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MOLYBDENUM EVIDENCE FOR INHERITED PLANETARY SCALE ISOTOPE HETEROGENEITY OF THE PROTOSOLAR NEBULA

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ABSTRACT

Isotope anomalies provide important information about early solar system evolution. Here we report molybdenum isotope abundances determined in samples of various meteorite classes. There is no fractionation of molybdenum isotopes in our sample set within 0.1 ‰ and no contribution from the extinct radionuclide ^{97}Tc at mass 97 (^{97}Tc/^{92}Mo $< 3 \times 10^{-6}$). Instead, we observe clear anomalies in bulk iron meteorites, mesosiderites, pallasites, and chondrites characterized by a coupled excess in *p*- and *r*- or a mirror deficit in *s*-process nuclides (Mo-HL). This large scale isotope heterogeneity of the solar system observed for molybdenum must have been inherited from the interstellar environment where the sun was born, illustrating the concept of "cosmic chemical memory". The presence of molybdenum anomalies is used to discuss the filiation between planetesimals.

Subject headings: ISM: abundances—minor planets, asteroids—nuclear reactions, nucleosynthesis, abundances—solar system: formation

1. INTRODUCTION

Variations of isotope abundances within the solar system that depart from mass-dependent fractionation and nuclear effects may occur as a result of inheritance of presolar nucleosynthetic anomalies (Anders and Zinner 1993) and mass-independent isotope effects (Thiemens 1999). Such variations have been detected in bulk meteorite samples for a variety of elements including oxygen (Clayton 1993), sulfur (Thiemens and Jackson 1995; Farquhar et al. 2000), titanium (Niemeyer 1988), chromium (Shukolyukov and Lugmair 1998; Podosek et al. 1999), zirconium (Yin et al. 2001), molybdenum (Yin et al. 2000), and barium (Harper et al. 1992), although some of these observations need confirmation (Thiemens and Jackson 1995; Farquhar et al. 2000; Yin et al. 2001, 2000; Harper et al. 1992). These variations bear information on important subjects such as stellar nucleosynthesis, galactic chemical evolution, heterogeneity of the protosolar nebula, and filiation of planetary objects.

Molybdenum is a promising element to use to address most of these points. Indeed, unprocessed presolar carbide and graphite grains carry extreme molybdenum signatures inherited from the stellar environment where they formed (Nicolussi et al. 1998a,b; Pellin et al. 1999, 2000) and subtle nucleosynthetic anomalies have been detected in macroscopic meteorite samples (Yin et al. 2000). In addition, the *p*-process nuclide ^{97}Tc which decays by electron capture to ^{97}Mo with a mean life of 3.8 Ma may have been alive in the early solar system (Yin and Jacobsen 1998), raising the possibility that this element can be used as an extinct chronometer (Podosek and Nichols 1996). Molybdenum is a highly refractory element (Fegley et al. 1993), so it has largely avoided exchange between gas and dust in the forming solar system. Furthermore, it is a moderately siderophile element (Schmitt et al. 1989) and therefore is relatively abundant in all meteorite classes, so that possible anomalies could be used to trace the filiation between planetesimals.

2. MO-HL ISOTOPE ANOMALIES

A protocol based on solvent extraction, ion exchange, and plasma ionization mass spectrometry was developed that permits the precise and accurate determination of molybdenum isotope abundances in natural samples (Dauphas et al. 2001). The method takes advantage of the affinity of molybdenum for di(2-ethylhexyl) phosphate and AG1-X8 strongly basic anion exchanger in order to achieve fine separation of this element from interfering species (Dauphas et al. 2001; Qi-Lu and Masuda 1992a,b, 1994). Isotopic analyses were performed using a Micromass Isoprobe plasma ionization mass spectrometer. Molybdenum isotope abundances were corrected for zirconium (Nomura et al. 1983) and ruthenium (Huang and Masuda 1997) isobaric interferences by monitoring the ion beam signal at masses 91 and 99. As we were mostly interested in non mass-dependent variations, we employed an internal normalization procedure (^{98}Mo/^{96}Mo $= 1.4470$) in order to correct molybdenum isotope abundances for both natural and instrumental mass fractionation (Dauphas et al. 2001) using the exponential law (Maréchal et al. 1999). After internal normalization, no variation is observed among natural terrestrial samples, which demonstrates the reliability of the method (Dauphas et al. 2001). Molybdenum and rhenium concentrations were determined by use of the standard addition technique. Molybdenum isotopic composition is expressed in ϵ-units, which are relative deviations of the sample relative to terrestrial molybdenum isotopic composition in parts per 10^4 (‰),

