Inference on terrestrial genesis from molybdenum isotope systematics

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Received 25 October 2001; accepted 11 January 2002; published 21 March 2002.

It has been suggested that a genetic relationship exists between the Earth and enstatite chondrites. The discovery of non mass dependent molybdenum isotope anomalies (Mo-w) at a macroscopic scale raises the possibility of using this element as a tracer of genetic relationships. We have determined the molybdenum isotopic compositions of enstatite chondrites (EH and EL) and terrestrial lavas presumably derived from the deep mantle (Loihi seamount, Hawaii). The molybdenum isotopic compositions are identical, suggesting a common source reservoir. The conclusion is that although distinct, the Earth shares similarities with enstatite chondrites from a chemical and isotopic point of view because both formed in the inner regions of the solar system.

INDEX TERMS: 1040 Geochemistry: Isotopic composition/chemistry; 6240 Planetology: Solar System Objects: Meteorites and tektites; 1060
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1. Introduction

The Earth is a differentiated body and the composition of rocks found at its surface cannot be readily used to infer the nature of the material from which our planet formed. Isotopic variations that depart from usual mass dependent fractionation and nuclear effects represent faithful witnesses of Earth’s accretion because they cannot be erased by subsequent geological processes. Thus, comparison of the isotopic compositions of terrestrial and meteoritic samples provides a means of constraining the nature of terrestrial precursors.

Contrary to other undifferentiated meteorites, enstatite chondrites possess oxygen [Clayton et al., 1984; Clayton, 1993] and chromium [Lugmair and Shukolyukov, 1998; Shukolyukov and Lugmair, 1998] isotopic compositions very close to that of the Earth. Also, in the Urey-Craig diagram, the bulk Earth plots close to enstatite chondrites [Javoy, 1999]. Some have argued that these similarities provide evidence for a genetic relationship between enstatite chondrites and our planet [Smith, 1981; Javoy et al., 1986; Javoy, 1995, 1998, 1999]. Yet, inferred elemental ratios of the primitive mantle [Allègre et al., 2001] tend instead to support the view that the Earth was formed from material sharing similarities with carbonaceous chondrites.

Recently, molybdenum nucleosynthetic isotope anomalies have been found in differentiated meteorites [Dauphas et al., 2002a]. After oxygen [Clayton et al., 1973; Clayton, 1993] and chromium [Shukolyukov and Lugmair, 2001], this is the third piece of evidence for planetary scale isotope heterogeneity of the protosolar nebula. The Mo-w anomalies are characterized by a coupled excess in p (92 and 94) and r (95, 97, 98, and 100), or a mirror deficit in s (95, 96, 97, and 98) nuclides [Yin et al., 2000; Dauphas et al., 2002a, 2002b]. These anomalies were inherited from the interstellar environment where the sun was born, illustrating the concept of “cosmic chemical memory” [Clayton, 1982]. The virtue of molybdenum for tracing the relationships between planetesimals has been demonstrated in the case of chondrites, iron meteorites, pallasites, and mesosiderites [Dauphas et al., 2002a]. Accurate and precise determination of the molybdenum isotopic composition of enstatite chondrites and terrestrial samples is thus an important step towards definitive acceptance or rejection of the “enstatite model”.

2. Samples and Analyses

Enstatite chondrites are divided into EH and EL subtypes on the basis of their iron content [Sears and Dodd, 1988]. Despite the fact that the oxygen isotopic composition of these two groups are identical [Clayton et al., 1984; Newton et al., 2000], they are thought to originate from two distinct parent-bodies [Keil, 1989]. We measured enstatite chondrites Indarch (EH4), Saint Sauveur (EH4), and Pillistfer (EL6). Ocean island basalts (OIB) are the surface expression of mantle plumes. Many of these are thought to originate in the deep mantle, below the 660 km discontinuity and possibly at the core-mantle boundary. In this respect, samples from Loihi seamount, Hawaiian plume, are among the best available samples for examining possible isotopic heterogeneities of the silicate Earth. We measured Loihi submarine pillow basalt T4D2 #1 dredged at 4200 m 18°46.0N 155°11.3W by the R/V Thomas Washington [Valbracht et al., 1996].

A protocol based on solvent extraction, ion exchange, and plasma ionization mass spectrometry was developed [Dauphas et al., 2001]. In order to correct for natural and instrumental mass fractionation, molybdenum isotope abundances were normalized to 96Mo/98Mo = 1.4470 [Dauphas et al., 2001]. Ratios are expressed in e notation,

\[ e = \left( \frac{[\langle 96\text{Mo} \rangle]}{[\langle 98\text{Mo} \rangle]} \right) - 1 \times 10^4 \]

where the standard is an Alfa Aesar solution of unknown origin. We measured many sediments for molybdenum isotope abundances [Dauphas et al., 2001] and found no difference except for mass fractionation relative to the standard solution, indicating that this solution must be representative of the molybdenum isotopic composition of the crust. Results are given in Table 1 for both enstatite chondrites and Loihi. All ratios are within error of the terrestrial standard value.

