Geochemical Perspectives Letters

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

R. Bast[1]*, E.E. Scherer[1], A. Bischoff[2]

OPEN ACCESS

doi: 10.7185/geochemlet.1705

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 (^{176}Hf/^{177}Hf$_i$). To determine the cause of the discrepancies and presence of unsupported radiogenic ^{176}Hf, we collected Lu-Hf data for the ureilitic trachyandesite ALM-A, a fragment of the recent Almahata Sitta meteorite fall. The purest feldspar and pyroxene fractions and all 2 M HNO_3 washes (*i.e.* selectively dissolved phosphate minerals) yield a 13-point isochron with a reasonable age of 4569 ± 24 Ma and ^{176}Hf/^{177}Hf$_i$ of 0.279796 ± 0.000011. Most *impure* mineral fractions, in contrast, scatter above this regression. Terrestrial contamination causes the ^{176}Hf 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 ^{176}Lu decay constant, the Lu-Hf CHUR parameters, and robust estimates of the ^{176}Hf/^{177}Hf$_i$ of the Solar System from meteorites.

Received 1 June 2016 | Accepted 2 September 2016 | Published 16 September 2016

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).

1. Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, Corrensstr. 24, 48149 Münster, Germany
* Corresponding author (email: Rebecca.Bast@uni-muenster.de)
2. Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

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 ^{176}Lu-^{176}Hf 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 (Barfod *et al.,* 2003); therefore, it is potentially precise and robust against post-crystallisation heating and shock. Unsupported ^{176}Hf 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 (Albarède *et al.,* 2006; Thrane *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.

Samples and Methods

Almahata Sitta fell onto the Nubian Desert in Sudan on October 7th, 2008 (Jenniskens *et al.,* 2009). Among polymict ureilitic and chrondritic 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 5th, 2009. 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, troilite, and metal. Accessory phases include apatite, merrillite, ilmenite, Ti,Cr,Fe-spinel, troilite, 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 HNO_3 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.

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

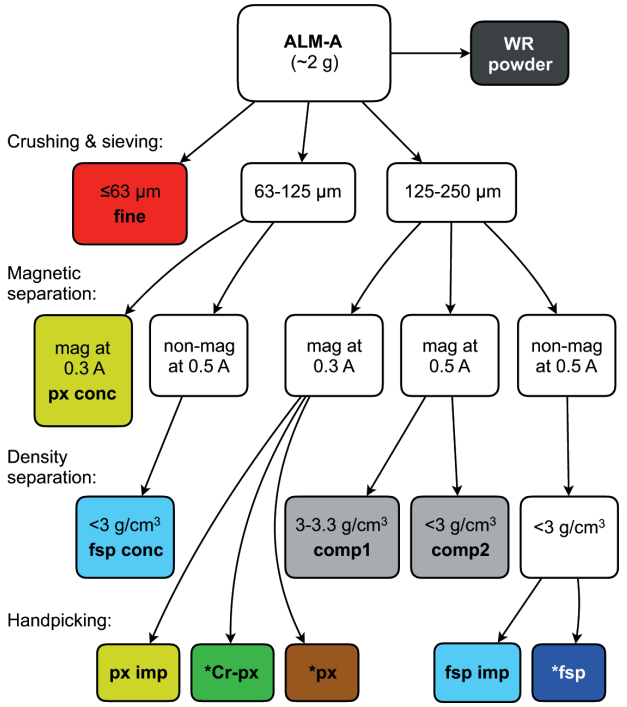

Figure 1 Mineral separation scheme. All fractions with coloured labels were analysed. Abbreviations: WR: whole-rock, fine: fine fraction, mag: magnetic, non-mag: non-magnetic, px: pyroxene, fsp: feldspar, conc: concentrate, comp: composite of mostly pyroxene and feldspar, imp: impure picking dregs, * pure: mono-mineralic fractions.

Table 1 Regressions for various fractions of ALM-A.

Fractions	n	Date (Ma)	^{176}Hf/^{177}Hf$_i$	MSWD	Fig.
All bulk & mineral fractions	20	4604 ± 84	0.279801 (39)	45	2
Washed residues, excl. fine	10	4578 ± 66	0.279807 (29)	15	2
Unwashed grains, excl. WR & fine	7	4659 ± 23	0.279765 (11)	2.1	2
All washes & purest mineral grains	13	4569 ± 24	0.279796 (11)	1.3	3
Purest mineral grains only	3	4571 ± 29	0.279796 (14)	0.012	3

The numbers in parentheses after ^{176}Hf/^{177}Hf$_i$ indicate the uncertainties in the least significant digits.