$$\epsilon^i = [(^i\text{Mo}/^{96}\text{Mo})/(^i\text{Mo}/^{96}\text{Mo})_{\text{std}} - 1] \times 10^4,$$

where $i = 92, 94, 95, 96, 97, 98$, or 100. We monitored the raw ratios for mass fractionation by comparison with an external standard but found no variation in our sample set within ~ 0.1 ‰/amu (Table 1).

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The Allende CV3.2 chondrite is a Rosetta stone for deciphering early solar system evolution. We confirm (Fig. 1a) the presence of molybdenum nucleosynthetic anomalies in macroscopic samples of this meteorite (Yin et al. 2000; Yin and Jacobsen 2000). As illustrated in Fig. 1b, the anomalous isotopic composition observed in Allende may result either from a coupled enrichment in p- and r- or a mirror deficit in s-nuclides (Anders and Grevesse 1989; Burbidge et al. 1957; Cameron 1957). It has been suggested that the molybdenum composition of Allende resulted from incomplete digestion of presolar grains that bear isotopic signatures typical of s-nucleosynthesis (Yin et al. 2000). Simple calculation (Becker et al. 1987; Huss and Lewis 1995; Nicolussi et al. 1998a,b; Dauphas et al. 2001) indicates that this cannot be the case because the resulting anomalies would be more than two orders of magnitude smaller than those observed (Yin and Jacobsen 2000). This implies that anomalous molybdenum in bulk Allende must be carried by another phase that needs to be identified, possibly metal, sulfide, or oxide presolar grains. In reference to Xe-HL (Anders and Zinner 1993; Reynolds and Turner 1964; Manuel et al. 1972), we denote the coupled anomalies in p- and r-nuclides Mo-HL.

Differentiation processes homogenize isotopic compositions originally existing within parent bodies. Thus, differentiated meteorites provide a means of examining isotopic heterogeneity in the protosolar nebula at scales comparable to the regions sampled by the parent bodies, which had masses inferred from metallographic cooling rates to be $10^{16} - 10^{19}$ kg (Wood 1964; Goldstein and Ogilvie 1965; Mittlefehldt et al. 1998). For this reason, we measured molybdenum isotope abundances in iron meteorites, mesosiderites, and pallasites (Fig. 1a, top right). Most meteorite groups exhibit similar anomalies to those observed in Allende but of lesser magnitude. Because we observe no decoupling within uncertainties between the p- and r-anomalies, we cannot decide whether they result from the presence of p-, r- or the absence of s-presolar phases. In either case, the observed anomalies provide evidence for large scale inherited isotope heterogeneity of the protosolar nebula.

The stellar environments where p-, r-, and s-nucleosynthesis develop are not identical (Burbidge et al. 1957; Cameron 1957) and the host phases for these signatures are variable (Anders and Zinner 1993) so that the interstellar medium must be chemically and isotopically heterogeneous. Thus, molybdenum isotope abundances were heterogeneously distributed in the solar system parental molecular cloud and the large scale variations we observe were inherited from the interstellar environment where the sun was born, illustrating the concept of "cosmic chemical memory" (Clayton 1982).

It was suggested that there might be a heterogeneous distribution of short-lived nuclides ^{53}Mn and ^{182}Hf in the early solar system (Lugmair and Shukolyukov 1998; Lee and Halliday 2000). Instead, the discovery of inherited isotope anomalies for molybdenum may support some form of "cosmic chemical memory" for stable isotopic ratios ^{53}Cr/^{52}Cr and ^{182}W/^{184}W.