3. Isotope Heterogeneity of the Earth?

There is no “non mass dependent” isotope heterogeneity of the Earth for oxygen [Robert et al., 1992]. Should we expect to observe some isotopic heterogeneity of the silicate Earth for molybdenum? Molybdenum is a moderately siderophile element [Schmitt et al., 1989] that was presumably delivered to the mantle in part by a late veneer after core formation. The molybdenum

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0094-8276/02/2001GL014237, 2002
concentration of the upper mantle is $5.2 \times 10^{-10}$ mol g$^{-1}$ [McDonough and Sun, 1995]. Given that osmium was essentially all delivered to the mantle by the late veneer [Morgan, 1985] and that the osmium content of the upper mantle is $1.8 \times 10^{-11}$ mol g$^{-1}$, it is straightforward to compute the fraction of molybdenum from this source using the chondritic ratio Mo/ Os = 3.8 [Anders and Grevesse, 1989]. It is thus estimated that approximately 87% of the molybdenum inventory of the upper mantle was left by core extraction and that 13% was delivered by the late veneer. Based on the osmium isotopic composition of the mantle, it was recently suggested that the late veneer was not completely homogenized in the whole mantle, its contribution being a factor of +3 or -1 higher in the deep mantle than in the lower mantle [Dauphas et al., 2002c]. In such a case, the contribution of the residual mantle and the late veneer in the deep mantle would be 95% and 5%, respectively. If there was a contrast of 1 e-unit between the proto-Earth and the late veneer, we should expect to observe a heterogeneity of the Earth of approximately 0.1 e-unit between the deep and the shallow mantle, which is not resolvable at present.

[8] As discussed previously, we measured a lava from Loihi seamount of T4D2#1 which is thought to have erupted material that was once deep in the Earth [Valbracht et al., 1996]. As illustrated in Figure 1, this sample presents no convincing anomaly relative to the standard or to crustal rocks, indicating that at our level of precision, the Earth is homogeneous for molybdenum isotopic composition after correction for possible mass dependent fractionation.

4. Implications for Planetary Genesis

[9] Determinations of molybdenum isotope abundances in enstatite chondrites allow us to discuss the possible relationships of these two meteorite groups both with each other and with the Earth. Keil [1989] presented convincing arguments that the parent-bodies of EH and EL chondrites were distinct. We measured the molybdenum isotopic composition of Indarch (EH4), Saint Sauveur (EH4), and Pillistfer (EL6). As illustrated in Figure 1, there is no obvious difference between EH and EL chondrites. Although EH and EL chondrites originated from two distinct parent-bodies, our results confirm the inference based on oxygen [Clayton et al., 1984; Newton et al., 2000] that they formed from the same isotopic reservoir.

[10] As discussed previously, the contribution of the late veneer to the molybdenum inventory of the silicate Earth was minor and the isotopic composition of the mantle must primarily reflect the composition of terrestrial precursors. There is no obvious anomaly in enstatite chondrites relative to the Earth (Figure 1). This result is consistent with the “enstatite model” of the Earth [Smith, 1981; Javoy et al., 1986; Javoy, 1995, 1998, 1999].

[11] A complication arises with Hf-W systematics because enstatite chondrites display deficits in $^{182}$W relative to the Earth [Lee and Halliday, 2000a]. However, this difference can be reconciled with an enstatite model for the Earth [Javoy, 2000].

[12] Despite having chondritic Hf/W ratios, enstatite chondrites display deficits in $^{182}$W relative to carbonaceous chondrites [Lee and Halliday, 2000a]. There are three alternative explanations for this puzzling observation: (i) the Hf/W ratio followed a complex evolution while $^{182}$Hf was still alive, (ii) the $^{182}$Hf extinct radiogenic nuclide was heterogeneously distributed in the early solar system, or (iii) as is observed for molybdenum [Dauphas et al., 2002a, 2002b], the non-radiogenic isotopic composition of tungsten was not uniform in the protosolar nebula. We propose that the Earth accreted from material having tungsten isotopic composition similar to enstatite chondrites and that core formation occurred while some $^{182}$Hf was still alive. In this case, the difference between the