Results

The Lu-Hf data for all bulk and mineral fractions are given in Table S-1 and shown in Figure 2 together with a reference isochron that is based on the ^{176}Lu-^{176}Hf parameters of the chondritic uniform reservoir (CHUR, Bouvier *et al.*, 2008) and the maximum age of the Solar System (4568 Ma, *e.g.*, Bouvier *et al.*, 2011). About 2/3 of the data plot above this reference, with the WR and fine fractions deviating the most. Regressing all 20 points yields an errorchron with an MSWD of 45 (Table 1) indicating excessive scatter (Wendt and Carl, 1991). The 10 washed mineral fractions (residues, filled symbols in Fig. 2) also yield an errorchron (4578 ± 66 Ma, MSWD = 15; Table 1). However, the unwashed, impure mineral separates (open circles in Fig. 2) define a low-scatter trend (MSWD = 2.1, n = 7; Table 1) with a slope of 0.09088, which corresponds to a date of 4659 ± 23 Ma and a ^{176}Hf/^{177}Hf$_i$ of 0.279765 ± 0.000011.

Washed residues generally have lower ^{176}Lu/^{177}Hf than their unwashed counterparts (Fig. 2), and the washes have complementary high ^{176}Lu/^{177}Hf (0.31–0.67), and radiogenic ^{176}Hf/^{177}Hf (Fig. 3). Owing to the low Lu- (0.6-1.9 ng) and

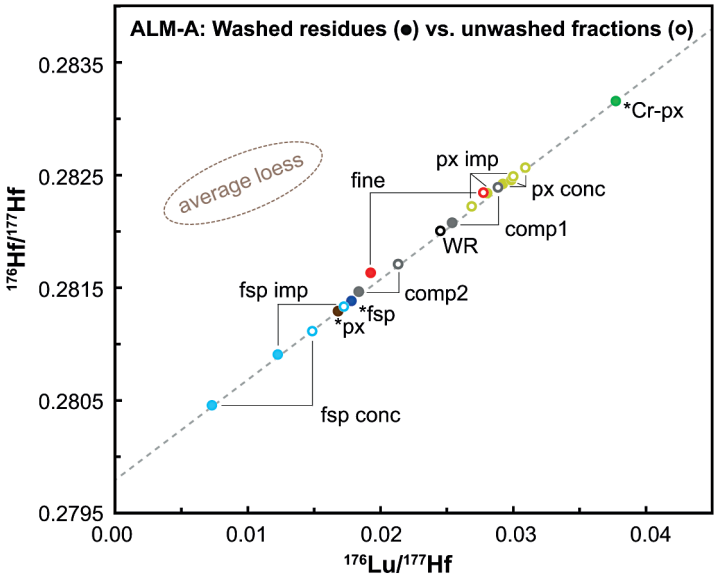

Figure 2 All bulk and mineral fractions of ALM-A (Table S-1). The washed residues are shown as filled circles and the unwashed fractions as open circles. The 2 s.d. error ellipses are smaller than the sample symbols. Isochron regressions are listed in Table 1. A Solar System isochron is plotted for reference (dashed grey line, ^{176}Lu-^{176}Hf parameters of the chondritic uniform reservoir of Bouvier *et al.*, 2008, t = 4568 Ma, *e.g.*, Bouvier *et al.*, 2011). In addition, average loess (Chauvel *et al.*, 2014) is shown, see Discussion. Abbreviations as in Figure 1.

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 $^{176}Hf/^{177}Hf_i$ of 0.279796 ± 0.000011 (Fig. 3).

