U-Th-Pb systematics of individual perovskite grains from the Allende and Murchison carbonaceous chondrites

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ABSTRACT

Ion microprobe U-Th-Pb isotopic measurements have been made of individual perovskite grains from the Allende (CV3) and Murchison (CM2) chondrites. These are the first chronological data reported for Murchison refractory inclusions. Several generations of perovskite were identified in polished thin sections of "fluffy" Type A inclusions 3529,44 and 4691 from Allende of which only the largest anhedral perovskites (> 20 μm) were analysed with the ion microprobe. The Allende perovskites are characterised by low U (typically < 3 ppm, but ranging up to 12 ppm in grain 7-1 from 3529,44), and Th/U of around 4 in 3529,44 and 10 in 4691. The 238Pb concentrations in the Allende perovskites range from 6 to 140 ppb. A precise age measurement could be obtained on grain 7-1 only; the U-Pb systematics of this grain are concordant with a 207Pb/206Pb age of 4565 ± 34 (2σ) Ma. Two of the Murchison perovskites occurred as individual 20-μm inclusions in spinel grains (7-309, 7-A52), while the third perovskite-bearing inclusion was a spherule dominated by perovskite with interstitial spinel (7-396). U concentrations range from 3.6 to 15 ppm with Th/U less than 0.5, and 206Pb concentrations ranging from 61 to 369 ppb. All analyses of the Murchison perovskites are consistent with a single formation age of 4569 ± 26 Ma. The ages determined by ion microprobe from these perovskites show good agreement with previous age estimates of Allende refractory inclusions measured by conventional mass-spectrometric techniques. There is no evidence in the U-Pb systematics of Allende and Murchison refractory inclusions for material that substantially predates the formation of the solar system.

1. Introduction

The purpose of this paper is to address the possibility of finding meteoritic phases that have radiometric ages measurably older than the accepted 4.57 Ga age of the solar system. The basis for such a possibility is that the solar nebula was formed from an initially cold and heterogeneous dust cloud [1]. The collapse of this dust cloud resulted in thorough mixing of the various components and heating such that sufficient temperatures were attained to isotopically homogenise even the refractory elements to a considerable extent, but not completely. What we seek is any material which survived the homogenisation events and may still hold direct evidence of a pre-solar parentage.

The most primitive material available for study, of course, comes from the carbonaceous chondrites. In geological terms, these meteorites should be regarded as polymict breccias which have sampled a wide variety of provenances. The main interest here is in the refractory Ca-Al-rich inclusions (CAI) that are composed predominantly of minerals such as melilite, spinel, Ti-rich pyroxene (fassaite) and anorthite. These phases are predicted to be amongst the earliest condensing out of a gas of solar composition [2]. Many CAI have been found to contain isotopic signatures that are dissimilar to terrestrial and, by extension, to the rest of the solar system [3] and yield indirect evidence that this material may have a pre-solar parentage. In addition, the lanthanide elements in some refractory inclusions are fractionated according to volatility and in these inclusions the most refractory of the REE are depleted. Fegley and Kornacki [4] have interpreted this pattern as due to an inherited pre-solar component and predicted that it should have a Nd age older than the solar system. The most direct way to verify this is to
undertake analyses of phases with suitable chronometers to produce absolute age constraints on this material.

CAI from the Allende (CV3) chondrite give both the highest U-Pb ages, up to 4.575 Ga [5–9], and lowest initial $^{87}\text{Sr}/^{86}\text{Sr}$ values, 0.69877 ± 2 [10], which are consistent with their formation as early condensates in the solar nebula. However, Jessberger and Dominik [11] determined release patterns of $^{40}\text{Ar}/^{39}\text{Ar}$ and found apparent ages in excess of 5 Ga for two inclusions. Stegmann and Begemann [12] measured the K isotopic composition in one of the inclusions analysed by Jessberger and Dominik [11] and found that the elevated $^{40}\text{Ar}/^{39}\text{Ar}$ ages were not due to an enhanced abundance of $^{40}\text{K}$ relative to $^{39}\text{K}$. The interpretation of these ages remains contentious and unclear in light of the ages of CAI determined by U-Pb and Sr systematics.