3. LIVE ^{97}TC IN THE EARLY SOLAR SYSTEM?

The positive anomaly at mass ^{97}Mo could potentially represent a radiogenic contribution from the decay of ^{97}Tc ($\tau = 3.8$ Ma) as well as a nucleosynthetic component. The ^{187}Re $-^{187}$Os system ($\tau = 62.8$ Ga) offers tempting evidence for diachronism of iron meteorite formation but the inferred chronologies are contradictory (Shen et al. 1996; Smoliar et al. 1996). The timescale inferred from the ^{53}Mn $-^{53}$Cr system ($\tau = 5.4$ Ma) is equivocal because these nuclides may have been redistributed during the extended cooling history of planetesimals. Yet, some iron meteorites have closure ages within ~ 7 Ma of Allende refractory inclusions (Hutcheon et al. 1992). The time span between metal condensation in the protosolar nebula and core crystallization in asteroids is best estimated from the ^{107}Pd $-^{107}$Ag system ($\tau = 9.4$ Ma) to be lower than 10 Ma (Chen and Wasserburg 1996). Thus, iron meteorites crystallized from a metallic magma within ~ 10 Ma of the solar system birth, when ^{97}Tc might have still been alive. Furthermore, the solid/liquid metal partition coefficient of rhenium (Fleet et al. 1999) and by inference technetium is higher than that of molybdenum (Liu and Fleet 2001), thus the Re(Tc)/Mo ratio (Yin and Jacobsen 1998) should have been extensively fractionated during metal crystallization (Table 1). The fractionation factor notation (Jacobsen and Wasserburg 1984) is employed for the Re(Tc)/Mo ratio,

$$f_{\text{Re/Mo}} = (^{185}\text{Re}/^{96}\text{Mo})/(^{185}\text{Re}/^{96}\text{Mo})_{\text{std}} - 1,$$

where the standard ratio is that of the chondritic uniform reservoir (chur), ^{185}Re/^{96}Mo $= 0.0454$ (Anders and Grevesse 1989). To test whether a significant radiogenic contribution exists on the ^{97}Mo peak, we use the fact that both ^{97}Mo and ^{100}Mo are r-nuclides, so there must be a relationship between the nucleosynthetic component at mass 97 and the anomaly at mass 100. Thus, we have corrected molybdenum isotope measurements for the nucleosynthetic contribution at mass 97 by using the observed anomaly at mass 100,

$$\epsilon^{97*} = \epsilon^{97} - (\rho^{97} - 0.5\rho^{98})/(1 - 2\rho^{98}) \times \epsilon^{100},$$

where $\rho^i = (^i\text{Mo}/^{100}\text{Mo})_r/(^i\text{Mo}/^{100}\text{Mo})_\oplus$, r and $\oplus$ denote the r-process and the Earth, respectively. The term ρ^{98} enters into the equation because ^{98}Mo/^{96}Mo is used to correct measurements for mass fractionation (Dauphas et al. 2001). It is estimated that $\rho^{97} = 0.43$ and $\rho^{98} = 0.25$, so $\epsilon^{97*} = \epsilon^{97} - 0.61 \times \epsilon^{100}$ (Arlandini et al. 1999). Rhenium is used as a proxy for technetium since these elements are likely to have very similar behavior during metal crystallization (Yin and Jacobsen 1998). If there were live ^{97}Tc when the iron meteorites formed and if all iron meteorites crystallized simultaneously (Chen and Wasserburg 1996), there should be a linear relationship (Jacobsen and Wasserburg 1984) between the radiogenic contribution at mass 97 (ϵ^{97*}) and the Re(Tc)/Mo fractionation factor ($f_{\text{Re/Mo}}$), the slope of which depends on the ^{97}Tc/^{185}Re ratio at the time of closure,