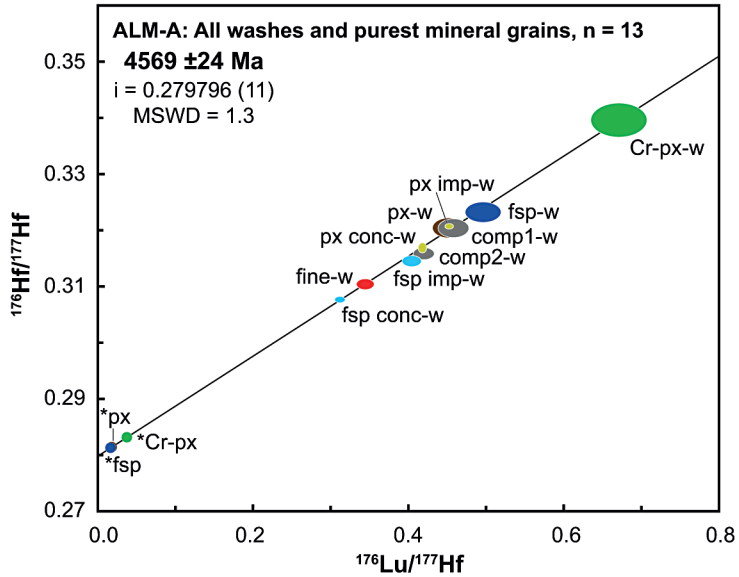

Figure 3 The purest mineral fractions (*i.e.* feldspar, low-Ca pyroxene, and Cr-pyroxene, all handpicked and washed) combined with all washes (error ellipses, denoted as -w). Abbreviations as in Table S-1.

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}Lu-^{176}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 in the meteorite or adhering to grains. To cause the observed deviations from the Solar System reference, the contaminant must be isotopically distinct (*i.e.* more radiogenic at lower $^{176}Lu/^{177}Hf$) from the meteorite minerals. Thus it is more likely that the contamination is terrestrial than introduced during parent body brecciation. We assume that the terrestrial contaminant is similar to average loess (*i.e.* 6.6 ppm Hf, $^{176}Lu/^{177}Hf = 0.0095 \pm 0.0049$, $^{176}Hf/^{177}Hf = 0.282428 \pm 0.000030$; Chauvel *et al.,* 2014). The deviations of, *e.g.,* the whole rock and fine fractions from the Solar System isochron can be explained by ~0.3 and 1.1 wt. % of this terrestrial contaminant, respectively (Table S-1).

Apparently, low-scatter trends that would not be immediately identified as errorchrons (*e.g.,* unwashed, impure fractions; MSWD of 2.1; Table 1) can yield spurious dates and low $^{176}Hf/^{177}Hf_i$ values. A similarly good isochron fit along a steep slope was previously observed for the quenched angrite Sahara 99555, and this was taken as evidence for accelerated ^{176}Lu decay caused by irradiation in the early Solar System (Bizzarro *et al.,* 2012). However, the requisite ^{176}Lu depletions have never been observed in meteorites (Scherer *et al.,* 2005; Wimpenny *et al.,* 2015). On the basis of our ALM-A Lu-Hf data, we argue instead that terrestrial contamination can also produce an apparently steep isochron if the high-Lu/Hf points included in the regression (*e.g.,* our impure pyroxene-rich fractions) are offset.

Evidently, terrestrial contamination can readily affect the ^{176}Lu-^{176}Hf systematics of meteorites, even during short terrestrial residence times. However, we infer from the accurate low-scatter isochron of the purest fractions (*i.e.* feldspar, low-Ca pyroxene, and Cr-pyroxene, 4571 ± 29 Ma, MSWD = 0.012, Table 1) that the terrestrial component is progressively removed during the mineral separation procedure. Sieving removes the fine-grained dust, which is most affected by contamination, and further sample handling during successive magnetic and density separations and the handpicking may help eliminate grain surface contamination. Washing minerals in 2 M HNO_3, in contrast, only increases the spread along isochrons toward lower $^{176}Lu/^{177}Hf$ values via phosphate removal without removing silicate-hosted contamination. The comparison of handpicked,