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**Table 1. Molybdenum Isotope Measurements**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>92</th>
<th>94</th>
<th>95</th>
<th>96</th>
<th>97</th>
<th>98</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indarch EH4</td>
<td>-0.44 ± 1.25</td>
<td>-0.26 ± 0.85</td>
<td>-0.05 ± 0.63</td>
<td>0</td>
<td>-0.21 ± 0.33</td>
<td>0</td>
<td>-0.61 ± 0.38</td>
</tr>
<tr>
<td>Indarch EH4</td>
<td>0.98 ± 0.86</td>
<td>0.58 ± 0.54</td>
<td>0.77 ± 0.47</td>
<td>0</td>
<td>0.49 ± 0.22</td>
<td>0</td>
<td>-0.10 ± 0.33</td>
</tr>
<tr>
<td>Saint Sauveur EH4</td>
<td>0.15 ± 0.62</td>
<td>0.13 ± 0.40</td>
<td>0.48 ± 0.21</td>
<td>0</td>
<td>0.26 ± 0.10</td>
<td>0</td>
<td>0.09 ± 0.28</td>
</tr>
<tr>
<td>Saint Sauveur EH4</td>
<td>0.09 ± 1.86</td>
<td>-0.15 ± 1.19</td>
<td>-0.04 ± 0.92</td>
<td>0</td>
<td>0.19 ± 0.23</td>
<td>0</td>
<td>1.22 ± 0.81</td>
</tr>
<tr>
<td>Pillistfer EL6</td>
<td>-1.03 ± 0.94</td>
<td>-0.74 ± 0.64</td>
<td>-0.27 ± 0.43</td>
<td>0</td>
<td>0.23 ± 0.21</td>
<td>0</td>
<td>0.66 ± 0.32</td>
</tr>
<tr>
<td>Pillistfer EL6</td>
<td>1.04 ± 1.15</td>
<td>0.69 ± 0.81</td>
<td>0.74 ± 0.62</td>
<td>0</td>
<td>0.45 ± 0.20</td>
<td>0</td>
<td>-0.07 ± 0.47</td>
</tr>
<tr>
<td>T4D2#1 OIB</td>
<td>-0.08 ± 0.67</td>
<td>0.01 ± 0.57</td>
<td>0.25 ± 0.30</td>
<td>0</td>
<td>0.31 ± 0.26</td>
<td>0</td>
<td>0.23 ± 0.49</td>
</tr>
<tr>
<td>T4D2#1 OIB</td>
<td>0.04 ± 1.03</td>
<td>0.05 ± 1.07</td>
<td>0.36 ± 0.37</td>
<td>0</td>
<td>0.30 ± 0.31</td>
<td>0</td>
<td>-0.10 ± 0.49</td>
</tr>
</tbody>
</table>

Molybdenum isotope abundances were normalized to $^{98}$Mo/96Mo = 1.4470 [Dauphas et al., 2001]. The isotopic composition is expressed as $\epsilon$ = ([Mo$^{68}$/96Mo]/[Mo$^{68}$/96Mo]std) - 1) × 10$^5$. Uncertainties are 2σ. The samples were digested in concentrated HF-HCl-HClO$_4$. The solution was then treated by solvent extraction using HDEHP and ion chromatography using AG1-X8. An Aridus desolvating sample introduction system was used to increase transport efficiency to the torch. The temperatures of the spray chamber and of the desolvator were set at 70 and 160°C, respectively. The sweep gas and nitrogen flows were fixed at 2.1 L/min and 0.16 mL/min, respectively. The acquisition scheme and data reduction technique are the same as those described in Dauphas et al. [2001].

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**Figure 1.** Molybdenum isotope spectra relative to the Earth's surface. The isotopic composition of the deep mantle (Loihi OIB) is given for comparison (broken line). (a) Mo-w isotope anomalies in the Allende CV3.2 carbonaceous chondrite [Dauphas et al., 2002a]. (b) Isotopic compositions of EH and EL enstatite chondrites.
tungsten isotopic composition of the Earth and enstatite chondrites might simply result from the decay of $^{182}$Hf in the terrestrial mantle. The $^{182}\text{W}/^{184}\text{W}$ ratios of the Earth and enstatite chondrites are taken to be 0.865000 and 0.864816 $\pm$ 0.000046 [Lee and Halliday, 2000a], respectively. The $^{180}\text{Hf}/^{184}\text{W}$ ratios of the silicate Earth and enstatite chondrites are estimated to be 13–53 [Newsom et al., 1996] and 1.1 ± 0.5 [Lee and Halliday, 2000a], respectively. In the case of a two-stage segregation model [Lee and Halliday, 1995], the $^{182}\text{Hf}/^{180}\text{Hf}$ at the time of core formation would have been 0.3 – 1.3 $\times$ $10^{-5}$. The initial 182$^{185}\text{Hf}/^{180}\text{Hf}$ of the solar system is 2.75 $\pm$ 0.24 $\times$ $10^{-4}$ [Lee and Halliday, 2000b]. Thus, the terrestrial core would have differentiated 50 ± 10 Ma after collapse of the protosolar nebula. This estimate is consistent with the timing of core formation inferred from lead isotope systematics to be 80 ± 40 Ma [Galer and Goldstein, 1996].

[13] Current modelling of planetary formation predicts that terrestrial precursors originated from a variety of heliocentric distances and that the Earth was built from the accretion of this odd assortment [Morbidelli et al., 2000]. Our opinion is that the Earth lacks a strict equivalent among available meteorites but that the enstatite model is still viable in a relaxed formulation: although distinct, the Earth shares similarities with enstatite chondrites from a chemical and isotopic point of view because both formed in the inner regions of the solar system.

[14] Acknowledgments. This work benefited from fruitful discussions with M. Javoy and U. Ott. We are grateful to M. Denise, G. Kurat, and H. Staudigel for generously donating the samples. We thank C. Zimmermann for analytical support. This work was funded by grants from the PNP (CNES/INSU) and PRISMS SMT4-C798-2220 (EC). This is contribution 1561 of the Centre de Recherches Pétrographiques et Géochimiques.

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