Refractory inclusions from the Murchison (CM2) chondrite are smaller than those from Allende and are typically less than 500 μm in diameter. The mineralogy also differs substantially from the Allende CAIs in that the most common phases are spinel, hibonite and perovskite. Ireland [13] found that the refractory objects in Murchison were of two main types. Platy crystal fragments of hibonite commonly have large Ca and Ti isotopic anomalies with the largest effects being excesses in $^{48}\text{Ca}$ and $^{50}\text{Ti}$ of +10 and +27% with respect to the terrestrial Ca and Ti isotopic compositions [14]. This type of inclusion does not appear to have excess $^{26}\text{Mg}$ associated with the decay of $^{26}\text{Al}$ ($t_{1/2} = 0.7$ Ma). The other major type of inclusion was spinel-hibonite inclusions with abundant perovskite. These grains do not have large Ca and Ti isotopic anomalies, but do have radiogenic $^{26}\text{Mg}$ at a level of $5 \times 10^{-5} \times ^{26}\text{Al}$. The trace-element patterns of these inclusions are also noteworthy in that spinel-hibonite-perovskite grains generally show the characteristics of condensates in that the most refractory of the REE are depleted whereas the crystal fragments show depletions in the relatively volatile REE Eu and Yb [15].

The systematics of the Murchison inclusions suggest that they formed earlier than the Allende inclusions. They commonly have larger isotopic anomalies, larger chemical abundance anomalies, and have a mineral assemblage (hibonite, perovskite, spinel) that equilibrates at a higher temperature than the Allende mineral assemblage (melilite, spinel, pyroxene). However, prior to this work, no direct age determinations have been made on Murchison CAI.

A minor, but important, oxide in refractory inclusions is perovskite, CaTiO$_3$. Perovskite is an important phase because it can contain significant concentrations of U and Th as has been shown in terrestrial kimberlites where accessory perovskite has been successfully used for age determinations [16]. However, the meteoritic perovskites are small, seldom greater than 20 μm in size, so that conventional analysis of individual grains would take a great deal of effort, if at all possible. We have developed techniques with the Sensitive High mass Resolution Ion Microprobe, SHRIMP, for the analysis of U-Pb ages in perovskites. These techniques have been applied to individual perovskite grains within refractory inclusions from both the Allende and Murchison meteorites. Preliminary results of this work were presented at the ICOG meeting in Cambridge [17].

2. Experimental techniques

2.1. Samples

Polished sections of “Fluffy” Type A inclusions [18] 3529.44 and 4691 contained abundant perovskite, often greater than 20 μm diameter, suitable for analysis with the ion microprobe. These inclusions were probably never molten; all are highly altered, and have melilite, spinel and perovskite as the most abundant primary phases. Several generations of perovskite are apparent within the CAIs ranging from the largest anhedral grains in the main mass of the CAI, to smaller euhedral perovskite through the same area, and abundant euhedral crystals in the Wark-Lovering rims, that are usually not larger than 2 μm. Owing to the size of the primary beam spot of the ion microprobe (25 μm), only the largest grains were analysed (Fig. 1a).

Suitable perovskite-bearing inclusions from the Murchison meteorite were identified in grain mounts prepared from density concentrates of crushed fragments [13]. Grains 7-309, 7-A52, and 10-11 contained single large (≈ 20 μm in diameter) perovskites as inclusions in spinel (Fig. 1b). Grain 7-396 is a spherule approximately 200 μm in diameter and is composed predominantly of perovskite with interstitial spinel (Fig. 1c). It is
rimmed by an Fe phyllosilicate phase surrounded by a diopside layer. Three of the perovskite-bearing inclusions analysed here were analysed previously for their trace-element abundances [15]. They were found to have volatility-fractionated patterns with large depletions in the most refractory trace elements and were therefore similar to the spinel-hibonite inclusions which also commonly have this signature. Unfortunately perovskite of sufficient size was not available in any of the isotopically anomalous hibonite crystal fragments.