impure, and bulk fractions reveals the importance of a thorough mineral purification, and we suggest the use of the most coarse-grained, mono-mineralic fractions 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}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 meteoritic and terrestrial minerals, not only disturbing isochrons but also rendering the contamination difficult to remove. Contaminated mineral and bulk fractions 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 fractions and all washes provide a crystallisation age for ALM-A of 4569 ± 24 Ma. The ^{176}Hf/^{177}Hf$_i$ 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 unequilibrated chondrites (Bouvier *et al.,* 2008) calculated back to the start of the Solar System using λ^{176}Lu = 1.867 ×10^{-11} yr^{-1} and 2) the value of 0.279781 ± 0.000018 measured in eucrite zircon by Iizuka *et al.* (2015). These estimates are all clearly higher than that of the Sahara 99555 regression (0.279685 ± 0.000019; Bizzarro *et al.,* 2012). Although some eucrite whole rock regressions yield ^{176}Hf/^{177}Hf$_i$ similar to our ALM-A value (*e.g.,* 0.279751 ± 0.000030 to 0.27977 ± 0.00008; Bouvier *et al.,* 2015), they generally exhibit elevated slopes and less precise ^{176}Hf/^{177}Hf$_i$ 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}Hf/^{177}Hf$_i$ estimates (*i.e.* our ALM-A isochron, average bulk chondrite compositions, and low-P/D 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}Hf/^{177}Hf$_i$ also applies to Earth. This, in turn, constitutes a vital reference for Hf isotope studies of Earth's early crust-mantle evolution.

Acknowledgements

We gratefully acknowledge funding by the Special Priority Program 1385 – "The first 10 Million Years of the Solar System – A Planetary Materials Approach" of the Deutsche Forschungsgemeinschaft (grant SCHE 1579/1-1/2/3). We thank editor Helen Williams and two anonymous reviewers for their constructive comments.

Editor: Helen Williams

Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1705

Cite this letter as: Bast, R., Scherer, E.E., Bischoff, A. (2017) The ^{176}Lu-^{176}Hf systematics of ALM-A: A sample of the recent Almahata Sitta meteorite fall. *Geochem. Persp. Let.* 3, 45-54.

References

Albarède, F., Scherer, E. E., Blichert-Toft, J., Rosing, M. T., Simionovici, A., Bizzarro, M. (2006) γ-ray irradiation in the early Solar System and the conundrum of the ^{176}Lu decay constant. *Geochimica et Cosmochimica Acta* 70, 1261–1270.

Amelin, Y., Koefoed, P., Bischoff, A., Budde, G., Brennecka, G., Kleine, T. (2015) Pb Isotopic Age of ALM-A - A Feldspar-Rich Volcanic Rock from the Crust of the Ureilite Parent Body. *LPI Contributions* 1856, 5344.

Barfod, G.H., Otero, O., Albarède, F. (2003) Phosphate Lu-Hf geochronology. *Chemical Geology* 200, 241–253.

Bast, R., Scherer, E.E., Sprung, P., Fischer-Gödde, M., Stracke, A., Mezger, K. (2015) A rapid and efficient ion-exchange chromatography for Lu–Hf, Sm–Nd, and Rb–Sr geochronology and the routine isotope analysis of sub-ng amounts of Hf by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry* 30, 2323–2333.

Bischoff, A., Horstmann, M., Pack, A., Laubenstein, M., Haberer, S. (2010) Asteroid 2008 TC3-Almahata Sitta: A spectacular breccia containing many different ureilitic and chondritic lithologies. *Meteoritics and Planetary Science* 45, 1638-1656.

Bischoff, A., Horstmann, M., Barrat, J.A., Chaussidon, M., Pack, A., Herwartz, D., Ward, D., Vollmer, C., Decker, S. (2014) Trachyandesitic volcanism in the early Solar System. *Proceedings of the National Academy of Sciences* 111, 12689-12692.

Bizzarro, M., Connelly, J.N., Thrane, K., Borg L.E. (2012) Excess hafnium-176 in meteorites and the early Earth zircon record. *Geochemistry Geophysics Geosystems* 13, doi: 10.1029/2011GC004003.

Blichert-Toft, J., Boyet, M., Télouk, P., Albarède, F. (2002) ^{147}Sm–^{143}Nd and ^{176}Lu–^{176}Hf in eucrites and the differentiation of the HED parent body. *Earth and Planetary Science Letters* 204, 167-181.

Bloch, E., Watkins, J., Ganguly, J. (2016) Diffusion kinetics of Lu in clinopyroxene and applications to Lu-Hf ages of eucrites. *Abstract submitted to the Goldschmidt conference in Japan.*

Bouvier, A., Verwoort, J.D., Patchett, P.J. (2008) The Lu–Hf and Sm–Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth and Planetary Science Letters* 273, 48-57.

