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 UO₂, coexisted in the nebular gas at high temperature, whereas Th existed exclusively as ThO₂; (2) chondrules*

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

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

1. Introduction

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

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

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

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

In contrast to CAIs, most chondrules have $^{238}\text{U}/^{235}\text{U}$ close to the terrestrial ratio (Connelly et al., 2017). Nevertheless, the long-standing fundamental question in U-Pb and Pb-Pb chronology of whether alignments in ^{207}Pb - ^{206}Pb - ^{204}Pb space represent true isochrons or are instead merely mixing lines is still open. Of course, any isochron can formally be considered a mixture of an initial component and a pure radiogenic component. Radiogenic ingrowth, however, preserves all alignments in isochron plots through time, and there is no feature intrinsic to the data guaranteeing that at the time the radiogenic system closes, it was isotopically homogeneous. If 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, 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 inquire whether original Pb was homogeneous or rather a mixture of genetically unrelated Pb components.

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

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

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

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

2. The power of the ^{232}Th - ^{208}Pb system

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

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

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

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

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

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

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

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 common non-radiogenic Pb component to be identified: when the samples have been substantially contaminated by terrestrial Pb, the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$ values at the intersection should be significantly different from primordial Pb (see below).

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

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

3. Material and Methods

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

The separated chondrules were processed for Pb isotopic analysis under clean laboratory conditions at the Ecole Normale Supérieure in Lyon (ENS Lyon). Because aggressive acid step leaching is known to achieve efficient separation of radiogenic and initial Pb (Frei and Kamber, 1995), after weighing each individual chondrule, or pool of multiple chondrules, into new, pre-cleaned Savillex beakers, they were leached successively in double-distilled hot 1M HBr, hot 6M HCl, and hot concentrated HNO₃, each acid a single leach for 1 hour at 120°C interspersed with

ultrasonication steps and clean ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) water rinses, then dissolved in a 3:1:0.5 mixture of double-distilled concentrated $\text{HF}:\text{HNO}_3:\text{HClO}_4$. All residue and leachate fractions were taken individually through 0.25 ml anion-exchange chromatographic columns to separate Pb (collected with double-distilled 6M HCl after elution of the sample matrix with double-distilled 1M HBr), which was analyzed for its isotopic composition by MC-ICP-MS, also at ENS Lyon. Total analytical blanks were processed in the same way as samples (see below).

Lead isotopic analyses were carried out on a Neptune Plus HR MC-ICP-MS (Thermo Scientific) using an Aridus II desolvating nebulizer system (Teledyne CETAC Technologies). Samples were dissolved in distilled 0.05M HNO_3 + 1 ppb Tl; the added Tl was used to correct the unknowns (samples and standards) for instrumental mass bias using an exponential law (Maréchal et al., 1999). Sample-standard bracketing was done by measuring, respectively, 5 ppb solutions of the Pb isotopic Standard Reference Material 981 from the National Institute of Standards and Technology (NIST) every two samples throughout the run sessions and normalizing to the values of Eisele et al. (2003) for NIST 981. The external reproducibility, estimated from repeat standard measurements of NIST 981, was better than 100-200 ppm (or 0.01-0.02%) for Pb isotope ratios based on $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and better than 50 ppm (or 0.005%) for $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, and $^{207}\text{Pb}/^{208}\text{Pb}$.

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

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

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

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

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

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

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

4. Results

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

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

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

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) is a novel observation. The range of apparent Th/U variations within individual chondrules (Fig. 5) is smaller than the range among chondrules (Fig. 4), although variations of up to 30% are significant compared with terrestrial rocks (Blichert-Toft et al., 2016; Elliott et al., 1999). Most residues of individual chondrules have apparent Th/U ranging from 3.0 to 5.2 (Figs. 4 and 5), consistent with the chondritic Th/U value of 3.9 ± 0.2 (Rocholl and Jochum, 1993) and the more recent and more precise planetary value of 3.876 ± 0.016 (Blichert-Toft et al., 2010a), but with extreme outliers at 0.65 (10R) and 14.6 (16R) (Figs. 4 and 5; sample 16R is off scale in Fig. 5). Likewise, the apparent Th/U of the six combined chondrule fractions (combined because each of the chondrules in these pooled samples was too small to be analyzed individually), de-emphasized here because of their rather unradiogenic Pb, varies between 2.9 and 5.1 (Table 2). 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 between the model Th/U and Pb-Pb ages calculated by subtracting primordial Pb from the sample, which discounts simple binary mixing.

5. Discussion

5.1 Isochrons vs mixing lines

Let us first address whether using the ^{232}Th - ^{208}Pb system helps validating isochrons vs mixing lines in the U-Pb system. First, the long-standing issue of the nature of the non-radiogenic end-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}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

U and Th have one carrier and initial Pb another. For these two samples, there is no evidence of separate carriers and the isochron claim holds. For CAI 22E, in contrast, even if initial Pb and radiogenic Pb components remain separated, there is evidence of separate carriers for U and Th. The Th carrier being much more soluble in HBr, HCl, and HNO₃, it is most likely associated with phosphate. The U carrier being preferentially liberated by HF has to be either silicates, oxides, or other titano-aluminates. Whether these minerals are genetically related is unclear.

