

MASS-INDEPENDENT ISOTOPE FRACTIONATION OF MOLYBDENUM AND RUTHENIUM IN MURCHISON. T. Fujii^{1,2}, F. Moynier², P. Telouk², and F. Albarède², ¹ Research Reactor Institute, Kyoto University, 2-1010 Asashiro Nishi, Kumatori, Sennan Osaka 590-0494, Japan (tosiyuki@HL.rri.kyoto-u.ac.jp), ² Laboratoire de Sciences de la Terre, UMR 5570 CNRS, Ecole Normale Supérieure de Lyon, 46, Allée d'Italie, 69364 Lyon Cedex 7, France.

Introduction: Dauphas et al. [1] and Yin et al. [2] reported molybdenum isotopic anomalies in bulk undifferentiated and differentiated meteorites and this was the first time that isotopic anomalies were found on the scale of a meteorite hand-specimen. Even more recently, Chen and Papanastassiou [3,4] identified ruthenium isotopic anomalies in meteorites. Dauphas et al. [5] used theoretical production ratios in stars to show that Mo and Ru isotopic anomalies correlate as predicted by nucleosynthetic models and concluded that such a correlation demonstrates the nucleosynthetic origin of the isotopic anomalies. The predicted correlation, however, fails for one sample, the Murchison CM3 chondrite, and the present study suggests a new mechanism to account for this discrepancy. This mechanism appeals to non-mass dependent isotopic fractionation processes, which Bigeleisen [6] ascribes to the finite size of the nucleus (nuclear field shift effect). A number of experiments mostly involving solvent extraction and liquid chromatography confirmed the existence of the mass-independent effects predicted by the nuclear field shift effect (see references in [7])

In the present work, we present experimental evidence of chemical mass-independent isotope fractionation for both Mo and Ru. Then, the nuclear field shift theory is applied to the actual isotopic anomalies found in Murchison.

Experiments and Results: Molybdenyl dichloride (MoO_2Cl_2) was dissolved in HCl to produce 0.1 M Mo(VI) solutions at various strength of HCl normalities. The organic phase was 0.1 M DC18C6 (Dicyclohexano-18-crown-6) in 1,2-dichloroethane. Aqueous and organic solutions were contacted (295 ± 0.5 K) in a glass vial, and after the equilibrium, the two phases were separated by centrifugation. An aliquot of the supernatant aqueous solution was taken for concentration determination. Mo was subsequently purified from leftover traces of organic materials left by the DC18C6 solution by employing an anion-exchange chromatographic separation. A solution containing 200 ppb Mo in 0.05 M HNO_3 was prepared for mass spectrometric analysis. Isotopic ratios of Mo in all samples were analyzed with the MC-ICPM-MS Nu plasma 500 HR coupled with a desolvating nebulizer Nu DSN-100. The instrumental mass bias was controlled by bracketing each sample with the unprocessed Mo solution. Isobaric interferences with Zr and Ru were below the detection limit of the mass spectrometer. The isotopic

ratios are reported as deviations of the measured values.

Hydrated ruthenium trichloride was dissolved in HCl to produce 0.07 M Ru(III) solutions at various HCl strengths. The details of the extraction procedure and purification from organic impurities follow those described for Mo. A solution containing 70 ppb Ru in 0.2 M HNO_3 was created for isotopic analysis. The measurement protocol of isotope ratio was same with the case of Mo. Isobaric interferences with Pd and Mo were below the detection limit of the mass spectrometer.

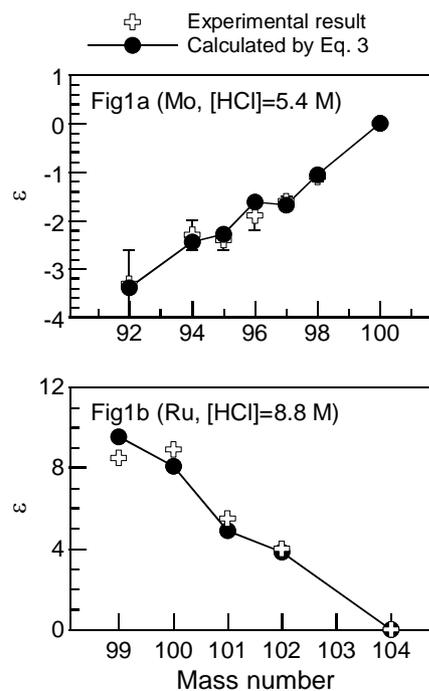
Let us define the isotope separation factor α as

$$\alpha_{m,m'} = ([^m\text{M}]/[^m\text{M}])_{\text{org}} / ([^m\text{M}]/[^m\text{M}])_{\text{aq}} \quad (1)$$

where m' and m indicate masses of light isotope and heavy isotope, respectively. $([^m\text{M}]/[^m\text{M}])_{\text{org}}$ and $([^m\text{M}]/[^m\text{M}])_{\text{aq}}$ are the isotope ratios of ^mM ($\text{M} = \text{Mo}$ or Ru) relative to ^mM found in the organic and aqueous phases, respectively. ($m = 100$ for Mo and 104 for Ru).

The isotope enrichment factor ε is defined as

$$\varepsilon_{m,m'} = (\alpha_{m,m'} - 1) \times 10,000 \quad (2)$$



The isotope enrichment factors between the organic and the aqueous phases are shown in ε units in Figure 1ab (representative examples). Substantial ($> 0.2 \varepsilon$

unit) deviation from the linearity indicates mass-independent isotope fractionation. The acidity dependence of mass-independent property was observed in this study. The even atomic mass isotopes show mostly mass-dependent fractionation, whereas the odd atomic mass isotopes show a breakdown of the mass-dependent law.

