

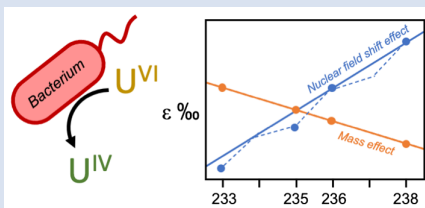
Contribution of the nuclear field shift to kinetic uranium isotope fractionation

A.R. Brown¹, Y. Roebbert², A. Sato³, M. Hada³, M. Abe^{3,4},
S. Weyer², R. Bernier-Latmani^{1*}

OPEN ACCESS

<https://doi.org/10.7185/geochemlet.2333>

Abstract



Isotopic fractionation of heavy elements (*e.g.*, >100 amu) often invokes the nuclear field shift effect, which is due to the impact of the elements' large nuclei on electron density. In particular, it has been explicitly described for uranium (U) at equilibrium and during kinetic isotope fractionation in abiotic mercury reactions. By following the fractionation of ²³³U, ²³⁵U, ²³⁶U and ²³⁸U during the enzymatic reduction of hexavalent U to tetravalent U by the bacterium *Shewanella oneidensis*, we provide the first direct evidence of the nuclear field shift effect during biologically controlled kinetic isotope fractionation. Here, we observed the odd-even staggering trend between

fractionation factors of each isotope and their nuclear masses, and show that fractionation factors are correlated better with the nuclear volume than the mass. Additionally, by computing the relative contributions of the conventional mass-dependent effect (vibrational energy) and the mass-independent effect (nuclear field shift), we demonstrate that the experimental nuclear field shift effect is smaller than the calculated equilibrium value and that this discrepancy is responsible for the kinetic fractionation factor being lower than that predicted at equilibrium.

Received 17 March 2023 | Accepted 8 September 2023 | Published 9 October 2023

Introduction

Redox transformations of uranium (U) lead to measurable fractionation of U isotopes. These fractionations typically result in the enrichment of the heavy isotope (²³⁸U) in the reduced state, the opposite direction of the mass-dependent fractionation observed for light elements (Andersen *et al.*, 2017). Further, isotope exchange reactions have revealed anomalous fractionations of the odd-mass isotopes, *i.e.* ²³³U and ²³⁵U, which deviate from the linear relationship between mass and fractionation magnitude observed for the even-mass isotopes (Fujii *et al.*, 1989a, 1989b; Nomura *et al.*, 1996). This odd-even staggering was observed to correlate with the isotope shifts in the atomic spectra of the isotopes, and specifically with the nuclear field shift, whereby distortions in the sizes and shapes of nuclei (the nuclear volume) between isotopes impact the electron densities surrounding the nucleus, which in turn impact ground state electronic energies. This led to the inclusion of a nuclear field shift (NFS) term in the theoretical calculation of isotopic enrichment factors for heavy elements (Bigeleisen, 1996).

These isotope exchange reactions have been assumed to be equilibrium processes (Fujii *et al.*, 2009), and the nuclear field shift effect (NFSE) itself has thus far been calculated only for equilibrium exchange reactions (Bigeleisen, 1996; Moynier *et al.*, 2013). Furthermore, given that hexavalent U (U^{VI}) reduction in the laboratory and nature display the same direction of

fractionation as predicted for equilibrium (Bigeleisen, 1996; Schauble, 2007; Stirling *et al.*, 2015), the nuclear field shift was also implicated for kinetically controlled reactions (Bopp *et al.*, 2010; Basu *et al.*, 2014, 2020; Stirling *et al.*, 2015). However, no direct evidence for the NFSE during kinetic U reduction has been provided to date; *i.e.* the odd-even staggering in the fractionation of isotopes has not yet been observed.

Whilst the NFSE has been observed during abiotic and kinetic fractionations of Hg isotopes (Zheng and Hintelmann, 2010), to our knowledge, there is no evidence of the NFSE during the biotic fractionation of any element. Indeed, mass-independent isotope fractionation of Hg has been observed in biological systems (*e.g.*, in fish) but this has been attributed to the nuclear spin effects or photochemical reactions, rather than to the NFSE (Krüte *et al.*, 2009; Epov *et al.*, 2011).

