and B and their residues for samples with at least 150 pg Pb showing  
770 evidence for both internal and external Th/U heterogeneities in Allende chondrules. The Th/U  
771 ratios are calculated by removing initial Pb with the composition of Nantan (the new “Canyon  
772 Diablo”) (Blichert-Toft et al., 2010a; see also caption to Fig. 3). Sample 16 with Th/U~14 is off-  
773 scale and therefore not shown. Leachates A and B correspond to leachates a and b in Tables 1  
774 and 2.

775 **Figure 6.** Lead isotope evidence of Th/U variability (right-hand scale) between samples of CAI  
776 (squares) and chondrules (circles) from the literature (Amelin et al., 2002; Connelly et al., 2012;  
777 2017), but also within individual samples.

778 **Figure 7.** Cumulated fractions of non-radiogenic Pb (purple), represented by  $^{204}\text{Pb}$ , uraniumogenic  
779  $^{206}\text{Pb}^*$  (blue, hidden) and  $^{207}\text{Pb}^*$ (tan), and thorogenic  $^{208}\text{Pb}^*$  (orange), extracted by progressive  
780 leaching and final dissolution from NWA 5697 chondrules C1 and C3 (top and middle panels)  
781 and Efremovka CAI 22E (bottom panel) (Connelly et al., 2012, 2017) as a function of the  
782 cumulated fraction of total Pb. The reagents used are summarily indicated in each figure. The  
783 curves for the two uraniumogenic Pb isotopes overlap almost perfectly, which reflects the lack of  
784 fractionation between  $^{238}\text{U}$  and  $^{235}\text{U}$ . The initial CD-type Pb component is extracted much more  
785 efficiently than uraniumogenic and thorogenic Pb, which argues for different Pb carriers. For CAI  
786 22E, thorogenic Pb is more efficiently extracted by HCl, HBr, and  $\text{HNO}_3$  than uraniumogenic Pb,  
787 which suggests that the major Th carrier is a phosphate. In each cases, HF dissolves silicates,  
788 oxides, and other refractory phases, which are the main carriers of radiogenic Pb.

789 **Figure 8.** The stability of U, UO, and UO<sub>2</sub> in the nebular gas calculated from the references  
790 provided in the text. The curves represent equivalence points (e.g.,  $P_{\text{UO}}=P_{\text{UO}_2}$ ). Thorium remains  
791 in the single ThO<sub>2</sub> form, while UO<sub>2</sub>(OH)<sub>2</sub> requires quite oxidizing conditions. Oxidation  
792 boundaries are also shown for C, Si, and H. Fields for chondrules and CAIs are from Grossman  
793 et al. (2012). Loss by dust condensation or hydrogen escape (change in total pressure) allows the  
794 gas to move across different fields.

795 **Table captions**

796 **Table 1.** Measured Pb isotope compositions of residues and leachates from single and pooled  
797 chondrules from Allende.

798 **Table 2.** Blank-corrected values and calculated parameters, including model ages and  $\kappa$ .