Bouvier, A., Brennecka, G.A., Wadhwa, M. (2011) Absolute chronology of the first solids in the Solar System. *LPI Contribution* 1639, 9054.

Bouvier, A., Blichert-Toft, J., Boyet, M., Albarède, F. (2015) ^{147}Sm–^{143}Nd and ^{176}Lu–^{176}Hf systematics of eucrite and angrite meteorites. *Meteoritics and Planetary Science* 50, 1896–1911.

Chauvel, C., Garçon, M., Bureau, S., Besnault, A., Jahn, B., Ding, Z. (2014) Constraints from loess on the Hf–Nd isotopic composition of the upper continental crust. *Earth and Planetary Science Letters* 388, 48-58.

Debaille, V., Yin, Q. Z., Amelin, Y. (2011) The Role of Phosphates for the Lu-Hf Chronology of Meteorites. *LPI Contributions* 1639, 9066.

Debaille, V., Yin, Q.-Z., Amelin, Y. (2013) Can diffusion cause discrepant Lu-Hf isochrons in meteorites? *Mineralogical Magazine* 77, 957.

Debaille, V., Van Orman, J., Yin, Q. Z., Amelin, Y. (2014) The Role of Diffusion During Metamorphism for the Lu-Hf Systematics of Chondrites. *Meteoritics and Planetary Science* 49, A5238.

Horstmann, M., Bischoff, A. (2014) The Almahata Sitta polymict breccia and the late accretion of Asteroid 2008 TC_3 - Invited Review. *Chemie der Erde - Geochemistry* 74, 149-184.

Iizuka, T., Yamaguchi, T., Hibiya, Y., Amelin, Y. (2015) Meteorite zircon constraints on the bulk Lu-Hf isotope composition and early differentiation of the Earth. *Proceedings of the National Academy of Sciences* 112, 5331–5336.

Jenniskens, P., Shaddad, M.H., Numan, D., Elsir, S., Kudoda, A.M., Zolensky, M.E., Le, L., Robinson, G.A., Friedrich, J.M., Rumble, D., Steele, A., Chesley, S.R., Fitzsimmons, A., Duddy, S., Hsieh, H.H., Ramsay, G., Brown, P.G., Edwards, W.N., Tagliaferri, E., Boslough, M.B., Spalding, R.E., Dantowitz, R., Kozubal, M., Pravec, P., Borovicka, J., Charvat, Z., Vaubaillon, J., Kuiper, J., Albers J., Bishop, J.L., Mancinelli, R.L., Sandford, S.A., Milam, S.N., Nuevo, M., Worden, S.P. (2009) The impact and recovery of asteroid 2008 TC3. *Nature* 458, 485–488.

Ludwig, K.R. (2003) Isoplot/Ex 3, A geochronological toolkit for Microsoft Excel. *Berkeley Geochronology Center Special Publication* No. 5.

Sanborn, M.E., Carlson, R.W., Wadhwa, M. (2015) ^{147,146}Sm–^{143,142}Nd, ^{176}Lu–^{176}Hf, and ^{87}Rb–^{87}Sr systematics in the angrites: Implications for chronology and processes on the angrite parent body. *Geochimica et Cosmochimica Acta* 171, 80–99.

Scherer, E.E., Cameron, K.L., Blichert-Toft, J. (2000) Lu-Hf garnet geochronology: Closure temperature relative to the Sm-Nd system and the effects of trace mineral inclusions. *Geochimica et Cosmochimica Acta* 64, 3413–3432.

Scherer, E.E., Münker, C., Mezger, K. (2001) Calibration of the Lutetium-Hafnium Clock. *Science* 293, 683-687.

Scherer, E.E., Mezger, K., Münker, C. (2003) The ^{176}Lu decay constant discrepancy: terrestrial samples vs. meteorites. *Meteoritics and Planetary Science* 38, A136.

Scherer, E.E., Münker, C., Kleine, T., Mezger, K. (2005) The isotopic composition of Lu in meteorites and lunar rocks: Implications for the decay constant of ^{176}Lu. *Geophysical Research Abstracts* 7, 10486.

Söderlund, U., Patchett, P.J., Vervoort, J.D., Isachsen, C.E. (2004) The ^{176}Lu decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions. *Earth and Planetary Science Letters* 219, 311–324.