2.2. Analytical details

The procedures developed for U-Th-Pb isotopic analyses of perovskite were analogous to those used for zircon [19], with only minor differences. The mass-resolving power of the mass analyser was 6500 \( (M/\Delta M) \) and the magnet was cyclically peak stepped seven times through a sequence including the \( \text{Pb}^+ \) species, \( \text{UO}^+ \), \( \text{ThO}^+ \), \( \text{UO}_2^+ \), and \( \text{CaTi}_2\text{O}_4^+ \) to produce one set of data.

The \( \text{Pb} \) isotopic ratios were taken as the measured \( \text{Pb}^+ \) ionic ratios. There are two effects that might influence the measured ratios: mass-dependent fractionation and the presence of \( \text{Pb} \) hydrides. Mass-dependent fractionation is a difficult parameter to quantify in the \( \text{Pb} \) isotopic system owing to the large variations in the isotopic composition of \( \text{Pb} \) in terrestrial minerals. The effect of mass fractionation is to enhance the light isotopes which reduces the \( ^{207}\text{Pb}/^{206}\text{Pb} \) ratio and leads to a slight underestimate of the age. In zircon, \( \text{Pb} \) isotopic mass fractionation may be approximately \(-0.25\%/\text{amu} \) [20], but as yet we have insufficient data to constrain the magnitude of this effect in perovskite. It is likely that the magnitude of isotopic mass fractionation will be similar in perovskite and zircon since the matrix effect appears to have a second order effect compared with the mass dependence of secondary ionisation [21]. At 4560 Ma, \( \text{Pb} \) isotopic mass fractionation of \(-0.25\%/\text{amu} \) corresponds to an age reduction of less than 4 Ma and so is negligible in comparison to the uncertainties of \( ^{207}\text{Pb}/^{206}\text{Pb} \) in our ion microprobe measurements.

While all major isobaric interferences are resolved from the peaks of interest at a mass resolving power of 6500 \( (M/\Delta M) \), \( \text{Pb} \) hydrides can be resolved only at a mass resolution in excess of 30,000 \( (M/\Delta M) \). The effect of a hydride inter-
ference is to enhance the \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio leading to an overestimate of the age. However, at the extreme ages expected for the meteoritic perovskites, the \(^{206}\text{PbH}^+\) contribution to \(^{207}\text{Pb}^+\) should be negligible. The effects of mass fractionation and \(\text{Pb}\) hydrides, as well as uncertainties of the \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio are demagnified in the age equation because of the low slope of the \(\text{Pb}\) growth curve at the expected formation time of the perovskites. At 4560 Ma, a 1% error in the \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio corresponds to an error in the age of only 0.3%.

The measurement of the abundance ratio of ionic species of two elements, such as \(^{206}\text{Pb}^+/^{238}\text{U}^+\), is a function of the analytical conditions, as well as the actual elemental ratio in the sample. It is not yet known how to control this effect and analyses of the same sample on different days, under apparently identical conditions, can show different \(^{206}\text{Pb}^+/^{238}\text{U}^+\) ratios. The variations can be empirically corrected by concurrent measurement of a suitable standard. A perovskite from skarn at Tazheran, Lake Baikal area, U.S.S.R., was selected as a standard because of its unusually high uranium concentration, in excess of 1000 ppm, which facilitates a good \(\text{Pb}/\text{U}\) calibration. Two perovskite cubes from this locality were analysed by Oversby and Ringwood [22] in a study of SYNROC stability for long-term radioactive waste management. Chemical analysis showed that the samples were relatively pure \(\text{CaTiO}_3\) with only minor amounts of \(\text{Nb}, \text{Fe}^{2+}\), and \(\text{REE}\). Besides high \(\text{U}\), the perovskite cubes analysed by Oversby and Ringwood had approximately 10 ppm common \(\text{Pb}\). This is a feature of perovskite in that it can accommodate significant amounts of \(\text{Pb}\) into its structure especially in comparison to zircon. However, the two samples were still highly radiogenic and had \(^{206}\text{Pb}/^{204}\text{Pb}\) ratios of approximately 500 and \(^{206}\text{Pb}/^{238}\text{U}\) ages of 464 ± 2 Ma and 461 ± 3 Ma. Since the samples are relatively young there is a large initial \(\text{Pb}\) correction resulting in large uncertainties in the \(^{205}\text{Pb}/^{206}\text{Pb}\) ages (509 ± 69 and 508 ± 46 Ma, respectively); the \(^{206}\text{Pb}/^{238}\text{U}\) and \(^{207}\text{Pb}/^{206}\text{Pb}\) ages are concordant within their 2\(\sigma\) error limits.

