The 176Lu–176Hf systematics of ALM-A: A sample of the recent Almahata Sitta meteorite fall

R. Bast*, E.E. Scherer¹, A. Bischoff²

Abstract

The application of Lu-Hf chronometry to meteorites has been compromised by arbitrary results such as dates up to 300 Myr older than the Pb-Pb age of the Solar System, unsubstantiated isochron scatter among different meteorite fractions, and varying initial Hf isotope ratios (176Hf/177Hf). To determine the cause of the discrepancies and presence of unsupported radiogenic 176Hf, we collected Lu-Hf data for the ureilic trachyandesite ALM-A, a fragment of the recent Almahata Sitta meteorite fall. The purest feldspar and pyroxene fractions and all 2 M HNO₃ washes (i.e. selectively dissolved phosphate minerals) yield a 13-point isochron with a reasonable age of 4569 ± 24 Ma and 176Hf/177Hf of 0.279796 ± 0.000011. Most impure mineral fractions, in contrast, scatter above this regression. Terrestrial contamination causes the 176Hf excesses, but is effectively removed by handpicking the purest mineral grains. Our study demonstrates 1) the successful application of the Lu-Hf chronometer to ALM-A, and 2) an internal consistency among the Pb-Pb age of the Solar System, the 176Lu decay constant, the Lu-Hf CHUR parameters, and robust estimates of the 176Hf/177Hf of the Solar System from meteorites.

Introduction

Early Solar System chronology is largely based on short-lived, currently extinct radioisotopes that only provide relative ages. Anchoring these ages to the absolute timescale requires long-lived chronometers that are accurate and precise. With the exception of Pb-Pb, such chronometers are based on the measured proportion of a radioactive parent isotope (P) to its decay product (daughter, D).

Samples and Methods

Almahata Sitta fell onto the Nubian Desert in Sudan on October 7th, 2008 (Jenniskens et al., 2009). Among polymict ureilite and chondritic fragments (Bischoff et al., 2010; Horstmann and Bischoff, 2014), the trachyandesitic sample ALM-A was found as a fresh 24.2 g piece on October 7th, 2008. It consists mostly of feldspar (anorthoclase and plagioclase), low-Ca pyroxene, and Cr-bearing Ca pyroxene with numerous inclusions of alkali-rich melt glass, feldspar, Ti-Fe oxides, ilmenite, and metal. Accessory phases include apatite, merrillite, ilmenite, Ti-Cr-Fe-spinel, ilmenite, and Fe-metal. All minerals appear unaltered in thin section.

ALM-A is a unique sample of the differentiated crust of the ureilite parent body (Bischoff et al., 2014). Its Pb-Pb age of 4562.0 ± 3.4 Ma (Amelin et al., 2015) is consistent with its Al-Mg model age of 6.5 ±0.5/–0.3 Myr after Ca-Al-rich inclusions (Bischoff et al., 2014), suggesting that ALM-A has not been disturbed by heating or shock after ~4.56 Ga. It is therefore ideal for investigating the cause of spurious Lu-Hf isochrons in meteorites.

A 2 g piece of ALM-A devoid of fusion crust was crushed in an agate mortar and sieved to <63, 63–125, and 125–250 µm fractions. Mineral concentrates were prepared using standard magnetic separation and heavy liquid techniques (see Supplementary Information for more details). Pure, mono-mineralic grains were handpicked under a binocular microscope, but impure separates dominated by one of the major minerals were also analysed (Fig. 1). When enough material was available, fractions were split, washing one aliquot with 2 M HNO₃ for 30 minutes, while leaving the other aliquot unwashed. The wash solutions were carefully pipetted off and analysed separately. The analytical procedure follows that of Bast et al. (2015) and is detailed in the Supplementary Information.

Thus in addition to high-temperature (diffusional) isotopic re-equilibration, these systems may also be disturbed by recent changes in P/D, which can occur even during low-temperature processes such as alteration and weathering.

