MOLYBDENUM ISOTOPIC COMPOSITION OF IRON METEORITES, CHONDRITES AND REFRACTORY INCLUSIONS

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Introduction. Recent Mo isotopic studies of meteorites reported evidence for differences in isotopic compositions for whole rocks of some primitive [1-3] and differentiated meteorites [2,4], relative to terrestrial materials. Enrichments of *r*- and *p*-process isotopes of up to 3-4 ε units (ε unit = parts in 10^4) over *s*-process dominated isotopes are the most prominent features. Certain types of presolar grains show large enrichments in *s*-process isotopes [5], however, it was concluded on grounds of mass balance that incomplete digestion of such grains cannot explain the enrichments of of *r*- and *p*-process isotopes in whole rocks of primitive chondrites [2]. If the reported variability in *r*- and *p*-process isotope enrichments reflects the true isotopic characteristics of the whole rocks, the implications are quite profound. It would suggest the presence of large scale Mo isotopic heterogeneity within the solar accretion disk with likely collateral effects for other elements. However, such effects were not found for Ru isotopes [6,7], nor for Zr isotopes [8]. Another recent Mo isotopic study by multi collector ICP-MS could not confirm the reported deviations in Allende, Murchison or iron meteorites [9]. Here, we present new results for the Mo isotopic composition of iron meteorites, chondrites and CAIs obtained by negative thermal ionization mass spectrometry (N-TIMS). We discuss analytical aspects and the homogeneity of Mo isotopic compositions in solar system materials.

Analytical Techniques. Iron meteorites (1-2.7 g) were dissolved in conc. HCl. Chondrites (~1g) were digested overnight at 235°C using reverse aqua regia in borosilicate Carius tubes. CAIs were also digested in Carius tubes and Mo was collected during Re separation by solvent extraction. Molybdenum was separated from sample matrices by a three-step ion exchange procedure using HF-HCl on AG1-X8 resin and HCl on AG50-X8 resin. Molybdenum was loaded on outgassed Re filaments, metalized for 1 h, and covered with La nitrate. Mo isotopic compositions were measured on the UMD Sector 54 multi collector TIMS in the form of MoO_3^-, at 1370-1420°C, and corrected for oxygen isotopic compositions. Signal intensities were 200-1900 mV for Mo standards, and 100-900 mV for samples on mass 146 (^{98}Mo). Data were collected in two cycles. In the first cycle all Mo isotopes were measured. In the second cycle, Ru interferences were monitored on mass 149 ($^{101}RuO_3^-$). Mass discrimination was corrected using the exponential law and a value of $^{92}Mo/^{98}Mo = 0.607898$, consistent with $^{94}Mo/^{98}Mo = 0.3802$ proposed by [10]. The $^{92}Mo/^{98}Mo$ ratio was chosen because it covers the large mass range necessary to obtain accurate mass bias corrections on other Mo isotopes. The Ru interference ($^{101}Ru/^{95}Mo = 0.000068 \pm 18$) required corrections of 0.2, 0.05, and 0.8 ε units on ^{96}Mo, ^{98}Mo, and ^{100}Mo, respectively. No interferences from Zr isotopes were detected. Filament blanks for Mo range between 0.5 and 0.9 ng. Carius tube blanks were 5-6 ng. Chemistry blanks range between 2 and 3 ng. Total blanks are insignificant for the present study because minimum quantities of processed meteoritic Mo were near 1 µg.

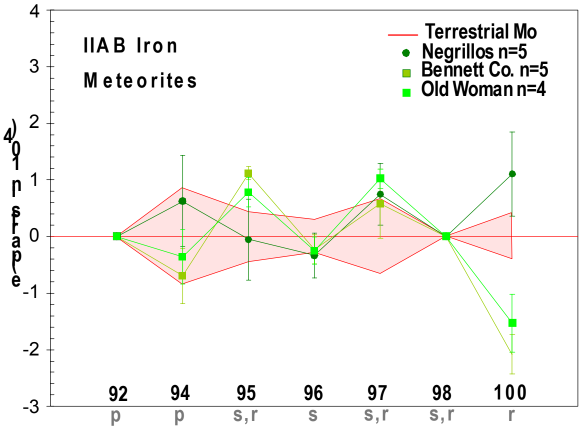

Fig. 1. Isotopic composition of Mo in IIAB iron meteorites, normalized to terrestrial Mo measured at UMD and displayed as deviations in ε units. Data are means of multiple analyses. Uncertainties are $2\sigma_m$.