The ion microprobe measurements of the Baikal perovskite had \(^{204}\text{Pb}/^{206}\text{Pb}\) within a range of 0.0010 to 0.0025 (\(^{206}\text{Pb}/^{204}\text{Pb}\) of 250 to 1000) which is consistent with the average values of Oversby and Ringwood [22]. The dispersion in the \(\text{Pb}\) isotopic compositions resulting from the variable ratio of common to radiogenic \(\text{Pb}\) indicated that the Baikal perovskite standard contained a rather “old” initial \(\text{Pb}\), with \(^{206}\text{Pb}/^{206}\text{Pb}\) of 0.0622, \(^{207}\text{Pb}/^{206}\text{Pb}\) of 0.935, and \(^{208}\text{Pb}/^{206}\text{Pb}\) of 2.206. The initial \(\text{Pb}\) in the Baikal standard corresponds to 1.76 to 4.48% of the total \(^{206}\text{Pb}\). The average \(^{207}\text{Pb}/^{206}\text{Pb}\) age, following correction for initial lead, was 514 ± 54 Ma, again in good agreement with the conventional analyses. However, the consistent measurement of the \(^{207}\text{Pb}/^{206}\text{Pb}\) age might indicate that the Baikal perovskite has suffered recent lead loss as suggested by Oversby and Ringwood [22]. If the Baikal perovskite is 500 Ma rather than \(\approx 460\) Ma as indicated by the conventional \(^{206}\text{Pb}/^{238}\text{U}\) measurements, then normalisation to the Baikal standard will result in an overestimate of the \(^{206}\text{Pb}/^{238}\text{U}\) in the meteoritic perovskites by approximately 9%.

Hinthorne et al. [23] first used \(\text{UO}^+ / \text{U}^+\) to calculate the \(\text{Pb}/\text{U}\) in zircons using an expression derived from their theory of the sputtering process. Compston et al. [19] developed an empirical treatment based on this relationship for the measurement of \(\text{Pb}/\text{U}\) in zircons with SHRIMP. We attempted to use the same basic procedure for the perovskites, but found that the \(\text{U}^+\) intensity from perovskite was too low for satisfactory precision. However, in perovskite the \(\text{UO}_2^+\) intensity was found to be higher than the \(\text{UO}^+\), and the same type of correlation was observed between \(^{206}\text{Pb}^+ / \text{UO}^+\) and \(^{206}\text{Pb}^+ / \text{UO}_2^+\) for perovskite as between \(^{206}\text{Pb}^+ / \text{U}^+\) and \(^{206}\text{Pb}^+ / \text{UO}_2^+\) in zircon analyses. The relationship is illustrated in Fig. 2, with data obtained from the standard Baikal perovskite over a period of some 18 months. The analyses fall into two groups. The first set of analyses (solid symbols) define a working curve which is adequately described by a quadratic function. The fact that a smooth relationship is observed, with scatter no more than about 2.0%, as for the standard zircon, suggests that the Baikal perovskite has a uniform \(^{206}\text{Pb}^+ / \text{U}\) and is therefore concordant in its \(\text{U-Pb}\) ages. The second group of analyses define a parallel trend (open symbols; analyses 12A-19). These data were collected over a 2-week period with exactly the same analytical conditions as for the first group. It is this type of difference in the measured ratios under identical analytical condi-
tions that the working curve calibration is designed to monitor.