$$\epsilon^{97*} = Q\,(^{97}\text{Tc}/^{185}\text{Re})_0 \times f_{\text{Re/Mo}},$$

where $Q = 10^4 \times (^{185}\text{Re}/^{97}\text{Mo})_{\text{chur}}$, $Q \sim 791$ (Anders and Grevesse 1989). It follows from the definition of ϵ^{97*} that this relationship holds only if the Earth evolved with a chondritic Tc/Mo while ^{97}Tc was still alive. This will be true if the core formed after the extinction of ^{97}Tc, which seems to be the case (Allègre et al. 1995; Galer and Goldstein 1996; Lee and Halliday 1995; Halliday et al. 1996).

There is no correlation between $f_{Re/Mo}$ and ϵ^{97*} which indicates that ^{97}Tc was extinct when the iron meteorites formed ($^{97}Tc/^{92}Mo < 3 \times 10^{-6}$, ^{92}Mo is used for normalization because both are p-nuclides and were synthetized in the same stellar environment). This result is consistent with information retrieved from modelling of the chemical evolution of the Galaxy in the solar neighborhood (in preparation).

4. INFERENCE ON PLANETARY GENETICS

Because there is no radiogenic contribution on ^{97}Mo and because ϵ^{97} is measured much more precisely and accurately than other isotopic ratios, we used ϵ^{97} to trace the filiation between parent bodies (Fig. 2). Terrestrial rocks (stream sediments, porphyry copper millhead, and synthetic glass) are within 0.05 ‰ of the terrestrial standard value (Dauphas et al. 2001), which demonstrates that the analytical procedure is accurate. The molybdenum isotopic composition of the silicate Earth is representative of the bulk Earth value because the mantle molybdenum content is largely dominated by the component derived from the proto-Earth rather than from a late accreting veneer (Righter and Drake 1997). Within each meteorite class, measurements on various specimens are consistent with derivation from a common source, which reinforces the genetic significance of the chemical classification (Scott and Wasson 1975; Sears and Dodd 1988). On the basis of oxygen (Clayton 1993) and chromium (Shukolyukov and Lugmair 1998; Podosek et al. 1999; Shukolyukov and Lugmair 2001) isotopic ratios, a genetic relationship between Eagle Station pallasites and some carbonaceous chondrites (ES-PAL/CV) has been inferred. This link is corroborated by molybdenum isotope measurements, which demonstrates the virtue of this element for tracing the relationships between planetsimals. The isotopic data support the proposed genetic associations between type IIIAB iron meteorites, mesosiderites, and main group pallasites (II-IAB/MES/MGPAL) but do not substantiate the link between types IAB and IIICD iron meteorites (IAB/IIICD) (Mittlefehldt et al. 1998).

Further analyses must be conducted on both macroscopic samples and separated phases in order to confirm and extend molybdenum isotope taxonomy and search for the presolar carriers of Mo-HL.