Discussion: Bigeleisen shows that the isotope fractionation factor α in the presence of field effect can be expressed as:

$$\ln \alpha = \left(\frac{hc}{kT} \right) f_s \times A + \frac{1}{24} \left(\frac{h}{2\pi kT} \right)^2 \left(\frac{1}{m'} - \frac{1}{m} \right) \times B \quad (3)$$

(detail of theory can be seen elsewhere [6]). We fitted the theoretical ϵ values to the experimental isotopic variations and Figure 1 shows that the observations are correctly explained by Bigeleisen's theory of non-mass dependent fractionation.

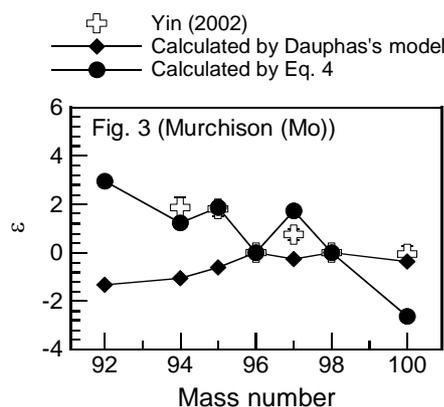
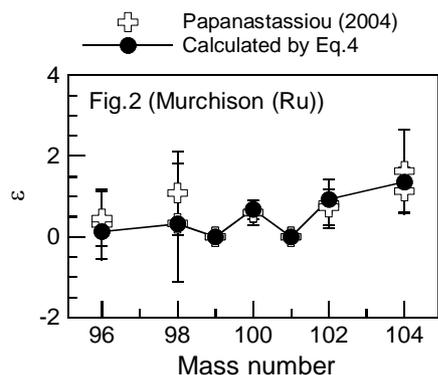
We apply Bigeleisen's theory to ϵ 's found in meteorites, in which the isotopic variations are normalized by using a standard value for an isotope ratio. Under a constant temperature, Eq. 3 can be simplified as [8],

$$\epsilon_{m,m_i} = 10^4 \times \left(\delta \langle r^2 \rangle_{m_1,m_i} - \frac{m_2(m_i - m_1)}{m_1(m_2 - m_1)} \delta \langle r^2 \rangle_{m_1,m_2} \right) \times a \quad (4)$$

in which m_1 and m_2 are masses of isotopes using for normalization (e.g., $m_1=96$ and $m_2=98$ for Mo, and $m_1=101$ and $m_2=99$ for Ru) and a an adjustable parameter. $\langle r^2 \rangle$ is the mean-square charge radius.

We explain the Ru isotopic pattern observed in a carbonaceous chondrite, Murchison [4]. Figure 2 shows the observed isotopic variations and the calculated values. The agreement for Murchison with our predicted values is, in general, excellent. A possible exception is an excess of ^{98}Ru which may reveal the presence of live ^{98}Tc ($T_{1/2} = 4.2$ My); the abundance of ^{98}Ru is, however, very small (1.86 percent) and, at least for Murchison, the error bar makes this anomaly probably insignificant. In addition, ^{98}Tc is shielded and as pointed by Becker et al. [9], the fractionation of the Re/Ru ratio (a proxy for Tc/Ru) in carbonaceous chondrites is < 2 [10,11]. ^{98}Ru anomalies are therefore expected to be difficult to detect. Dauphas et al. [5] proposed a model in which Mo and Ru nucleosynthetic anomalies are correlated. We attempted to use their model on Ru and Mo data on Murchison [2,4] (Figure 3). The ^{92}Mo abundance can be predicted from the observed ^{100}Ru abundance [4,5] and, from there on, all the Mo isotopic abundances predicted by their model can be inferred. In particular, negative ^{100}Ru anomalies should be associated with positive Mo anomalies at masses 94, 95, 97, and 100 (Figures 1 and 3 in [5]). The positive ^{100}Ru anomaly of Murchison ($\sim 0.6 \pm 0.2$, [4]) shows that this meteorite is a notable exception; it

supports our suggestion that the Ru isotopic anomalies found in this meteorite result from the nuclear field shift effect and not from nucleosynthetic processes.



As shown in Figure 3., the nuclear field-shift theory accounts for isotopic abundances at mass 95 (in addition to 96 and 98) but still leaves positive anomalies at mass 94 and particularly at mass 100. As discussed in references [1,2], these anomalies reveal the presence of a p -process component at mass 94 and of a r -process component at mass 100, the most abundant r -process Mo. As for the mass 97, taking the nuclear field-shift effect into account makes the anomaly *negative* instead of positive as previously found [1,2], which has been suggested that ^{97}Mo anomaly may attest to the presence of live ^{97}Tc ($T_{1/2} = 3.8$ My) while the last Tc/Mo fractionation took place.

References: [1] Dauphas N. et al. (2002) *Ap. J.*, 565, 640-644. [2] Yin Q. et al. (2002) *Nature*, 415, 881-883. [3] Chen J. H. et al. *LPS XXXIV*, Abstract #1789. [4] Papanastassiou D. A. *LPS XXXV*, Abstract #1828. [5] Dauphas N. et al. (2004) *EPSL*, 226, 465-475. [6] Bigeleisen J. (1996) *JACS*, 118, 3676-3680. [7] Fujii T. et al. (2002) *JPC A*, 106, 6911-6914. [8] Fujii et al. *submitted*. [9] Becker H. and Walker R. J. (2003) *CG*, 196, 43-56. [10] Jochum K. P. et al. (1996) *GCA*, 60, 3353-3357. [11] Horan M. F. et al. (2003) *CG*, 196, 5-20.