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Non-nucleosynthetic heterogeneity in non-radiogenic stable Hf isotopes: Implications for early solar system chronology

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ABSTRACT

Nucleosynthetic heterogeneity and secondary neutron capture reactions may have important implications for ^{176}Lu–^{176}Hf chronology and modelling of early planetary evolution. So far, the relevance of these phenomena for the Lu–Hf system has not been explored. We therefore have analyzed the non-radiogenic stable Hf-isotope composition (^{177}Hf, ^{178}Hf, ^{179}Hf, and ^{180}Hf) of meteorites, meteorite components, and terrestrial rock samples to identify nucleosynthetic or neutron capture-induced variations. All analyzed chondrites have uniform ^{178}Hf/^{177}Hf and ^{180}Hf/^{177}Hf values that cannot be resolved from the average terrestrial composition. Thus, there is no evidence for nucleosynthetic heterogeneity in chondrites or Earth and these data support the use of a chondritic reference value for the Hf-isotope composition of the Bulk Silicate Earth. This homogeneity contrasts with nucleosynthetic heterogeneities found in lighter elements and provides evidence for a separate synthesis of light and heavy r-process nuclei.

Various mesosiderite samples and one lunar meteorite display coupled ^{178}Hf/^{177}Hf and ^{180}Hf/^{177}Hf anomalies that are associated with neutron capture-induced deviations in ^{149}Sm/^{154}Sm and ^{150}Sm/^{154}Sm. However, the analyzed chondrites and an aubrite show only Sm-isotope anomalies, and these are the result of neutron capture. The Hf-isotope anomalies require substantial capture of epithermal neutrons, whereas Sm anomalies result primarily from thermal neutron capture. The non-radiogenic stable isotope composition of Hf is thus a suitable monitor for epithermal neutron capture reactions. The data reveal distinct neutron energy spectra: mesosiderites are characterized by high epithermal-to-thermal neutron fluence ratios, whereas the remaining samples show low epithermal-to-thermal ratios.

Secondary neutron capture may significantly increase the measured ^{176}Hf/^{177}Hf in whole-rock meteorite samples without causing a resolvable shift in ^{176}Lu/^{177}Hf. Thus it could potentially induce scatter in Lu–Hf whole-rock isochrons and produce spurious initial ^{176}Hf/^{177}Hf values. However, the slopes of internal (i.e., mineral) isochrons cannot be increased significantly by secondary neutron capture. This process therefore cannot account for the unrealistically old ^{176}Lu–^{176}Hf 'ages' (e.g., ~4.75 Ga) of some meteorites.

1. Introduction

The long-lived ^{176}Lu–^{176}Hf decay system provides a powerful geochronometer and isotopic tracer for geochemical modelling (e.g., Patchett, 1983). When applied to Archean rocks and minerals, it can be used to reconstruct timing and degree of large-scale silicate differentiation events early in Earths' history (e.g., Vervoort et al., 1996; Amelin et al., 1999). The system, however, can only be fully utilized if the bulk Lu/Hf and the initial ^{176}Hf/^{177}Hf of the planetary body in question and the ^{176}Lu decay constant are well constrained.

Being refractory and lithophile elements, Lu and Hf are assumed not to have been fractionated significantly from each other during processes of nebular evaporation, condensation, or planetary core formation. This assumption is supported by the tightly defined chondritic Lu/Hf value of Bouvier et al. (2008). Thus, the solar composition and also that of the bulk silicate portion of terrestrial planetary bodies are taken to have a chondritic Lu/Hf (e.g., Palme and Jones, 2007). Different classes and petrologic types of chondrites form a correlated array in ^{176}Hf/^{177}Hf vs. ^{176}Lu/^{177}Hf space (e.g., Blichert-Toft and Albarède, 1997). A chondritic reference value for the Lu–Hf system has been defined as the ^{176}Hf/^{177}Hf

