

MASS-INDEPENDENT ISOTOPE FRACTIONATION OF CHROMIUM IN LIGAND EXCHANGE REACTION AND REDOX REACTION. T. Fujii¹, F. Moynier², and Q-Z. Yin², ¹Research Reactor Institute, Kyoto University, 2-1010 Asashiro Nishi, Kumatori, Sennan Osaka 590-0494, Japan (tosiyuki@HL.rr.i.kyoto-u.ac.jp), ²Department of Geology, University of California Davis, One Shields Avenue, Davis CA, 95616.

Introduction: Recently, the classic theory of stable isotope fractionation of the Bigeleisen-Mayer equation [1] has been expanded by the original author to include the mass-independent term named the nuclear field shift effect [2]. The improved theory successfully explained the observed non-linear isotope effect on ²³⁵U in a chemical exchange system [2]. Since then, researchers have applied the new Bigeleisen theory to explain other unusual isotope effects (see, e.g. [3] and references therein). How such mass independent isotopic fractionation would affect interpretations of isotopic anomalies observed in the primitive meteorites were discussed subsequently by [4,5]. The matter clearly requires further attention. In this context, we conducted experiments to verify the magnitude of the mass-independent isotope fractionation induced by laboratory experiments. We present experimental evidence of the mass-independent isotope fractionation of Cr in a ligand exchange reaction and a redox reaction (electron exchange reaction).

We chose Cr as our target element for the following reason: first, because of its magic number neutrons $N=28$, ⁵²Cr has the smallest nuclear charge radius [6] among the stable chromium isotopes, ⁵⁰Cr, ⁵²Cr, ⁵³Cr, and ⁵⁴Cr (see Fig. 1). This pronounced nuclear property of Cr makes it a most favorable element in the periodic table for identification of non-linear isotopic effect in chemical systems; second, Cr plays an increasingly important role in modern isotope cosmochemistry and geochemistry. ⁵³Mn-⁵³Cr system ($T_{1/2}=3.7$ Myr) has been successfully applied as a high resolution chronometer in the early solar system [7-10]. ⁵⁴Cr anomalies observed in primitive meteorites and planetary bodies [9,10] are now accepted as widespread nebula wide phenomena. There are some unresolved issues in Cr isotope cosmochemistry, however. For example ⁵⁴Cr anomalies were observed by one laboratory [9] but not by the other [7] in the same materials thought to come from Vesta. Whether ⁵³Cr anomalies reflect heterogeneous distribution of ⁵³Mn in the solar nebula, Mn/Cr fractionation, or ⁵³Cr heterogeneity is still to be understood [7]. How chemical mass-independent fractionation a la Bigeleisen may affect Cr isotope systematics is an important question to be addressed.

Experimental: Experiment (a) Liquid-liquid extraction with macrocyclic compounds is known to be effective to show larger chemical isotope fractionation

[3]. Hydrated chromium trichloride ($\text{CrCl}_3 \cdot \text{H}_2\text{O}$, 99.99% purity) was dissolved in HCl to produce 0.36 mol/L (M) Cr(III) solutions at various strength of HCl. The organic phase was 0.1 M DC18C6 (dicyclohexano-18-crown-6) in 1,2-dichloroethane. Aqueous and organic solutions were contacted (297 ± 0.5 K) in a glass vial, and after the equilibrium, the two phases were separated by centrifugation. Cr in the organic phase was back extracted into pure H₂O and was analyzed by ICP-AES to determine the distribution ratio ($D \sim 10^{-5}$). The leftover Cr in the back-extracted water solution was further purified by employing a cation-exchange chromatographic separation. A solution containing 400 ppb Cr in 0.1 M HNO₃ was prepared for mass spectrometric analysis. Isotopic ratios of ⁵⁰Cr/⁵²Cr and ⁵³Cr/⁵²Cr were analyzed with a Nu Plasma HR-MC-ICP-MS at UC Davis coupled with a desolvating nebulizer, Nu DSN-100. The instrumental mass bias was controlled by bracketing each sample with the unprocessed Cr solution under identical condition. Isobaric interferences with Ti and V were below the detection limit of the mass spectrometer.

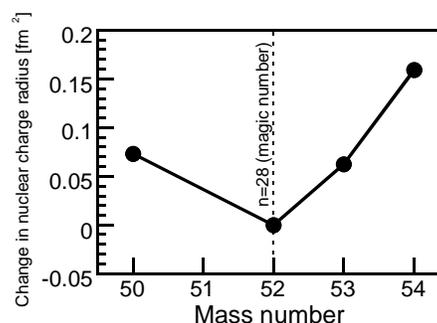


Fig. 1 Variations of nuclear charge radius vs mass number for Cr stable isotopes.

Experiment (b) Pyrometallurgical bi-phase extraction, a reprocessing technique in nuclear science [11], is the redox system at high temperature investigated in this study. Anhydrous CrCl_3 (99.99% purity) was dissolved in LiCl-KCl eutectic and this was contacted with liquid zinc (Zn metal, 99.999% purity) in a quartz tube at temperatures of 723K, 873K, and 1023K. Cr(III) in the molten salt phase was reduced and extracted by metallic Zn. After achieving the extraction equilibrium (after 24 hours), the molten salt phase was drawn into a quartz tube for analysis. The extraction experiment was carried out in a glove box filled with dry Ar continuously purified to remove oxygen and humidity. The O₂ and H₂O contents were maintained

to less than 1 ppm. The Cr in the drawn salt sample was analyzed by ICP-AES (>99% Cr was extracted). The purification of Cr and its isotopic analysis were performed using the same protocol of experiment (a).