Thrane, K., Connelly, J.N., Bizzarro, M., Meyer, B.S., The, L.-S. (2010) Origin of excess ^{176}Hf in meteorites. *Astrophysical Journal Letters* 717, 861–867.

Wendt, I., Carl C. (1991) The statistical distribution of the mean squared weighted deviations. *Chemical Geology* 86, 275–285.

Wimpenny, J., Amelin, Y., Yin, Q.-Z. (2015) The Lu isotopic composition of achondrites: Closing the case for accelerated decay of ^{176}Lu. *Astrophysical Journal Letters* 812, L3–5.

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

R. Bast[1]*, E.E. Scherer[1], A. Bischoff[2]

Supplementary Information

The Supplementary Information includes:

- Analytical Procedure
- Additional Details on the Terrestrial Contamination in ALM-A
- Table S-1
- Supplementary Information References

Analytical Procedure

Two grams of ALM-A were crushed in an agate mortar and sieved to <63, 63-125, and 125-250 µm fractions. A 100 mg chip was reserved for the whole rock powder. The chip was treated in an ultrasound ethanol bath, rinsed with ethanol, dried, and then powdered in agate. Minerals were separated by magnetic properties using a Frantz® magnetic barrier separator and by density using methylene iodide (MI, 3.3 g/cm^3) and an MI-acetone mixture (3.0 g/cm^3). Density fractions were rinsed several times in acetone to remove all heavy liquid residues. Feldspar, low-Ca pyroxene, and Cr-bearing Ca pyroxene were further purified by dry hand-picking mono-mineralic grains from the respective mineral concentrates (125-250 µm; Fig. 1). Care was taken to avoid grains with any adhering material or coatings. The bulk and mineral fractions were weighed into Savillex Teflon® vials, in which some aliquots (Table S-1) were washed in 2 M HNO_3 and rinsed multiple times with milli-Q water. The HNO_3 plus water rinses were all collected in another Savillex vial and constitute the "washes". The residual samples after

1. Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, Corrensstr. 24, 48149 Münster, Germany
* Corresponding author (email: Rebecca.Bast@uni-muenster.de)
2. Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

the HNO_3 washing procedure are referred to as "washed samples" or "residues". All samples and washes were spiked with a mixed ^{176}Lu-^{180}Hf tracer. The wash solutions were dried down with a drop of $HClO_4$. The mineral fractions were digested in 2:1 HF:HNO_3 on a hotplate at 120 °C for 2 days, whereas the whole-rock powder was autoclave-digested at 180 °C for 5 days. After drying the samples, fluorides were evaporated three times with 1 ml of concentrated HNO_3, and complete dissolution was achieved when converting the samples to chlorides using 10 M HCl.

Hafnium was separated from the rare earth elements (REE) on an initial 2 ml cation column (AG 50W-X8, 200-400 mesh) and further purified using a dedicated 2 ml Ln-Spec column (Bast *et al.*, 2015). Both Hf and Lu cuts were analysed on a Neptune Plus MC-ICP-MS following the procedure described in Bast *et al.* (2015). For most bulk and mineral fractions, the Hf isotope composition was measured at concentrations around 40 ppb in sufficiently clean solutions (Zr/Hf ≤ 1, ^{175}Lu/$^{176}\Sigma$ monitors ≤ 0.0005). For the washes, Hf was analysed at the 1 ppb-level with ≤0.35 V on ^{177}Hf, and the ^{175}Lu/$^{176}\Sigma$ monitors were somewhat elevated at 0.0001 to 0.006. These Lu interferences were corrected using 1) natural Lu, and 2) the ^{176}Lu/^{175}Lu of the spiked sample. An average ^{176}Hf/^{177}Hf is reported, and the reported uncertainties enclose both end-member values. Procedural blanks were continuously monitored and ranged from 1 to 20 pg Hf and 1 to 5 pg Lu. To ensure a robust blank correction for samples with low sample-to-blank ratios (*i.e.* ~20-140 for the washes), the reported error ellipses include additional uncertainties for subtracting minimum and maximum blanks. Otherwise, the external reproducibility is estimated as described in Bast *et al.* (2015). The results reported in Table S-1 are normalised to ^{176}Hf/^{177}Hf = 0.282160 for the Ames Hf-standard, which is isotopically equivalent to JMC-475.