The relationship illustrated in Fig. 2 is used to determine the (unknown) $^{206}\text{Pb}^{+}/^{238}\text{U}^{+}$ in the meteoritic perovskites in terms of the known ratio in the Baikal perovskite. Following the zircon treatment, the only assumption used in the ion microprobe procedures is simply that:

$$\frac{y_u}{y_{st}} = \frac{Y_u}{Y_{st}}$$

where $y$ denotes the $^{206}\text{Pb}^{+}/^{238}\text{U}^{+}$ for the unknown (u) and standard (st) perovskites at the same value of $^{238}\text{U}^{+}$ in the two perovskites.

The measured $^{232}\text{Th}^{+}/^{238}\text{U}^{+}$ ratios are linearly proportional to $^{208}\text{Pb}^{*}/^{206}\text{Pb}^{*}$, and hence to $^{232}\text{Th}^{+}/^{238}\text{U}^{+}$ in a closed system, by the relationship:

$$\frac{^{208}\text{Pb}^{*}}{^{206}\text{Pb}^{*}} = \frac{^{232}\text{Th}(e^{\lambda_2t} - 1)}{^{238}\text{U}(e^{\lambda_8t} - 1)}$$

where $\lambda_2$ and $\lambda_8$ denote the decay constants for $^{232}\text{Th}$ and $^{238}\text{U}$, respectively, and $t$ is the age. The discrimination is taken to be constant here with:

$$\text{Th}/\text{U} = 1.02 \frac{^{232}\text{Th}^{+}}{^{238}\text{U}^{+}}$$

and is a satisfactory approximation owing to the large initial Pb concentrations in the meteoritic perovskites. Analyses of the Baikal standard and a range of other terrestrial perovskites have indicated that the discrimination between the measured $^{232}\text{Th}^{+}/^{238}\text{U}^{+}$ and $^{232}\text{Th}^{+}/^{238}\text{U}^{+}$ in the target does vary slightly with $^{238}\text{U}^{+}$.

Approximate values for U concentration have been calculated using an empirical relationship between $\text{CaTi}_2\text{O}_4^{+}/\text{UO}^{+}$ and $\text{UO}_2^{+}/\text{UO}^{+}$ in a similar fashion to the Pb/U calibration (Fig. 3). The U concentration of the unknown is expressed in terms of the U concentration of the Baikal perovskite which is 1050 ppm [24]; the Th concentration then follows from equation (3) for the measured $\text{ThO}^{+}/\text{UO}^{+}$. The $^{204}\text{Pb}$ concentration, expressed in ppb, was also determined from the Pb/U working curve calibration.

Data from the meteoritic perovskites were corrected for initial Pb with the Canyon Diablo troilite Pb isotopic composition and the measured $^{204}\text{Pb}/^{206}\text{Pb}$ to obtain radiogenic Pb isotope ratios for concordia plots.

3. Results and discussion

3.1. Allende perovskites

A number of perovskite grains were analysed from Allende 3529,44 and 4691 but were generally characterised by very low U concentrations (less than 3 ppm) and were not fully analysed. Only one grain, 7-1 from 3529,44, had significantly higher U at 12 ppm. Th/U ratios were 2.6–3.8 in 3529,44 and 7–10 in perovskites from 4691. Initial Pb in these perovskites was less than 140 ppb. All
of the perovskites analysed had $^{207}\text{Pb}/^{206}\text{Pb}$ ages consistent with a formation age of 4.5–4.6 Ga within large uncertainties. A precise age determination could only be made for grain 7-1 from 3529,44 (Table 1) which had high U as well as very low initial Pb. The initial $^{206}\text{Pb}$ in the two analyses is approximately 0.7% of the total lead. The concordia plot for the two analyses of this perovskite are concordant within measurement uncertainties and the mean $^{207}\text{Pb}/^{206}\text{Pb}$ age was $4565 \pm 34$ Ma ($2\sigma_m$) (Fig. 4).