5.2 The origin of Th/U variations

Th/U variations in chondrules and CAIs may result from a number of processes. Large isotopic heterogeneities exist both within and among different meteorite classes in general and among chondrules in particular. Early observations of clear correlations between neutron-rich isotopic anomalies (⁵⁴Cr, ⁵⁰Ti), (s/r nuclide abundances), stable nuclide abundances (Zn, Cu), and Δ¹⁷O (Dauphas et al., 2002; Luck et al., 2003; 2005; Trinquier et al., 2007; 2009; Moynier et al., 2010) led Warren (2011) to describe the Solar Nebula as a mixture of different components that were not thoroughly homogenized in the accretion disk. Most chondrules formed from dust aggregates derived from pre-solar cloud material and condensates of the nebular gas, including the carriers of these heterogeneities (e.g., Krot et al., 2009). Precursors of variable origin (refractory grains, CAI fragments, olivine, Fe metal) were variously thermally processed during chondrule melting events. Relict Mg-rich olivine crystals can be present in chondrules as shown by their ¹⁶O-enriched isotopic compositions relative to the glassy mesostasis and the main silicate phases (e.g., Weinbruch et al., 1993; Jones et al., 2004; Pack et al., 2004; Chaussidon et al., 2008; Rudraswami et al., 2011; Tenner et al., 2013; Marrocchi et al., 2019). This implies that olivine crystals did not completely evaporate or melt during chondrule formation. Precursor refractory dust (either CAI fragments or refractory condensates) would have behaved similarly. Exchanges

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

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

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

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

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

The major fraction of precursor silicate dust condensed at lower temperatures, possibly under various oxygen fugacities. This would control the U-Th speciation in the nebular gas and thus the Th/U ratio in chondrule melts at equilibrium. Variations of oxygen fugacity in the chondrule-forming region can result from transport and vaporization of H₂O ice (Cuzzi and Zahnle, 2004) and from partial evaporation of precursor silicate dust (Ebel and Grossman, 2000). Available oxygen can combine with carbon and silicon to form CO and SiO. A series of equations can be written such as

The equivalence point of the first equation, defined by $P_{\text{Si}} = P_{\text{SiO}}$, defines the oxygen partial pressure P_{O_2} as

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

where ΔG° is the change in Gibbs free energy of the first reaction. These values can be found in JANAF tables (Chase et al., 1998) and the variation of the equivalence point with temperature calculated in a T-log P_{O_2} plot as shown in Fig. 8. It is well established that, at high temperatures, uranium vapor can be oxidized as UO, UO₂, and UO₃ as P_{O_2} increases. Likewise, Th may be oxidized as ThO and ThO₂. Under strongly oxidizing conditions, U can also be hydrated as UO₂(OH)₂ (Olander, 1999; Alexander, 2005). The thermodynamic data for U, Th, and their oxides can be found in Green (1980), Cox et al. (1989), Guillaumont and Mompean (2003), and Konings et al. (2014). At low P_{O_2} , in a vapor dominated by Si, CO, and H₂, U tends to be in the UO₂ 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 H₂, and the dominant U form
410 becomes UO₃, which is believed to represent the environment of chondrules. The form
411 UO₂(OH)₂ is only stable under unrealistic values of P_{O_2} . In contrast, Th remains in its ThO₂
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 ThO₂ form, Th/U fractionation essentially reflects the
415 UO₂/(UO₂ + UO₃) 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

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

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

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

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

6. Conclusions

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

rather than mixing lines requires caution. A planetary, or “normal”, Th/U ratio is a minimum condition for proceeding further with Pb-Pb dating of any given chondrule or CAI.

Th/U variability can result from the presence of components with a different early nebular or pre-nebular history. Redox-dependent U speciation in the gas, loss of hydrogen, and/or introduction of foreign nucleosynthetic components are all possible non-exclusive explanations for the presence of large Th/U variations in chondrules and their refractory precursors. Pb-Pb ages of chondrules and CAIs may date the formation of their precursor materials rather than the formation of the chondrules and the CAIs themselves.

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Figure captions

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

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

Figure 3. Inverse isochron ($^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{204}\text{Pb}/^{206}\text{Pb}$) plots of Pb from leachates and residues for 14 single chondrules. Only fractions with >150 pg Pb after blank correction have been plotted. Solid (blue) circles: residues. Open (white) circles: leachates. The best-fit line for the 41 samples with >150 pg Pb, including leachates and residues, defines an age of 4561.2 ± 0.6 Ma (2 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 ± 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

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

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

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

Figure 7. Cumulated fractions of non-radiogenic Pb (purple), represented by ^{204}Pb , uranogenic $^{206}\text{Pb}^*$ (blue, hidden) and $^{207}\text{Pb}^*$ (tan), and thorogenic $^{208}\text{Pb}^*$ (orange), extracted by progressive leaching and final dissolution from NWA 5697 chondrules C1 and C3 (top and middle panels) and Efremovka CAI 22E (bottom panel) (Connelly et al., 2012, 2017) as a function of the cumulated fraction of total Pb. The reagents used are summarily indicated in each figure. The curves for the two uranogenic Pb isotopes overlap almost perfectly, which reflects the lack of fractionation between ^{238}U and ^{235}U . The initial CD-type Pb component is extracted much more efficiently than uranogenic and thorogenic Pb, which argues for different Pb carriers. For CAI 22E, thorogenic Pb is more efficiently extracted by HCl, HBr, and HNO_3 than uranogenic Pb, which suggests that the major Th carrier is a phosphate. In each cases, HF dissolves silicates, oxides, and other refractory phases, which are the main carriers of radiogenic Pb.

789 **Figure 8.** The stability of U, UO, and UO₂ 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 ThO₂ form, while UO₂(OH)₂ 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 κ .