Additional Details on the Terrestrial Contamination in ALM-A

In the main text, the accuracy and lack of excess scatter in the isochrons of 1) handpicked minerals alone, and 2) handpicked minerals plus selectively dissolved phosphate minerals (washes) were used to eliminate several explanations (irradiation, diffusive resetting, and terrestrial alteration) for the excess ^{176}Hf found in most of the bulk and fine-grained samples. Given that the coarse, handpicked grains were devoid of excess ^{176}Hf, the simplest remaining way to explain its presence in bulk and fine fractions is the presence of very fine grained (<63 µm) terrestrial material that infiltrated (dry or suspended in water) the meteorite along cracks or grain boundaries. Considering the sample preparation method used, we would thus expect the whole rock (powdered directly from a chip) and the <63 µm fractions to be affected the most by contamination. Owing to geochemical cycling over Earth's history, low-Lu/Hf terrestrial samples are generally more radiogenic than low-Lu/Hf meteoritic minerals that have been isolated since ~4.56 Ga. Thus mixtures of meteoritic material with terrestrial contamination will be displaced above (and to the left of) the true isochron (Fig. 2, main text). That the contamination is effectively removed by sieving for coarse grains

Table S-1 Lutetium-Hafnium concentration and isotope data for ALM-A.

Fraction	Sample weight (mg)	Washed?	Lu (ng)	Hf (ng)	Lu (ppm)	Hf (ppm)	$^{176}Lu/^{177}Hf$	est. % 2 s.d.	$^{176}Hf/^{177}Hf$	2 s.e.	est. % 2 s.d.	wt. % terr. comp.
WR	48.57	no	10.8	62.5	0.222	1.29	0.02451	0.25	0.282005	(3)	0.0015	0.3
fine	24.05	no	5.34	27.3	0.222	1.14	0.02776	0.27	0.282344	(4)	0.0028	0.8
fine-r	24.95	yes‡	3.57	26.3	0.143	1.05	0.01925	0.25	0.281629	(4)	0.0029	1.1
fine-w			1.4	0.6			0.3421	2.8	0.310141	(30)	0.26	
px conc	50.81	no	20.5	94.1	0.403	1.85	0.03091	0.27	0.282567	(3)	0.0018	0.3
px conc-r1	48.68	yes‡	19.2	91.1	0.394	1.87	0.02985	0.25	0.282455	(3)	0.0019	0.1
px conc-r2	49.60	yes	19.3	93.7	0.389	1.89	0.02922	0.26	0.282421	(3)	0.0021	0.4
px conc-w			1.4	0.5			0.4160	1.1	0.316665	(120)	0.25	
*px-r	14.22	yes‡	6.76	57.1	0.476	4.01	0.01681	0.27	0.281293	(4)	0.0023	0.1
px-w			0.4	0.1			0.4500	3.9	0.320195	(72)	0.45	
*Cr-px-r	24.42	yes‡	13.4	50.3	0.547	2.06	0.03773	0.27	0.283156	(3)	0.0023	0.1
Cr-px-w			0.6	0.1			0.6698	4.4	0.339548	(76)	0.74	
px imp-1	5.08	no	1.92	10.2	0.379	2.00	0.02688	0.25	0.282222	(7)	0.0035	0.6
px imp-2	50.48	no	21.2	100	0.419	1.98	0.03000	0.25	0.282489	(3)	0.0019	0.4
px imp-r	53.14	yes‡	21.6	109	0.407	2.06	0.02804	0.26	0.282340	(3)	0.0022	0.9
px imp-w			1.7	0.5			0.4504	1.0	0.320497	(34)	0.13	
comp1	33.14	no	14.5	71.3	0.438	2.15	0.02886	0.28	0.282391	(3)	0.0017	0.5
comp1-r	11.46	yes	4.53	25.3	0.396	2.21	0.02540	0.26	0.282077	(5)	0.0031	0.4
comp1-w			1.0	0.3			0.4559	3.6	0.320205	(47)	0.43	
comp2	49.78	no	7.39	49.2	0.148	0.988	0.02131	0.25	0.281706	(4)	0.0057	0.1
comp2-r	51.75	yes	6.66	51.4	0.129	0.994	0.01837	0.25	0.281464	(3)	0.0025	0.3
comp2-w			1.3	0.4			0.4176	2.6	0.315563	(53)	0.28	
fsp conc	105.2	no	3.72	35.5	0.0353	0.337	0.01486	0.25	0.281114	(3)	0.0020	0.0
fsp conc-r	100.8	yes‡	1.90	37.1	0.0189	0.368	0.007290	0.25	0.280456	(3)	0.0022	0.0
fsp conc-w			1.9	0.9			0.3098	1.9	0.307352	(25)	0.15	
*fsp-r	95.44	yes	1.73	13.8	0.0181	0.144	0.01781	0.25	0.281383	(4)	0.0026	0.0
fsp-w			1.3	0.4			0.4944	3.8	0.323039	(31)	0.48	
fsp imp	99.99	no	5.89	48.5	0.0589	0.485	0.01724	0.25	0.281332	(3)	0.0017	0.0
fsp imp-r	104.9	yes	4.41	51.1	0.0421	0.487	0.01226	0.25	0.280906	(4)	0.0022	0.1
fsp imp-w			1.3	0.5			0.4023	2.5	0.314287	(26)	0.26	