### 3.2. Murchison perovskites

The possibility of a non-terrestrial U isotopic composition in Murchison perovskite was addressed by U isotopic analysis of the perovskite inclusion in grain 10-11. The Baikal standard gave a value for $^{238}\text{U}/^{235}\text{U}$ of 133 $\pm$ 6 ($2\sigma_m$) as compared to the terrestrial value of 137.88. The value obtained for perovskite 10-11 was 127 $\pm$ 11 ($2\sigma_m$) and has lower precision owing to the lower U content of the meteoritic perovskite. Both analyses lie within their $2\sigma$ error bounds of the normal composition although both appear to be marginally lower than the terrestrial value. This may be related to mass-dependent fractionation within the ion microprobe which enhances the lighter isotopes. The fractionation measured in the Baikal standard corresponds to a mass fractionation of $-12 \pm 13%$/amu, whereas the meteoritic perovskite has a fractionation of $-26 \pm 26%$/amu. However, since there was no evidence of a non-terrestrial U isotopic composition, the terrestrial $^{238}\text{U}/^{235}\text{U}$ ratio of 137.88 was used. The perovskite in grain 10-11 was essentially exhausted after the U isotopic analysis and a U-Th-Pb analysis was not undertaken.

U-Th-Pb analyses of three Murchison perovskite-bearing inclusions are listed in Table 1. The two perovskite inclusions in spinel, 7-309 and 7-A52, gave very similar results. Only one data set was collected from each perovskite because of their small size. Uranium is around 5 ppm with low Th, less than 1 ppm, and Th/U is less than 0.1. Initial Pb was 127 and 168 ppb $^{204}\text{Pb}$ for 7-A52 and 7-309, respectively, and corresponds to

### Table 1

<table>
<thead>
<tr>
<th>Grain, area</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>$^{204}\text{Pb}$ (ppb)</th>
<th>Th/U</th>
<th>$^{238}\text{U}$</th>
<th>$^{207}\text{Pb}$</th>
<th>$^{204}\text{Pb}$</th>
<th>$^{206}\text{Pb}$</th>
<th>$^{206}\text{Pb}$*</th>
<th>$^{207}\text{Pb}$*</th>
<th>$^{207}\text{Pb}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murchison grain mount No. 7</td>
<td>396, 1-1</td>
<td>10</td>
<td>3.3</td>
<td>100</td>
<td>0.32 $\pm$ 2</td>
<td>0.872 $\pm$ 30</td>
<td>0.691 $\pm$ 11</td>
<td>0.0098 $\pm$ 9</td>
<td>0.397 $\pm$ 7</td>
<td>1.042 $\pm$ 38</td>
<td>93.2 $\pm$ 4.1</td>
</tr>
<tr>
<td>396, 1-2</td>
<td>15</td>
<td>3.8</td>
<td>61</td>
<td>0.26 $\pm$ 2</td>
<td>1.169 $\pm$ 27</td>
<td>0.675 $\pm$ 13</td>
<td>0.0056 $\pm$ 8</td>
<td>0.328 $\pm$ 8</td>
<td>0.810 $\pm$ 27</td>
<td>72.8 $\pm$ 3.0</td>
<td>0.651 $\pm$ 14</td>
</tr>
<tr>
<td>396, 2-1</td>
<td>5.8</td>
<td>2.5</td>
<td>86</td>
<td>0.43 $\pm$ 2</td>
<td>0.822 $\pm$ 36</td>
<td>0.676 $\pm$ 14</td>
<td>0.0143 $\pm$ 15</td>
<td>0.567 $\pm$ 12</td>
<td>1.054 $\pm$ 49</td>
<td>88.6 $\pm$ 5.2</td>
<td>0.609 $\pm$ 18</td>
</tr>
<tr>
<td>396, 3-1</td>
<td>12</td>
<td>5.1</td>
<td>269</td>
<td>0.41 $\pm$ 2</td>
<td>0.690 $\pm$ 22</td>
<td>0.725 $\pm$ 8</td>
<td>0.0241 $\pm$ 11</td>
<td>0.862 $\pm$ 10</td>
<td>1.125 $\pm$ 38</td>
<td>95.3 $\pm$ 4.0</td>
<td>0.615 $\pm$ 13</td>
</tr>
<tr>
<td>396, 3-2</td>
<td>12</td>
<td>3.5</td>
<td>88</td>
<td>0.30 $\pm$ 2</td>
<td>0.930 $\pm$ 29</td>
<td>0.653 $\pm$ 9</td>
<td>0.0083 $\pm$ 77</td>
<td>0.324 $\pm$ 6</td>
<td>0.992 $\pm$ 31</td>
<td>84.1 $\pm$ 3.2</td>
<td>0.615 $\pm$ 11</td>
</tr>
<tr>
<td>A52, 1-1</td>
<td>3.6</td>
<td>0.2</td>
<td>127</td>
<td>0.06 $\pm$ 1</td>
<td>0.721 $\pm$ 43</td>
<td>0.736 $\pm$ 19</td>
<td>0.0294 $\pm$ 25</td>
<td>0.632 $\pm$ 17</td>
<td>1.008 $\pm$ 69</td>
<td>83.0 $\pm$ 7.6</td>
<td>0.597 $\pm$ 32</td>
</tr>
<tr>
<td>309, 1-1</td>
<td>5.5</td>
<td>0.5</td>
<td>168</td>
<td>0.09 $\pm$ 1</td>
<td>0.624 $\pm$ 39</td>
<td>0.720 $\pm$ 18</td>
<td>0.0224 $\pm$ 23</td>
<td>0.748 $\pm$ 18</td>
<td>1.268 $\pm$ 87</td>
<td>108.1 $\pm$ 9.2</td>
<td>0.618 $\pm$ 26</td>
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</tbody>
</table>