The long-lived 176Lu-176Hf chronometer benefits from a large range in P/D among different minerals and a high closure temperature in silicates (e.g., Scherer et al., 2000) and apatite (Barford et al., 2003); therefore, it is potentially precise and robust against post-crystallisation heating and shock. Unsupported 176Hf has been observed in many meteorites however, resulting in Lu-Hf dates that are up to 300 Myr older than the Pb-Pb age of the Solar System (e.g., Blichert-Toft et al., 2002; Bizzarro et al., 2012). The origin of this component is vigorously debated, with hypotheses including high-energy irradiation (Albarede et al., 2006; Thran et al., 2010) and diffusive re-equilibration on the meteorite parent body (Debaille et al., 2011, 2013, 2014; Bloch et al., 2016). However, our investigation of a sample of the recent Almahata Sitta meteorite fall precludes these mechanisms. Instead, we propose that the observed discrepancies may in general arise from terrestrial contamination, terrestrial weathering, or both.

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Isochron regressions (Table 1) are calculated using Isoplot/Ex v3.76 (Ludwig, 2003) and the $^{176}\text{Lu}$ decay constant $\lambda = 1.867 \times 10^{-11}$ yr$^{-1}$ (Scherer et al., 2001; 2003; Söderlund et al., 2004).

Table 1  Regressions for various fractions of ALM-A.

<table>
<thead>
<tr>
<th>Fractions</th>
<th>n</th>
<th>Date (Ma)</th>
<th>$^{176}\text{Hf}/^{177}\text{Hf}_{i}$</th>
<th>MSWD</th>
<th>Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>All bulk &amp; mineral fractions</td>
<td>20</td>
<td>4604 ± 84</td>
<td>0.279801 (39)</td>
<td>45</td>
<td>2</td>
</tr>
<tr>
<td>Washed residues, excl. fine</td>
<td>10</td>
<td>4578 ± 66</td>
<td>0.279807 (29)</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>Unwashed grains, excl. WR &amp; fine</td>
<td>7</td>
<td>4659 ± 23</td>
<td>0.279765 (11)</td>
<td>2.1</td>
<td>2</td>
</tr>
<tr>
<td>All washes &amp; purest mineral grains</td>
<td>13</td>
<td>4569 ± 24</td>
<td>0.279764 (11)</td>
<td>1.3</td>
<td>3</td>
</tr>
<tr>
<td>Purest mineral grains only</td>
<td>3</td>
<td>4571 ± 29</td>
<td>0.279796 (14)</td>
<td>0.012</td>
<td>3</td>
</tr>
</tbody>
</table>

The numbers in parentheses after $^{176}\text{Hf}/^{177}\text{Hf}_{i}$ indicate the uncertainties in the least significant digits.
HF contents (0.1-0.9 ng) of the washes, the isochron points have relatively large uncertainties (see Supplementary Information), but they are not systematically offset from the Solar System reference. A regression of the purest, handpicked mineral grains and all washes yields a 13-point isochron (MSWD = 1.3) with an age of 4569 ± 24 Ma and $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.279796 ± 0.000011 (Fig. 3).

Discussion

A reasonable Lu-Hf age that is concordant with the Pb-Pb age of the sample is obtained for the purest major mineral fractions and the 2 M HNO$_3$ washes, which are interpreted to represent selectively digested phosphate minerals. Thus, the $^{176}\text{Lu}/^{177}\text{Hf}$ systematics of ALM-A have not been disturbed after initial closure with respect to feldspars, pyroxenes, and phosphate minerals. Because irradiation, resetting during parent body brecciation, or terrestrial alteration would have disturbed those minerals, such processes can be ruled out for ALM-A. Nevertheless, most of the bulk and impure mineral fractions scatter above the Solar System reference (Fig. 2) – a feature that has previously been observed in other achondrite samples (e.g., Blichert-Toft et al., 2002; Bouvier et al., 2015; Sanborn et al., 2015).