* Pure, handpicked mineral separate. For each mineral fraction, one aliquot (-r, residue) was washed in 2 M HNO_3 for 30 min at room temperature or ‡ at 65 °C, and the wash solutions (-w) were analysed separately. Abbreviations as in Figure 1 in the main text, est. % 2 s.d.: estimated external reproducibility in %, 2 s.e.: absolute internal measurement uncertainty on $^{176}Hf/^{177}Hf$ in the 6th digit, wt. % terr. comp.: weight % of terrestrial component needed to explain the positive deviation from the reference isochron, calculated assuming average Lu-Hf parameters (see main text) and 6.6 ppm Hf in the loess (Chauvel *et al.*, 2014).

and hand-picking suggests that it is hosted by a separate, particulate material that has not chemically reacted, or combined, with the meteorite minerals *e.g.,* by hydrous alteration. This may explain why the meteorite can be contaminated yet still appear fresh and unaltered. We speculate that the contamination was derived from ambient desert material over the 1 year residence time between the Almahata Sitta fall and the collection of ALM-A. (We consider it unlikely that contamination was introduced by sample curation, but cannot rule out this possibility.) If the terrestrial contamination is indeed the result of even short residence times on Earth, then potentially all meteorite finds (and many falls) may subject to similar effects. In cases such as ALM-A, where the contamination is not accompanied by chemical alteration or weathering, simple physical means, such as sieving, may be effective at removing the contamination. For whole rock analyses, it might be better to first isolate a coarse grained bulk fraction by sieving (*e.g.,* Amelin *et al.,* 2015) rather than simply powdering a rock chip as we have done here. However, the result may not be representative of the bulk meteorite if fine-grained meteoritic components (*e.g.,* accessory minerals) are removed along with the contaminant. If the contamination occurs in connection with the chemical alteration that commonly affects meteorite finds (*e.g.,* Crozaz and Wadhwa, 2001; Crozaz *et al.,* 2003) and perhaps recently found pieces of earlier falls, it might prove more difficult to remove.

Supplementary Information References

Amelin, Y., Koefoed, P., Bischoff, A., Budde, G., Brennecka, G., Kleine, T. (2015) Pb Isotopic Age of ALM-A - A Feldspar-Rich Volcanic Rock from the Crust of the Ureilite Parent Body. *LPI Contributions* 1856, 5344.

Bast, R., Scherer, E.E., Sprung, P., Fischer-Gödde, M., Stracke, A., Mezger, K. (2015) A rapid and efficient ion-exchange chromatography for Lu–Hf, Sm–Nd, and Rb–Sr geochronology and the routine isotope analysis of sub-ng amounts of Hf by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry* 30, 2323–2333.

Crozaz, G., Wadhwa, M. (2001) The terrestrial alteration of Saharan shergottites Dar al Gani 476 and 489: a case study of weathering in a hot desert environment. *Geochimica et Cosmochimica Acta* 65, 971–977.

Crozaz, G., Floss, C., Wadhwa, M. (2003) Chemical alteration and REE mobilization in meteorites from hot and cold deserts. *Geochimica et Cosmochimica Acta* 67, 4727-4741.