Results

Here, we provide direct evidence of the NFSE during kinetic isotope fractionation *via* the enzymatic reduction of U^{VI} by the bacterium, *Shewanella oneidensis* strain MR-1. To achieve this result, we measured the simultaneous fractionation of ²³³U, ²³⁵U, ²³⁶U and ²³⁸U throughout this reaction and report the odd-even staggering trend only previously seen during abiotic chemical exchange reactions.

1. École Polytechnique Fédérale de Lausanne (EPFL), Environmental Microbiology Laboratory, CH-1015 Lausanne, Switzerland
2. Institute of Mineralogy, Leibniz University Hannover, D-30167 Hannover, Germany
3. Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan
4. Department of Chemistry, Hiroshima University, Hiroshima, Japan

* Corresponding author (email: rizlan.bernier-latmani@epfl.ch)



First, we prepared an isotope mix of the IRMM-184 natural U standard and the IRMM-3636 ^{233}U and ^{236}U “double spike”, typically used to correct for instrumental mass bias during MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry) analyses of the $^{238}\text{U}/^{235}\text{U}$ ratio. The isotope mix was supplied to anoxic reactors containing *S. oneidensis* MR-1 in the presence of lactate, which serves as the electron donor for U^{VI} reduction, and 30 mM sodium bicarbonate, which complexes the U^{VI} to give aqueous tri- and dicarbonate species (Fig. S-1). This well documented reaction leads to the reductive precipitation of solid phase U^{IV} through the extracellular transfer of electrons *via* enzymes on the bacterial surface (Wall and Krumholz, 2006).

Here, we show that for duplicate systems, aqueous U concentrations decreased over several days, indicative of the precipitation of U^{IV} (Fig. 1a). This reaction was accompanied by the fractionation of ^{238}U and ^{235}U , such that the light ^{235}U was enriched in the residual unreacted aqueous U^{VI} , as evidenced by the progressively negative $\delta^{238}\text{U}$ values (Fig. 1b). This fractionation is well described by Rayleigh distillation models, from which the derived fractionation factors (ϵ) are $\sim 1\%$. These values are very typical for these biologically mediated reactions and

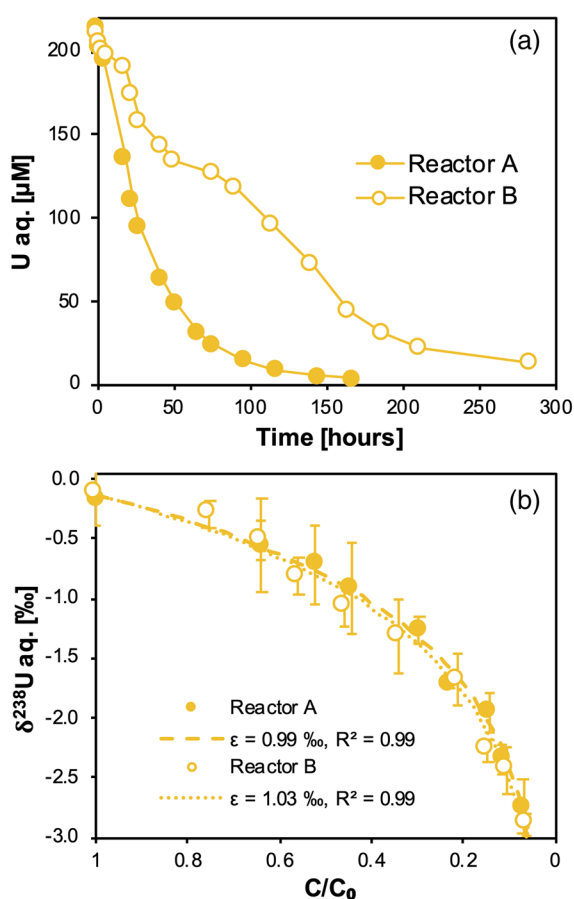


Figure 1 (a) Concentration of aqueous U (representing U^{VI}), as a function of time, in reactors containing 200 μM U^{VI} and 30 mM sodium bicarbonate incubated with *S. oneidensis*. Filled and open symbols depict duplicate reactors. (b) $\delta^{238}\text{U}$ values for aqueous U reported as a function of the remaining aqueous U fraction. Filled and open symbols depict duplicate reactors and error bars show 2 standard deviations of the mean of triplicate measurements. Rayleigh model curves for each duplicate reactor are shown in dashed lines, along with their corresponding isotope enrichment factors (ϵ). See [Supplementary Information](#) for definition of $\delta^{238}\text{U}$.