On the basis of our ALM-A Lu-Hf data, we infer that terrestrial contamination is the source of the excess radiogenic Hf that affects the most impure separates, especially the fine fraction. (See Supplementary Information for more details on the terrestrial contaminant.) This terrestrial component is not effectively removed by washing in 2 M HNO$_3$ (Table S-1), as indicated by the scatter among the washed residues of the impure fractions (i.e. pyroxene and feldspar concentrates, impure picking dregs, both composites, and the fine fraction, Table 1). This is consistent with the isotope compositions of the washes, which reflect meteoritic phosphate minerals that were selectively dissolved from all fractions. These observations suggest that the terrestrial contaminant comprises fine-grained silicate material that, while insoluble in 2 M HNO$_3$ does dissolve during the HF–HNO$_3$ digestion. The contaminant was not identified optically. We assume that only small amounts of terrestrial material are present in cracks and density separations and the handpicking may help eliminate grain surface contamination. Washing minerals in 2 M HNO$_3$, without removing silicate-hosted contamination. The comparison of handpicked,
impure, and bulk fractions reveals the importance of a thorough mineral purifica-
tion, and we suggest the use of the most coarse-grained, mono-mineralic frac-
tions available when applying the Lu-Hf chronometer to meteorites.

**Conclusion**

Despite its short terrestrial residence and lack of visible alteration, ALM-A bears evidence – in the form of unsupported $^{176}\text{Hf}$ – of terrestrial contamination. Meteorites having longer residence times (i.e. finds and some falls) may be affected in a similar manner, but with the added complication of aqueous alteration. The latter could potentially redistribute parent and daughter isotopes among mete-
oritic and terrestrial minerals, not only disturbing isochrons but also rendering
the contamination difficult to remove. Contaminated mineral and bulk frac-
tions can define overly steep trends, potentially without obvious geologic scatter
if some data are excluded from the regression. The possibility of such effects
should be carefully evaluated before invoking such exotic mechanisms as early Solar System irradiation to explain spuriously old Lu-Hf dates. For ALM-A, the contamination was effectively removed by our elaborate mineral separation
procedure based on grain size, magnetic properties, density, and, importantly,
handpicking to optically identify and exclude impurities. The purest mineral frac-
tions and all washes provide a crystallisation age for ALM-A of 4569 ± 24 Ma. The $^{176}\text{Hf}/^{177}\text{Hf}$ of the ALM-A isochron, 0.279796 ± 0.000011, is identical to 1) the value of 0.279794 ± 0.000011 derived from the average composition of unequi-
librated chondrites (Bouvier et al., 2008) calculated to the start of the Solar System using $^{176}\text{Lu}$ = 1.967 ×10$^{-11}$ yr$^{-1}$ and 2) the value of 0.279781 ± 0.000018 measured in eucrite zircon by Izuka et al. (2015). These estimates are all clearly higher than that of the Sahara 995555 regression (0.279685 ± 0.000019; Bizzarro et al., 2012). Although some eucrite whole rock regressions yield $^{176}\text{Hf}/^{177}\text{Hf}$ similar to our ALM-A value (e.g. 0.279751 ± 0.000030 to 0.279777 ± 0.000008; Bouvier et al., 2015), they generally exhibit elevated slopes and less precise $^{176}\text{Hf}/^{177}\text{Hf}$ values whose meaning remains unclear because of unexplained excess scatter (MSWD = 4.5–11; e.g. Blichert-Toft et al., 2002; Bouvier et al., 2015). We therefore agree with the assessment of Bouvier et al. (2015) that existing eucrite isochron data cannot be used to precisely constrain the Lu-Hf parameters of the Solar System or Earth. Nevertheless, the consistency among three kinds of independent $^{176}\text{Hf}/^{177}\text{Hf}$ estimates (i.e. our ALM-A isochron, average bulk chondrite compositions, and low-1D mineral compositions) for samples from different parent bodies provides evidence for the isotopic homogeneity of Hf at the beginning of the Solar System and suggests that the chondritic $^{176}\text{Hf}/^{177}\text{Hf}$ also applies to Earth. This, in turn, constitutes a vital reference for Hf isotope studies of Earth’s early crust-mantle evolution.

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**Additional Information**

Supplementary Information accompanies this letter at http://www.
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**References**