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value of this array at its mean $^{176}Lu/^{177}Hf$ (Blichert-Toft and Albarède, 1997). Using an alternative approach, Patchett et al. (2004) concluded by comparing combined Lu–Hf and Sm–Nd data of chondrites and terrestrial samples that the mean of carbonaceous chondrites might represent a plausible alternative reference value for the Bulk Silicate Earth (BSE). Most recently, Bouvier et al. (2008) improved upon earlier studies by analyzing unequilibrated chondrites (types 1–3, mostly falls), thereby significantly reducing the spreads in Lu/Hf and $^{176}Hf/^{177}Hf$, and the uncertainties on their mean values. However the possibilities of 1) initial nucleosynthetic Hf-isotope heterogeneity or 2) secondary nuclear effects have not yet been thoroughly investigated. A uniform initial $^{176}Hf/^{177}Hf$ of the solar system requires that the Hf nuclides were homogeneously distributed in the solar nebula. To determine this initial value, the effects of secondary processes such as radiogenic ingrowth, secondary chemical fractionation, and nuclear reactions must be identified and accurately quantified. Here we evaluate the possible extent of nucleosynthetic heterogeneities and secondary nuclear effects by analyzing the non-radiogenic stable Hf-isotope composition of meteorites, meteorite components, and terrestrial rocks. The importance of such a study is highlighted by recent findings of isotope anomalies in *bulk* meteorite samples for elements such as Ba, Cr, Fe, Nd, Mo, Ni, Sm, and Ti (e.g., Rotaru et al., 1992; Yin et al., 2002; Hidaka et al., 2003; Bizzarro et al., 2007; Carlson et al., 2007; Quitté et al., 2007; Leya et al., 2008a; Regelous et al., 2008), which indicate that initial nucleosynthetic heterogeneities have been preserved.

Hafnium isotopes are produced in a variety of nucleosynthetic processes. The neutron-deficient ^{174}Hf isotope and possibly ~3% of ^{176}Hf (Klay et al., 1991) were produced by the p-process, which has been attributed to environments such as supernovae or massive stars in their pre-supernova phase (Arnould and Goriely, 2003). The majority of ^{176}Hf, however, is of s-process origin. In contrast, ^{177}Hf, ^{178}Hf, ^{179}Hf, ^{180}Hf, and ^{182}Hf had contributions from both s- and r-process (Wisshak et al., 2006; Vockenhuber et al., 2007). The s-process is commonly attributed to thermally pulsing, low-mass, asymptotic giant branch (AGB) stars (Busso et al., 1999). The r-process is thought to comprise different rapid neutron capture processes that occur in various stellar environments such as supernovae or neutron star mergers. The common characteristic of these processes is a high neutron density, which is possible in various temperature regimes (e.g., Meyer and Adams, 2006; Arnould et al., 2007). Further nuclear reactions, including charged particle reactions, can contribute to the r-process synthesis of lighter nuclei ($\sim Z \leq 56$; e.g., Qian and Wasserburg, 2007).

Quantifying radiogenic ^{176}Hf ingrowth requires that the decay constant of ^{176}Lu is accurately and precisely known. There is however an unsolved discrepancy between ^{176}Lu decay constant determinations based on meteorites (e.g., Patchett and Tatsumoto, 1980; Bizzarro et al., 2003) and those based on terrestrial samples (Scherer et al., 2001, 2003; Söderlund et al., 2004). Possible explanations for the apparently accelerated decay of ^{176}Lu in meteorites include the excitation of ^{176}Lu via γ-irradiation (Albarède et al., 2006) or interactions with ultra-relativistic cosmic-rays or neutrinos (Thrane et al., 2006; Meyer et al., 2008). Given the good agreement among ^{176}Lu decay constant calibrations that are based on terrestrial samples, the application of the ^{176}Lu decay constant to terrestrial data sets appears to be justified (Söderlund et al., 2004). Yet, the discrepancy is still the subject of ongoing research.