Results and discussion: The isotope fractionation factor α_m ($m=50$ or 53) is defined as

$$\alpha_m = ([^m\text{Cr}]/[^{52}\text{Cr}])_X / ([^m\text{Cr}]/[^{52}\text{Cr}])_Y \quad (1)$$

where X and Y stand for organic phase and aqueous phase for experiment (a) and molten salt phase and liquid metal phase for experiment (b). Because of the extreme distribution coefficient D , $([^m\text{Cr}]/[^{52}\text{Cr}])_Y$ can be replaced by $([^m\text{Cr}]/[^{52}\text{Cr}])_{\text{init}}$, where *init* refers to the starting composition. $\delta^m\text{Cr}$ is defined as

$$\delta^m\text{Cr} = (\alpha_m - 1) \times 1,000 \quad (2)$$

We present isotopic anomaly found in ^{53}Cr in ϵ unit. ϵ_{53} is defined as parts per 10,000 deviation from the mass dependent line. A mass-independent isotope fractionation was observed for both systems, as a function of acidity in experiment (a), and a weak temperature dependency in experiment (b). We have thus experimentally demonstrated the existence of mass-independent isotope fractionation of Cr in both ligand exchange reaction and redox reaction.

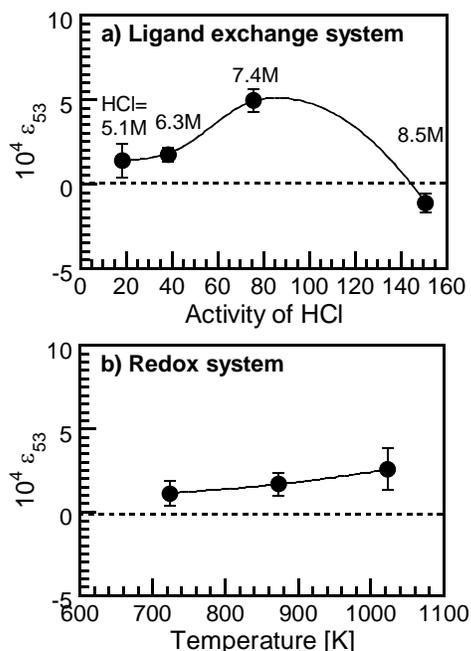


Fig.2. Mass-independent isotope fractionation of ^{53}Cr

The conventional mass-dependent theory of the Bigeleisen-Mayer equation [1] has been extended to include the nuclear field shift effect [2],

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

(see [2] for details of the theory). The field shift results from the isotopic difference in nuclear size and shape [6], and hence, it is totally mass-independent.

We fitted the theoretical α values ($\ln \alpha_m \sim \delta^m\text{Cr}/1,000$) to the experimental isotopic variations (the most drastic case, experiment (a), $[\text{HCl}]=7.4\text{M}$). The observation can be explained by the Bigeleisen's theory of nuclear field shift effect.

Table 1 Cr isotope results

$\delta^{50}\text{Cr}$	$\delta^{52}\text{Cr}$	$\delta^{53}\text{Cr}$	$\delta^{54}\text{Cr}^a$
2.30 ± 0.06	0	-0.64 ± 0.04	-1.08

^a) Estimated by using Eq. (3).

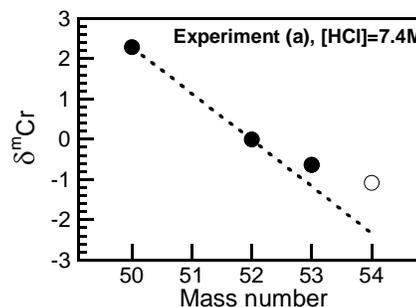


Fig 3. $\delta^m\text{Cr}$ values in a ligand exchange system. Dotted line is mass dependent fractionation line.

Except for one case (experiment (a), $[\text{HCl}]=8.5\text{M}$, $[\delta^{50}\text{Cr}]=1.49 \pm 0.05$, $\delta^{53}\text{Cr}=-0.85 \pm 0.03$), all results showed similar trends as shown in Fig. 3. (Scaling factors A and B in Eq. 3 are variables which strongly depend on the experimental condition. In this study, concentrated HCl may have strengthened the complexation of Cr-Cl, which may have shifted A and B). $\delta^{53}\text{Cr}$ showed distinguishable excesses from the mass-dependent line. The most important result in this study is the evidence of the mass-independent isotope fractionation in redox reaction at high temperature. To our knowledge, this is the first observation in laboratory scale experiment. Redox reactions at high temperature should have been prevalent in the early solar nebula processes, and hence, we may need to pay more attention to the mass-independent isotope fractionation in these reactions.

References: [1] Bigeleisen J. and Mayer M. G. (1947) *JCP*, 15, 261-267. [2] Bigeleisen J. (1996) *JACS*, 118, 3676-3680. [3] Fujii T. et al. (2002) *JPC*, A106, 6911-6914. [4] Fujii T. et al. (2006) *EPSL*, 247, 1-9. [5] Fujii T. et al. (2006) *Ap. J.*, 647, 1506-1516. [6] King, W. H. (1984) *Isotope Shifts in Atomic Spectra*; Plenum Press, New York. [7] Lugmair G. W. and Shukolyukov A. (1998) *GCA*, 62, 2863-2886. [8] Moynier F. et al. (2007) *LPS XXXVIII*, submitted. [9] Trinquier A. (2005) PhD thesis, Univ. Paris 7, France. [10] Shukolyukov A. and Lugmair G. W. (2006) *EPSL*, 250, 200-213. [11] Yamana H. et al. (2000) *J. Nucl. Mater.* 278, 37-47.