demonstrate the sequestration of the isotopically heavy U^{IV} product from the reactants, as shown previously for U isotope fractionation (Basu *et al.*, 2014; Stirling *et al.*, 2015; Stylo *et al.*, 2015).

The inclusion of ^{233}U and ^{236}U in the isotope mix allowed the fractionation of these additional odd- and even-mass isotopes to be monitored (Fig. S-2), in order to reveal the presence of the odd-even staggering that would implicate the role of the NFSE in the fractionation of U isotopes. Here, three-isotope plots revealed that the fractionation behaviour did not conform to the theoretical relationship for mass-dependent isotope fractionation (Figs. 2, S-3). Total fractionation between ^{236}U and ^{235}U was larger than expected for a mass difference of 1 amu, compared to the fractionation of ^{238}U and ^{235}U ($\Delta m = 3$ amu). Additionally, the fractionation between the two odd-isotopes, ^{233}U and ^{235}U ($\Delta m = 2$ amu) was less than expected compared to the fractionation of ^{238}U and ^{235}U . These anomalous fractionations are consistent with those observed previously for U isotopes in chemical exchange reactions, in which fractionation factors for each isotope scale better with the mean square nuclear charge radii rather than the isotope mass (Fig. S-4), indicating that the nuclear volume dominates the fractionation (Fujii *et al.*, 2009; Moynier *et al.*, 2013). Here, we also observe odd-even isotope staggering in the relationship between isotopic mass and fractionation factors and demonstrate this same trend between ϵ and the mean square nuclear charge radii (Fig. 3) (Angeli and Marinova, 2013). Thus, in addition to the direction of U isotope fractionation, these data offer strong evidence that the NFSE is also responsible for the mass-independent nature of isotope fractionation observed for this kinetic reaction.

To probe whether the observed mass-independent fractionation arose from ongoing abiotic equilibrium isotope exchange between reactant U^{VI} and the solid U^{IV} product, or from the kinetically controlled enzymatic reduction, we performed isotope exchange experiments between isotopically heavy aqueous U^{VI} carbonate (initial $\delta^{238}\text{U} = \sim 5\%$) and the U^{IV} products of the bioreduction experiment (initial $\delta^{238}\text{U} = 0\%$). Here, we controlled the U speciation to be the same as during bioreduction using the same solution composition and ensured no further biologically mediated redox change by inactivating bacterial cells *via* sonication. Over several months, we observed the progressive depletion of the heavy ^{238}U from aqueous U^{VI} (Fig. S-5) as it

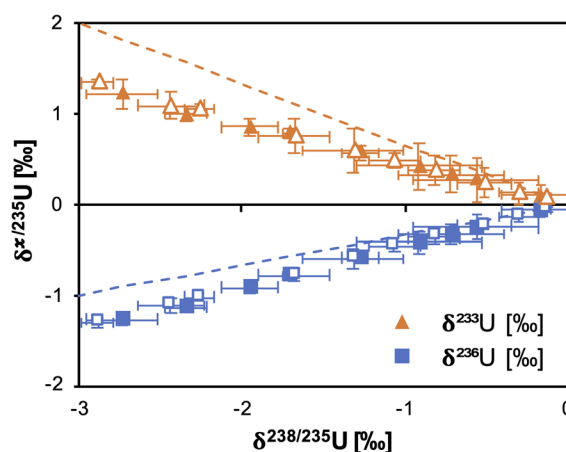


Figure 2 Three-isotope plots for delta values of all samples. Filled and open symbols depict duplicate reactors and error bars show two standard deviations of the mean of triplicate measurements. Dashed lines represent theoretical relationships for mass-dependent fractionation.