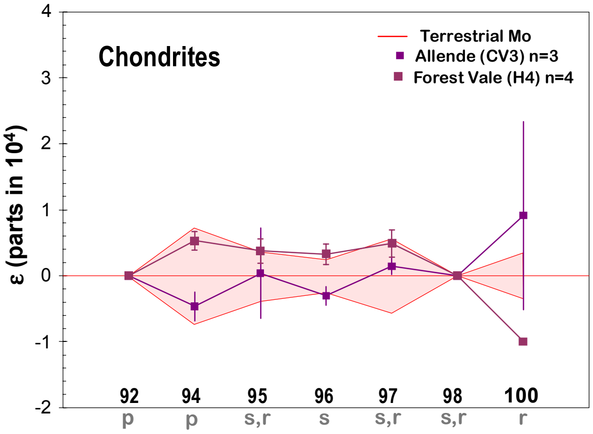

Fig. 2. Mo isotopic composition of chondrites Allende (CV3) and Forest Vale (H4), normalized like in Fig. 1. Data are means of multiple analyses. Uncertainties are $2\sigma_m$.

Mo standard. The isotopic composition and external precisions for a terrestrial Mo ammonium molybdate solution from Fisher (140-1000 ng of Mo on the filament) was monitored between 7/1999 and 7/2002 (n = 35) and represents our primary reference material. External precisions (2σ in ε units) over this period are ±1.68 ($^{94}Mo/^{98}Mo$), ±1.75 ($^{95}Mo/^{98}Mo$), ±0.89 ($^{96}Mo/^{98}Mo$), ±1.87 ($^{97}Mo/^{98}Mo$), and ±2.59 ($^{100}Mo/^{98}Mo$). These precisions can be improved by a factor of two by multiple analysis of samples and standards

($2\sigma_m$, n=4-6) over shorter periods of time (see Figs. 1-3). Our results for the Mo isotopic composition of the ammonium molybdate solution overlap within 1.5 ε units with the data by Qi-Lu and Masuda [10], who used ^{94}Mo/^{98}Mo for normalization. We noted somewhat larger differences up to 2.5 ε units on the high mass side compared to the study by [1], who used ^{98}Mo/^{96}Mo for normalization.

Iron meteorites. In Fig. 1, the mean Mo isotopic compositions of multiple runs of Group IIAB magmatic iron meteorites are plotted as deviations in ε units from the mean of the Fisher Mo standard. Except for ^{100}Mo, the data for Negrillos, Bennett County and Old Woman overlap with terrestrial Mo within ±1 ε unit. Negrillos shows a slight positive deviation for ^{100}Mo compared to the Mo standard, although with a large uncertainty, while Bennett County and Old Woman show resolvable negative deviations by –2.1 and –1.5 ε units, respectively.

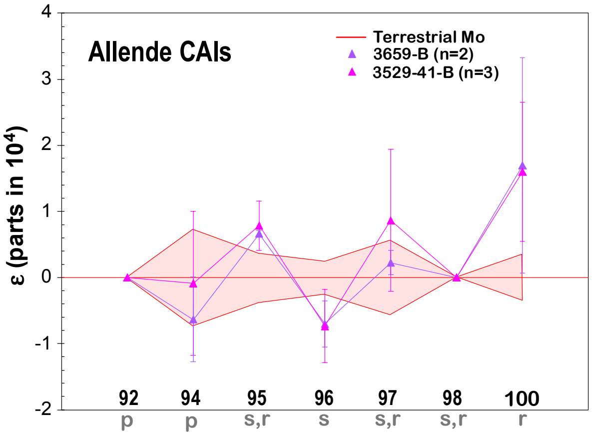

Fig. 3. Mo isotopic composition of CAIs from Allende, normalized like in Fig. 1. Data are means of multiple analyses. Uncertainties are $2\sigma_m$.

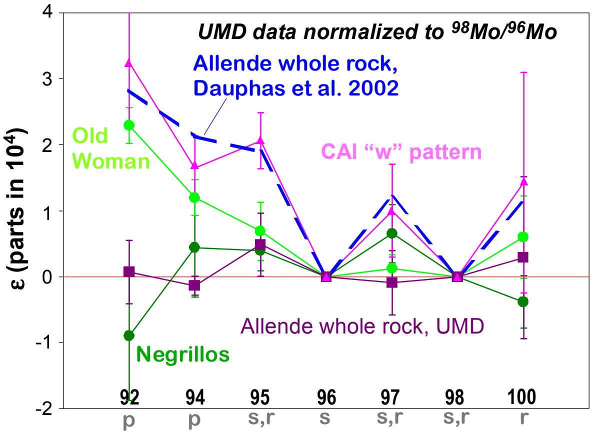

Fig. 4. Selected samples from Figs. 1-3, renormalized to ^{98}Mo/^{96}Mo.