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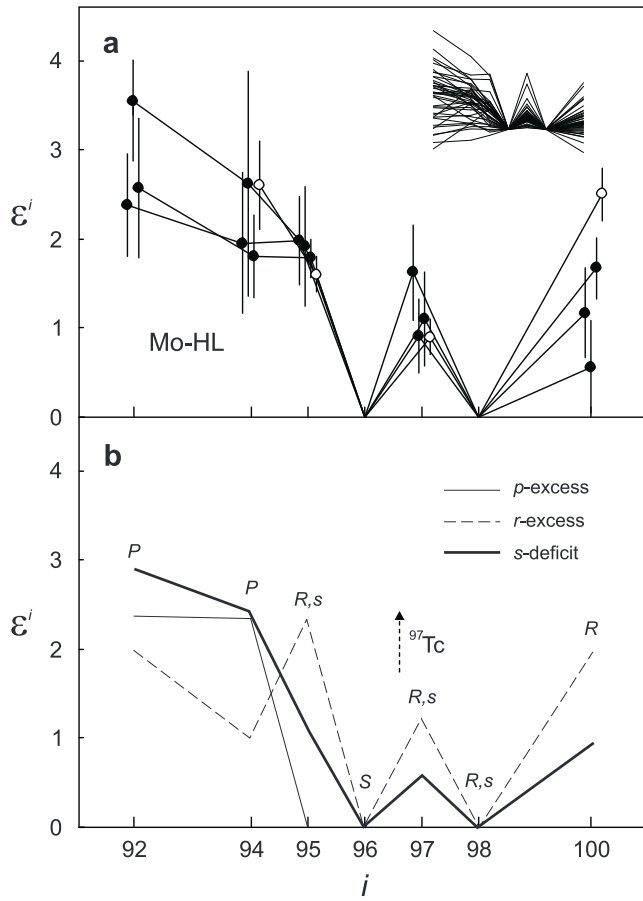
FIG. 1.— Molybdenum isotopic spectra relative to the Earth. a. Molybdenum isotope abundances in Allende [black (this study) and white (Yin et al. 2000) dots] depart from usual mass-dependent fractionation. Similar anomalies are observed in iron meteorites, mesosiderites, and pallasites (top right) which provides evidence for large scale isotopic heterogeneity of the protosolar nebula. The top curves of the inset are those of Allende. The isotopic spectrum we observe is denoted Mo-HL in reference to Xe-HL (Anders and Zinner 1993; Reynolds and Turner 1964; Manuel et al. 1972). Uncertainties are 2 . b. Synthetic spectra obtained by adding or substracting pure p, r, and s nucleosynthetic abundances (Arlandini et al. 1999). The nucleosynthetic sources (Burbidge et al. 1957; Cameron 1957; Anders and Grevesse 1989) of the different nuclides are indicated. There is a possible contribution at mass 97 from the decay of now extinct ^{97}Tc (= 3:8 Ma). The spectrum closest to observations is that corresponding to a deficit in s- or a mirror excess in p- and r- nuclides.
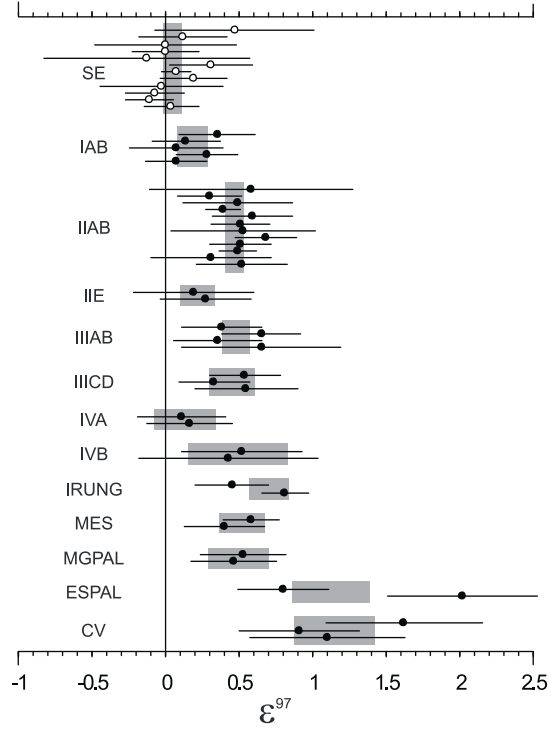
Fig. 2.— Molybdenum isotope taxonomy. SE-silicate Earth (Dauphas et al. 2001). IAB/IRUNG-iron meteorite. MES-mesosiderite. MGPAL/ESPAL-pallasite. CV-carbonaceous chondrite. The shaded rectangles are the mean composition for each group. Uncertainties are 2 .