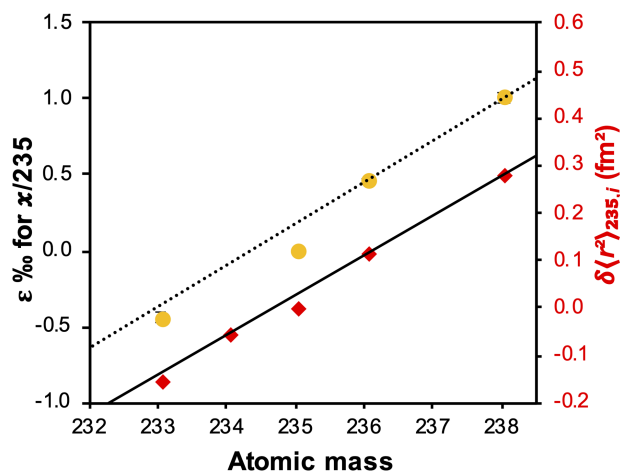


Figure 3 Fractionation factors (ϵ) for each atomic mass. Symbols and error bars depict the mean and standard deviation of duplicate reactors. Where not visible, the error is within the size of the symbol. Mean square nuclear charge radii ($\delta\langle r^2 \rangle_{235,i} = \delta\langle r^2 \rangle_i - \delta\langle r^2 \rangle_{235}$) for each atomic mass were taken from [Angeli and Marinova \(2013\)](#). The lines represent linear regressions of ϵ and $\delta\langle r^2 \rangle_{235,i}$ for even-mass numbers only.

became enriched in the U^{IV} species, as expected. However, this process was minor and theoretical equilibrium was not achieved (e.g., $\epsilon^{eq} = 1.1$ to 2.7 ‰ from *ab initio* calculation; [Table S-1](#)). That is to say, the aqueous U^{VI} remained isotopically heavier than the U^{IV} solid phase after several months, compared with the few days required to generate isotopically heavy U^{IV} during bioreduction. Additionally, the slight increase in aqueous U suggests that at least part of the decrease in $\delta^{238}U_{aq}$ may have actually been due to release of light U from the solid, rather than isotope exchange between dissolved and solid phases. These observations suggest that, whilst ongoing equilibrium isotope exchange may make a minor contribution to the observed direction of the fractionation (enrichment of the heavy isotope in the U^{IV} product, as demonstrated by [Wang et al., 2015](#)), it does not account for the magnitude of isotope fractionation during the kinetic reaction of biological reduction.

To calculate the contribution of the NFSE and the mass effect to the fractionation factors obtained for each isotope during the enzymatic reduction, we used the methods of [Fujii et al. \(2009\)](#) and [Moynier et al. \(2009\)](#) to obtain the scaling factors of the conventional mass effect and the nuclear field shift term that appear in [Bigeleisen's \(1996\)](#) theory ([Figs. 4, S-6](#)). Whilst this analysis was developed initially for isotopic equilibrium conditions, it succeeds in reproducing the odd-even staggering trend (highlighted by the regression of the even isotopes in [Fig. S-6](#)) and suggests the dominant contribution of the NFSE to the overall observed kinetic fractionation factors.

Kinetic fractionations of U isotopes in the laboratory and nature consistently show lower fractionation than that predicted or measured at equilibrium ([Fujii et al., 2006](#); [Abe et al., 2008, 2010](#); [Basu et al., 2014](#); [Wang et al., 2015](#); [Stirling et al., 2015](#); [Stylo et al., 2015](#); [Andersen et al., 2017](#); [Brown et al., 2018](#); [Sato et al., 2021](#); [Li and Tissot, 2023](#)). However, the extent to which the relative contributions of the mass effect and the NFSE lead to this discrepancy has not been explored. This is of fundamental importance to the understanding of how isotope fractionation observed during kinetic reactions relates to that calculated for isotopic equilibrium. Thus, we compared the magnitudes of the decomposed mass and field shift effects from the experimental kinetic reaction (ϵ^{kin}), to the mass and field shift effect contributions determined for full equilibrium fractionation