Uncertainties refer to last digits of datum and are $\pm 1\sigma$. Errors in concentration measurements by ion microprobe are approximately $\pm 10%$ for U, Th and $\pm 20%$ for $^{204}\text{Pb}$. Pb isotopic ratios with subscript m refer to measured ratios whereas those with superscript * have been corrected for common lead from the $^{204}\text{Pb}/^{206}\text{Pb}$ assuming a common lead composition of Canyon Diablo troilite [5].

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Fig. 4. Concordia plot of U-Pb data for perovskite grain 7-1 from Allende CAI 3529,44.
20.8% and 27.4% of the total $^{206}$Pb being present as initial Pb. Grain 7-396 was analysed in three different locations for a total of five sets. It has somewhat higher U and Th concentrations, ranging from 6 to 15 and 2 to 5 ppm respectively, and has a low Th/U around 0.4. Initial Pb is variable and ranges from 60 to 369 ppb $^{204}$Pb and corresponds to a range of 5.2 to 22.4% of the total $^{206}$Pb being present as initial Pb.

A concordia plot of the Murchison perovskite data is shown in Fig. 5. Four of the analyses are concordant within the 1σ uncertainties of the measurements, one is discordant (indicating Pb loss), while two are apparently reversely discordant (indicating U loss or Pb gain). Normal discordancy is a common feature in zircons and is attributed to Pb loss during a thermal episode where Pb is excluded from the structure. Reverse discordancy is an uncommon phenomenon. It has been described from zircons where it is apparently due to Pb redistribution during metamorphism resulting in localised enrichments of radiogenic Pb [25]. However, it should be noted that the reverse discordancy of the two meteoritic perovskite samples is rather marginal with both analyses lying within 3σ of concordia. An added margin of error could be included with the meteoritic perovskite analyses because of some uncertainty in the Pb/U calibration. Firstly, the concordancy of the Baikal standard has not been proven to a high degree and the Pb/U could be underestimated by up to 9% thereby moving the Pb/U of the meteoritic perovskites down by the same factor. Secondly, the $\text{UO}_2$/U values for the meteoritic perovskites were consistently less than 1.5 whereas only one of the Baikal perovskite standards was within this range. The reason for the difference in the ranges of $\text{UO}_2$/UO for the two perovskite types is not clear but may be related to differences in the intrinsic oxygen fugacity of the perovskites, or the presence of spinel in the sputtered areas from the meteoritic perovskites. A more definitive assessment of the Baikal standard will be made after more extensive analyses in conjunction with geochemistry of other terrestrial perovskites.