TABLE 1

MOLYBDENUM ISOTOPE MEASUREMENTS

#	Class	[Mo] (ppm)	†Re=Mo	92	94	95	96	97	98	100	h /amu
Bitburg	IAB	6:9 0:7	< 0:8	1:20 1:62	0:34 0:81	0:15 0:40	0	0:35 0:26	0	0:49 0:77	0:01 0:16
Bitburg	IAB	6:9 0:7	< 0:8	0:15 0:72	0:22 0:42	0:10 0:32	0	0:14 0:23	0	0:11 0:22	0:04 0:21
Canyon Diablo	IAB	5:1 0:8	0:05 0:04	0:48 0:90	0:39 0:49	0:21 0:54	0	0:07 0:32	0	0:17 0:28	0:34 0:17
Canyon Diablo	IAB	5:1 0:8	0:05 0:04	0:59 0:82	0:45 0:58	0:33 0:38	0	0:28 0:21	0	0:21 0:44	0:08 0:16
Canyon Diablo	IAB	5:1 0:8	0:05 0:04	0:19 1:35	0:01 0:45	0:00 0:33	0	0:07 0:21	0	0:28 0:64	0:12 0:27
Braunau	IIAB	7:6 0:1	1:05 0:11	2:50 0:93	1:54 0:71	0:28 0:78	0	0:58 0:69	0	0:29 0:83	0:09 0:16
Braunau	IIAB	7:6 0:1	1:05 0:11	1:53 0:77	1:90 0:83	0:83 0:40	0	0:30 0:22	0	0:26 0:41	0:04 0:17
Coahuila	IIAB	7:5 0:5	2:39 0:18	2:15 0:92	1:11 0:27	0:39 0:33	0	0:49 0:37	0	0:39 0:26	0:17 0:16
Coahuila	IIAB	7:5 0:5	2:39 0:18	1:29 0:75	1:41 0:99	0:71 0:37	0	0:39 0:12	0	0:51 0:16	0:00 0:16
Coahuila	IIAB	7:5 0:5	2:39 0:18	0:77 1:79	0:70 1:43	0:74 0:74	0	0:59 0:27	0	0:46 0:55	0:01 0:16
Guadalupe Y Calvo	IIAB	7:0 0:4	6:41 0:37	1:56 0:39	1:48 0:56	0:69 0:28	0	0:51 0:20	0	0:25 0:22	0:05 0:17
Guadalupe Y Calvo	IIAB	7:0 0:4	6:41 0:37	0:03 0:87	0:93 0:88	0:47 0:46	0	0:53 0:49	0	0:08 0:70	0:23 0:45
Guadalupe Y Calvo	IIAB	7:0 0:4	6:41 0:37	1:31 0:60	1:19 0:48	0:66 0:39	0	0:68 0:21	0	0:15 0:26	0:02 0:18
Scottsville	IIAB	6:8 0:8	8:46 0:47	1:57 0:62	1:06 0:57	0:43 0:23	0	0:51 0:21	0	0:06 0:26	0:06 0:19
Scottsville	IIAB	6:8 0:8	8:46 0:47	2:07 0:85	1:59 0:50	0:83 0:25	0	0:49 0:13	0	0:23 0:30	0:02 0:16
Sikhote-Alin	IIAB	5:9 0:5	< 0:8	1:15 1:10	0:86 0:85	0:30 0:64	0	0:31 0:41	0	0:48 0:44	0:07 0:20
Sikhote-Alin	IIAB	5:9 0:5	< 0:8	1:66 1:23	1:34 0:35	0:82 0:36	0	0:52 0:31	0	0:23 0:66	0:08 0:24
Mont Dieu	IIE	6:8 0:4	0:02 0:05	1:47 0:64	1:18 0:44	0:66 0:29	0	0:19 0:15	0	0:18 0:41	0:01 0:16
Mont Dieu	IIE	6:8 0:4	0:02 0:05	1:21 0:89	0:91 0:42	0:97 0:26	0	0:27 0:19	0	0:84 0:48	0:28 0:39
Cape York	IIIAB	6:3 0:1	0:32 0:07	1:34 0:54	1:00 0:54	0:45 0:15	0	0:38 0:27	0	0:16 0:30	0:06 0:17
Cape York	IIIAB	6:3 0:1	0:32 0:07	2:87 0:76	1:81 0:52	0:88 0:36	0	0:65 0:27	0	0:26 0:26	0:05 0:16