via *ab initio* calculations (ϵ^{eq}) ([Fig. 4](#)). This comparison reveals that the contribution of the mass effect to ϵ^{kin} approximates that predicted for equilibrium, no matter whether the tri- or dicarbonate U^{VI} species is assumed to be preferentially reduced by the bacterium ([Fig. 4](#); trend (i)). On the other hand, the analysis indicates that the contribution of the NFSE to ϵ^{kin} is typically much smaller than that for ϵ^{eq} , but varies depending on the calculation method (density functional theory (DFT) versus Hartree-Fock (HF)) and the U^{VI} species used ([Fig. 4a-c](#); trend (ii)). Indeed, calculations using DFT and the dicarbonate U^{VI} species appear to suggest that the isotope fractionation of the kinetic reaction approaches full equilibrium ([Fig. 4d](#); trend (iii)). However, previous calculations using the HF method showed better agreement with the experimental ϵ^{eq} for the U^{VI}/U^{IV} -chloride isotope exchange reaction compared with DFT calculations, suggesting that the results of the HF method may be more accurate ([Wang et al., 2015](#); [Sato et al., 2021](#)). Whilst *ab initio* calculations of ϵ^{eq} are not easy to verify due to a lack of experimental data with which to validate them, these data suggest that the mass effect has reached equilibrium, whilst the NFSE has not. This raises the question of how these two effects are manifested during kinetic reactions and what controls their relative expressions.

A recent study by [Brown et al. \(2018\)](#) explored the effect of abiotic U^{VI} reduction rates, controlled by U speciation, on attendant U isotope fractionation. To explain the inverse reaction rate-fractionation relationship, a model was developed incorporating a variable contribution of the NFSE that was dependent on the ratio of forward to backward reactions, but that also required isotopic exchange between U^{VI} and U^{IV} . However, in our study we observed only a minor contribution from equilibrium isotope exchange that cannot explain the magnitude of isotope fractionation during the kinetic reaction and this suggests that kinetic fractionation may also include the NFSE.

The mathematical basis for the inclusion of NFSE in kinetic fractionation has been derived by [Sato et al. \(2021\)](#). The authors introduced a model of kinetic uranium isotope fractionation that incorporates transition state theory to allow the inclusion of the NFSE within a multi-step U^{VI} reduction reaction, independent of subsequent equilibrium isotope exchange between the oxidised and reduced U. The model was then employed to re-interpret the data of [Brown et al. \(2018\)](#), demonstrating that the observations can arise from kinetic fractionation components that include the NFSE, without the requirement for independent equilibrium isotope exchange between the initial reactant and the final product. Rather, the model indicates that the magnitude of NFSE expression is dependent on the degree of reverse electron transfer (back reaction). This has since been confirmed experimentally using purified U^{VI} reducing proteins of various redox states. Fully reduced proteins facilitated rapid electron transfer with limited back reaction and little isotopic fractionation, whereas partially reduced proteins permitted significant NFSE-dominated fractionation linked to the allowance for extensive reverse electron transfer ([Brown et al., 2023](#)).

Our data support the view that the mass effect is both an equilibrium and kinetic isotope fractionation, in which the full fractionation at equilibrium can be expressed during kinetically controlled reactions. On the other hand, the NFSE may be exclusively an equilibrium fractionation between the instantaneous products and transition state(s), and the transition state(s) and the reactants, and as such, its expression during kinetic fractionation within the reduction reaction may be dependent on reaction reversibility ([Fujii et al., 2009](#); [Moynier et al., 2013](#); [Yang and Liu, 2016](#); [Sato et al., 2021](#)). This would explain the range of fractionation factors observed in the laboratory and nature, including both mass-dependent and mass-independent directions of fractionation.