Chondrites and CAIs. Fig. 2 shows the Mo isotopic composition for multiple analyses of the carbonaceous chondrite Allende (CV3) and the ordinary chondrite Forest Vale (H4). With the exception of ^{100}Mo, the chondrite data overlap with terrestrial Mo at the ± 1ε level or better. Forest Vale shows a resolvable deviation of –1.0 ε for ^{100}Mo, relative to the Mo standard. Mo isotopic data for two CAIs from Allende overlap with terrestrial Mo within ±1 ε unit (Fig. 3). The data for ^{100}Mo are also consistent with a slight positive deviation of +1.5 ε, however, with large uncertainties.

Discussion. With the exception of ^{100}Mo, the Mo isotopic composition of the meteorites and CAIs analyzed here overlap with terrestrial Mo within ±1 ε unit, when normalized to ^{92}Mo/^{98}Mo. Analysis of our data shows that ε^{100}Mo for individual sample runs correlate negatively with the fractionation factor β. Run conditions for Negrillos (positive ε^{100}Mo) were significantly different from Old Woman and Bennett County (negative ε^{100}Mo). ^{100}Mo is the only Mo isotope outside the mass range used for normalization, and hence, may yield the least accurate results. Our results on IIAB iron meteorites and the Allende whole rock show no evidence for a +1.0 to +2.6 ε unit enrichment in *p*-process ^{94}Mo, relative to pure s-process ^{96}Mo [1,2]. In Fig. 4, we show some of our data normalized to ^{98}Mo/^{96}Mo. We note large discrepancies for light Mo isotopes in some samples. CAI 3529-41-B shows a "w"-pattern that has been noted for Allende whole rock and some differentiated meteorites in studies that normalized data to ^{98}Mo/^{96}Mo [1,2]. Using this normalization, Old Woman (and Bennett Co., not shown) displays resolvable positive deviations for ^{92}Mo (+2.3 ε) and ^{94}Mo (+1.2 ε). In contrast, Negrillos is close to terrestrial Mo, but with a slightly negative ^{92}Mo. Even for the different normalization, our Allende whole rock shows a normal isotopic composition. Run conditions in this case more closely matched those for the standards. The variable results for different normalization ratios indicate a potential for analytical biases, depending on what the run conditions were (fractionation factors) and which normalizing ratio was chosen. Because of the larger mass range, ^{92}Mo/^{98}Mo may provide a more accurate mass bias correction for the light Mo isotopes than ^{98}Mo/^{96}Mo, particularly, in cases where run conditions for samples and standards diverge.

The new Mo isotopic data yield no conclusive evidence for large-scale and systematic isotopic heterogeneities in the inner solar system at the 1-3 ε level for elements in the mass range near A = 100. These results are consistent with Ru and Zr isotopic data [6-8].

This work was partially supported by NASA grant NAG 54769. We thank R. Clarke and G. MacPherson of the USMNH for providing the meteorite samples.

References. [1] Yin, Q. et al. *Nature* 415, 881, 2002; [2] Dauphas, N. et al. *Ap. J.* 565, 640, 2002; [3] Dauphas, N. et al. *Lunar and Planetary Science* XXXIII, Abstr. 1198, 2002; [4]; Masuda, A. & Qi-Lu *61th Meteoritical Society Meeting*, Abstr. 5010, 1998; [5] Nicolussi, G. et al. *Geochim. Cosmochim. Acta* 62, 1093, 1998; [6] Becker, H. and Walker, R. J., *Lunar and Planetary Science* XXXIII, Abstr. 1018, 2002; [7] Becker, H. & Walker, R. J., *Chemical Geology* in press, 2003; [8] Schönbächler, M. et al. *Lunar and Planetary Science* XXXIII, Abstr. 1283, 2002; [9] Lee, D-C. & Halliday, A. N. *65th Meteoritical Society Meeting*, Abstract 5135, 2002; [10] Qi-Lu & Masuda, A. *Int. J. Mass Spectrom. Ion Proc.* 130, 65, 1994.