One particularly important nuclear effect that has long been known to significantly modify primary isotope compositions is the capture of secondary neutrons (n-capture) by nuclides having large n-capture cross sections (e.g., Lingenfelter et al., 1972; Leya et al., 2000). Highly energetic galactic cosmic-rays (~0.1 to ~10 GeV) interact with matter and produce fast to moderately fast secondary neutrons. These are moderated to epithermal (~0.025 eV to a few keV) and thermal (~0.025 eV at room temperature) energies by elastic scattering and other nuclear reactions (e.g., Lingenfelter et al., 1972; Gosse and Phillips, 2001). The resulting neutron energy spectrum depends on the size and chemical compositions of the target body and the depth within the target (e.g., Leya, 1997; Kollár et al., 2006). In particular, H, O, Si and Fe contents have a strong influence on the moderation of neutrons to thermal energies and thus on the relative magnitudes of thermal and epithermal neutron fluences (Lingenfelter et al., 1972; Kollár et al., 2006). Capture of epithermal and thermal neutrons by nuclei changes the isotope abundances of the target material. The average probability for capturing a neutron (cross section) scales with the inverse of the neutron velocity (i.e. capture probability $\sim 1/v$). Superimposed on this dependence are discrete energies at which the n-capture probability is enhanced, the so-called resonances. For thermal neutrons, the $1/v$ dependence usually is sufficient for predicting capture rates, and thus the thermal neutron capture cross sections are defined. In the epithermal region, however, resonances are important for defining the epithermal analogue to the thermal cross section, the resonance integral (RI). The destruction (i.e., burnout) and production of isotopes important to the Lu–Hf system depend on the energy spectrum of the secondary neutrons and the integrated neutron flux (n/cm²). At *epithermal* energies, the most probable reactions are n-capture on ^{177}Hf and ^{178}Hf, i.e., $^{177}Hf(n,\gamma)^{178}Hf$ (RI of ~7210 barn) and $^{178}Hf(n,\gamma)^{179}Hf$ (RI of ~1910 barn), respectively. These affect all ^{177}Hf-referenced Hf-isotope ratios directly via changing the ^{177}Hf abundance and indirectly by increasing $^{179}Hf/^{177}Hf$, which is commonly used for mass-bias correction. Because all Hf-isotope abundances are modified, such n-capture effects cannot be avoided by using a different normalizing ratio. At *thermal* energies, the most probable n-capture reaction is the transformation of ^{176}Lu to ^{177}Hf, i.e., $^{176}Lu(n,\gamma)^{177}Lu \rightarrow {}^{177}Hf + e^- + \bar{\nu}$, with a thermal n-capture cross section (σ_{th300K}) of ~3640 barn. Another sensitive monitor of secondary n-capture reactions is the transformation of ^{149}Sm to ^{150}Sm (e.g., Lingenfelter et al., 1972; Nyquist et al., 1995; Hidaka et al., 2000): ^{149}Sm has a large capture cross section for both thermal and epithermal neutrons (σ_{th300K} ~70,040 barn and RI of ~3480 barn). Here, using measurements of non-radiogenic stable Sm- and Hf-isotope compositions, the first findings of neutron-capture-induced changes of Hf-isotope abundances in meteorites are reported. The implications for geochemical modelling and for ^{176}Lu–^{176}Hf chronology are discussed.

2. Sample description and analytical techniques

A variety of terrestrial and extra-terrestrial rock samples were selected for this study. The terrestrial samples comprise Archean to Quaternary igneous and metamorphic rocks ($n = 20$), including four international rock standards (AGV-2, BCR-2, BHVO-2, and JG-2). This selection was made to test for potential temporal variations in the non-radiogenic stable Hf-isotope compositions in terrestrial rocks. The extra-terrestrial samples include chondrites, mesosiderites, one lunar meteorite (DAG 262), one aubrite (Peña Blanca Springs), three dark inclusions (two from NWA 753, one from Allende), and two Ca–Al-rich inclusions (CAI) from Allende. The chondrite suite includes four carbonaceous chondrites (Allende — CV3, Dar al Gani 275 — CK4/5, Dar al Gani 137 — CO3, and Murchison — CM2), eight ordinary chondrites (Dar al Gani 318 — H3, Acfer 105 — H4, El Hammami — H5, Acfer 111 — H3-6, Dar al Gani 216 — L3, Acfer 029 — L6, Dar al Gani 301 — L6, and Acfer 066 — LL3-6), and one Rumuruti chondrite (NWA 753 — R3.9). The chondritic regolith breccias Acfer 066 and Acfer 111 were chosen because of their known regolith irradiation histories and high solar noble gas contents (Pedroni and Begemann, 1994; Jäckel et al., 1997; Scherer et al., 1998). The mesosiderite samples comprise five 'basaltic' pebbles, two pyroxene fractions from two 'basaltic' pebbles, and one 'gabbroic' pebble (see classification of Rubin and Mittlefehldt, 1992) from Vaca Muerta (hereafter VM), as well as silicate inclusions from Estherville and Mincy.