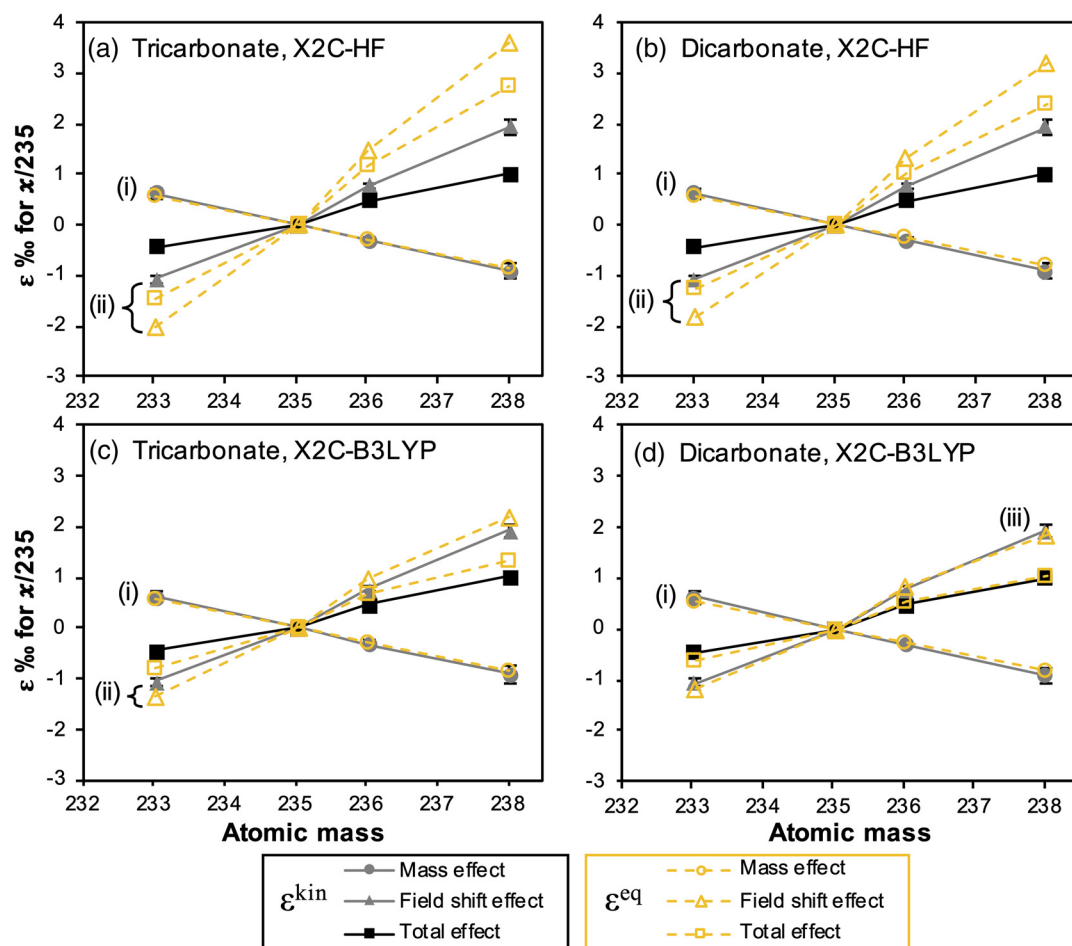


Figure 4 Isotope enrichment factors from the bacterial reduction experiment (ϵ^{kin}) and *ab initio* calculated equilibrium isotope enrichment factors (ϵ^{eq}) for the mass effect, the nuclear field shift effect and their sum (total effect) for each atomic mass. Equilibrium calculations were performed for either (a, c) tricarbonate, $\text{UO}_2(\text{CO}_3)_3^{4-}$, or (b, d) dicarbonate, $\text{UO}_2(\text{CO}_3)_2^{2-}$, as the U^{VI} species. Calculations of $\ln K_{\text{IV}}$ for ϵ^{eq} were performed using either (a, b) the Hartree-Fock method (X2C-HF) or (c, d) density functional theory (DFT) with the B3LYP functional (X2C-B3LYP). Symbols and error bars depict the mean and standard deviation of values derived from analysis of the data from duplicate reactors. A comparison of experimentally measured ϵ and recalculated total ϵ (after decomposition of the experimental data into the field shift and mass effect terms) is presented in Figure S-6. Trend (i) points to the consistent values obtained for MDF from theory and experiment, (ii) points to the discrepancy between theory and experiment for the NFSE contribution in three of the four cases, and (iii) points to the agreement between NFSE theory and experiment in the case of dicarbonate speciation and DFT calculations.