Apart from a degree of uncertainty in the Pb/U, all of the Murchison perovskites have the same $^{207}$Pb/$^{206}$Pb within error which is consistent with a single formation age of $4569 \pm 26 \text{ Ma (2σ m, } \chi^2 = 1.66)$. The Murchison perovskite data have also been evaluated by applying the three-dimensional discordia-plane method described by Wendt [26,27] which does not require knowledge of the initial lead present in the samples. However, the dispersion of the highly radiogenic perovskites was limited and so a common Pb isotopic composition of Murchison was used to better constrain the formation age. The data fit very well to a discordia plane (MSWD of 0.88) indicating a primary formation age of $4576 \pm 30 \text{ Ma with a poorly constrained secondary age within error of zero at } -1190 \pm 1700 \text{ Ma}$.

### 3.3. Synthesis

Murchison refractory inclusions commonly have larger isotopic anomalies, larger elemental abundance anomalies, and have mineral assemblages that equilibrate at higher temperatures than those in Allende inclusions. However we can resolve no differences in the formation times of these two different types of CAI. The age of perovskites from both Allende and Murchison refractory inclusions, as determined by the ion microprobe analyses, is consistent with a formation age of 4.57 Ga which is identical to that determined by conventional analyses of bulk Allende inclusions [5–9].

Terrestrial contamination has been a concern in the interpretation of conventional data because bulk samples generally have excess radiogenic lead that is not supported by the intrinsic U (see for example [7]). The two sources of terrestrial lead contamination most often considered are lead introduced during the analytical procedures and that introduced in the terrestrial environment prior to
meteorite recovery. Neither of these two processes can effect the perovskites we have analysed. Contamination of the samples during analytical procedures is not possible with ion microprobe techniques because sputtering removes any surface contamination prior to measurement. Similarly, any lead introduced in the terrestrial environment would only be a surface phenomenon and the perovskites we have analysed are essentially protected by the surrounding CAI material.

Fegley and Kornacki [4] have proposed that the Group II REE abundance pattern was an inherited component and would have a Sm-Nd age older than the canonical age of the solar system. Of the inclusions studied here, Allende 4691 and all three Murchison inclusions have REE patterns that are depleted in an ultrarefractory component of the REE [15,28], whereas 3529,44 has a Group VI REE pattern characterised by excesses of the relatively volatile REE Eu and Yb. There is no evidence in the perovskites with Group II-type patterns for any component with an age older than the Group VI perovskites, or any ages older than 4.57 Ga, as recorded in their U-Pb systematics.

However, this does not preclude the incorporation of older components into CAIs. At the temperatures necessary for the formation of CAIs, the U-Pb system would be completely reset since Pb is a highly volatile element. In order to determine whether the CAIs have components that predate the solar system, it will be necessary to determine radiogenic ages from a refractory parent-daughter system such as Nd-Sm as explicitly proposed by Fegley and Kornacki [4]. Papanastassiou et al. [29] have reported Sm-Nd data which suggest that this might be the case in that two inclusions they measured yielded isochrons with slopes corresponding to 4.8 Ga. However, they could not rule out the possibility of open-system behaviour as having caused the apparently old ages and proposed further work to verify the data.

The Group II pattern must form as a condensate since any residue will retain the ultrarefractory REE. However, the presence of condensate material in the CAIs does not necessarily require the formation of CAIs as condensates. The preservation of isotopic heterogeneities in refractory elements such as Ca and Ti, in volatile elements such as H and the noble gases, and in O which is present in both gas and solid phases, preclude total homogenisation of the solar nebula [30]. The distinctive isotopic compositions of small inclusions such as the hibonite crystal fragments require the preservation of isotopic heterogeneity on a very small scale and this appears to be compatible only with models involving partial evaporation of less refractory aggregates.

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