Henbury	IIIAB	8:6 2:4	2:96 0:20	1:70 1:55	0:88 0:59	0:09 0:54	0	0:35 0:30	0	0:02 0:81	0:07 0:17
Henbury	IIIAB	8:6 2:4	2:96 0:20	0:81 2:11	0:78 0:77	0:22 1:08	0	0:65 0:54	0	1:07 1:17	0:07 0:18
Magnesia	IIICD	7:4 0:9	< 0:8	1:88 0:61	1:28 0:48	0:58 0:31	0	0:54 0:24	0	0:01 0:33	0:08 0:15
Magnesia	IIICD	7:4 0:9	< 0:8	0:70 1:92	0:22 0:96	0:18 0:38	0	0:33 0:24	0	0:06 0:91	0:25 0:31
Magnesia	IIICD	7:4 0:9	< 0:8	1:32 1:41	1:30 0:98	0:74 0:50	0	0:55 0:35	0	0:11 0:56	0:04 0:16
Gibeon	IVA	5:7 0:1	0:27 0:04	0:84 0:71	0:97 0:77	0:75 0:25	0	0:11 0:30	0	0:21 0:36	0:01 0:17
Gibeon	IVA	5:7 0:1	0:27 0:04	0:44 1:28	0:50 0:78	0:70 0:32	0	0:16 0:29	0	0:04 0:26	0:01 0:19
Cape of Good Hope	IVB	25:0 0:2	1:58 0:13	2:05 1:26	1:80 0:60	0:86 0:59	0	0:52 0:41	0	0:38 0:65	0:06 0:17
Cape of Good Hope	IVB	25:0 0:2	1:58 0:13	1:75 0:49	1:21 0:16	0:99 0:24	0	0:43 0:61	0	0:68 1:11	0:06 0:34
Grand Rapids	IRUNG	11:5 0:1	1:07 0:10	1:28 0:62	1:15 0:40	0:89 0:25	0	0:45 0:25	0	0:48 0:36	0:09 0:17
Grand Rapids	IRUNG	11:5 0:1	1:07 0:10	0:40 0:70	0:21 0:68	0:73 0:24	0	0:81 0:16	0	0:60 0:31	0:04 0:16
Estherville	MES			1:90 0:62	1:64 0:55	1:00 0:30	0	0:58 0:19	0	0:17 0:50	0:03 0:25
Estherville	MES			0:52 1:42	0:98 0:83	0:60 0:56	0	0:40 0:27	0	0:30 0:48	0:18 0:23
Imilac	MGPAL			0:22 1:97	0:09 1:60	0:09 0:74	0	0:53 0:29	0	0:67 0:79	0:05 0:17
Imilac	MGPAL			0:08 1:58	0:18 1:26	0:04 0:73	0	0:46 0:29	0	1:10 0:48	0:12 0:18
Eagle Sation	ESPAL			1:57 0:42	1:21 0:53	0:86 0:35	0	0:80 0:31	0	0:84 0:30	0:03 0:16
Eagle Sation	ESPAL			0:43 1:55	1:43 1:24	1:35 0:55	0	2:02 0:51	0	1:54 0:68	0:03 0:17
Allende	CV			2:38 0:57	1:95 0:79	1:98 0:50	0	1:62 0:53	0	1:17 0:50	0:06 0:38
Allende	CV			3:54 0:67	2:62 1:26	1:92 0:67	0	0:91 0:41	0	0:56 0:52	0:17 0:23
Allende	CV			2:57 0:78	1:80 0:46	1:78 0:21	0	1:10 0:53	0	1:67 0:34	0:04 0:16

Note. — Molybdenum isotope measurements (Dauphas et al. 2001). †$_{Re=Mo}$ is the Re/Mo fractionation factor, ^{i} represents the molybdenum isotopic composition after internal normalization, and is the composition after external normalization of raw $^{98}Mo=^{96}Mo$ ratios. All uncertainties are 2 .