Further work is required to explore the factors that control the relative contributions of the two effects during kinetic isotope fractionations and rule out the contribution of other isotope effects, e.g., a nuclear spin effect or magnetic isotope effect (Epov *et al.*, 2011). Indeed, different reaction mechanisms of Hg reduction, e.g., photoreduction *versus* reduction by dissolved organic matter or SnCl_2 , resulted in different relative contributions of mass-dependent and mass-independent fractionation (Bergquist and Blum, 2007; Zheng and Hintelmann, 2010).

Collectively, the data presented here show unambiguous evidence for the contribution of the nuclear field shift to isotope fractionation during kinetic U reduction and confirm that previously observed fractionations (reporting enrichment of the heavy isotope in the product) arise from the dominance of the nuclear field shift effect.

Acknowledgements

Funding for this work was provided by an ERC consolidator grant awarded to RB-L (725675: UNEARTH: “Uranium isotope fractionation: a novel biosignature to identify microbial metabolism on early Earth”). This work was also supported by JSPS

KAKENHI Grant Numbers JP19K22171, JP21H01864 and JP22J12551. A part of the calculations was performed at the Research Center for Computational Science, Okazaki, Japan (Project: 21-IMS-C049 and 22-IMS-C049).

Editor: Claudine Stirling

Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2333>.



© 2023 The Authors. This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0

License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at <https://www.geochemicalperspectivesletters.org/copyright-and-permissions>.

Cite this letter as: Brown, A.R., Roebbert, Y., Sato, A., Hada, M., Abe, M., Weyer, S., Bernier-Latmani, R. (2023) Contribution of the nuclear field shift to kinetic uranium isotope fractionation. *Geochem. Persp. Let.* 27, 43–47. <https://doi.org/10.7185/geochemlet.2333>

References

- ABE, M., SUZUKI, T., FUJII, Y., HADA, M., HIRAO, K. (2008) An *ab initio* molecular orbital study of the nuclear volume effects in uranium isotope fractionations. *The Journal of Chemical Physics* 129, 164309. <https://doi.org/10.1063/1.2992616>
- ABE, M., SUZUKI, T., FUJII, Y., HADA, M., HIRAO, K. (2010) Ligand effect on uranium isotope fractionations caused by nuclear volume effects: An *ab initio* relativistic molecular orbital study. *The Journal of Chemical Physics* 133, 044309. <https://doi.org/10.1063/1.3463797>
- ANDERSEN, M.B., STIRLING, C.H., WEYER, S. (2017) Uranium Isotope Fractionation. *Reviews in Mineralogy and Geochemistry* 82, 799–850. <https://doi.org/10.2138/rmg.2017.82.19>
- ANGELI, I., MARINOVA, K.P. (2013) Table of experimental nuclear ground state charge radii: An update. *Atomic Data and Nuclear Data Tables* 99, 69–95. <https://doi.org/10.1016/j.adt.2011.12.006>
- BASU, A., SANFORD, R.A., JOHNSON, T.M., LUNDSTROM, C.C., LÖFFLER, F.E. (2014) Uranium isotopic fractionation factors during U(VI) reduction by bacterial isolates. *Geochimica et Cosmochimica Acta* 136, 100–113. <https://doi.org/10.1016/j.gca.2014.02.041>
- BASU, A., WANNER, C., JOHNSON, T.M., LUNDSTROM, C.C., SANFORD, R.A., SONNENTHAL, E.L., BOYANOV, M.I., KEMNER, K.M. (2020) Microbial U Isotope Fractionation Depends on the U(VI) Reduction Rate. *Environmental Science & Technology* 54, 2295–2303. <https://doi.org/10.1021/acs.est.9b05935>
- BERGQUIST, B.A., BLUM, J.D. (2007) Mass-Dependent and -Independent Fractionation of Hg Isotopes by Photoreduction in Aquatic Systems. *Science* 318, 417–420. <https://doi.org/10.1126/science.1148050>
- BIGEISEN, J. (1996) Nuclear Size and Shape Effects in Chemical Reactions. Isotope Chemistry of the Heavy Elements. *Journal of the American Chemical Society* 118, 3676–3680. <https://doi.org/10.1021/ja954076k>
- BOPP IV, C.J., LUNDSTROM, C.C., JOHNSON, T.M., SANFORD, R.A., LONG, P.E., WILLIAMS, K.H. (2010) Uranium $^{238}\text{U}/^{235}\text{U}$ Isotope Ratios as Indicators of Reduction: Results from an in situ Biostimulation Experiment at Rifle, Colorado, U.S.A. *Environmental Science & Technology* 44, 5927–5933. <https://doi.org/10.1021/es100643v>
- BROWN, A.R., MOLINAS, M., ROEBBERT, Y., SATO, A., ABE, M., WEYER, S., BERNIER-LATMANI, R. (2023) Electron flux is a key determinant of uranium isotope fractionation during bacterial reduction. *Communications Earth & Environment* 4, 329. <https://doi.org/10.1038/s43247-023-00989-x>
- BROWN, S.T., BASU, A., DING, X., CHRISTENSEN, J.N., DEPAOLO, D.J. (2018) Uranium isotope fractionation by abiotic reductive precipitation. *Proceedings of the National Academy of Sciences* 115, 8688–8693. <https://doi.org/10.1073/pnas.1805234115>
- EPOV, V.N., MALINOVSKIY, D., VANHAECKE, F., BÉGUÉ, D., DONARD, O.F.X. (2011) Modern mass spectrometry for studying mass-independent fractionation of heavy stable isotopes in environmental and biological sciences. *Journal of Analytical Atomic Spectrometry* 26, 1142–1156. <https://doi.org/10.1039/c0ja00231c>
- FUJII, T., MOYNIER, F., ALBARÈDE, F. (2009) The nuclear field shift effect in chemical exchange reactions. *Chemical Geology* 267, 139–156. <https://doi.org/10.1016/j.chemgeo.2009.06.015>
- FUJII, Y., NOMURA, M., OKAMOTO, M., ONITSUKA, H., KAWAKAMI, F., TAKEDA, K. (1989a) An Anomalous Isotope Effect of ^{235}U in U(IV)-U(VI) Chemical Exchange. *Zeitschrift für Naturforschung A* 44, 395–398. <https://doi.org/10.1515/zna-1989-0507>
- FUJII, Y., NOMURA, M., ONITSUKA, H., TAKEDA, K. (1989b) Anomalous Isotope Fractionation in Uranium Enrichment Process. *Journal of Nuclear Science and Technology* 26, 1061–1064. <https://doi.org/10.1080/18811248.1989.9734427>
- FUJII, Y., HIGUCHI, N., HARUNO, Y., NOMURA, M., SUZUKI, T. (2006) Temperature Dependence of Isotope Effects in Uranium Chemical Exchange Reactions. *Journal of Nuclear Science and Technology* 43, 400–406. <https://doi.org/10.1080/18811248.2006.9711111>
- KRITEE, K., BARKAY, T., BLUM, J.D. (2009) Mass dependent stable isotope fractionation of mercury during mer mediated microbial degradation of monomethylmercury. *Geochimica et Cosmochimica Acta* 73, 1285–1296. <https://doi.org/10.1016/j.gca.2008.11.038>
- LI, H., TISSOT, F.L.H. (2023) UID: The uranium isotope database. *Chemical Geology* 618, 121221. <https://doi.org/10.1016/j.chemgeo.2022.121221>
- MOYNIER, F., FUJII, T., TELOUK, P. (2009) Mass-independent isotopic fractionation of tin in chemical exchange reaction using a crown ether. *Analytica Chimica Acta* 632, 234–239. <https://doi.org/10.1016/j.aca.2008.11.015>
- MOYNIER, F., FUJII, T., BRENNER, G.A., NIELSEN, S.G. (2013) Nuclear field shift in natural environments. *Comptes Rendus Geoscience* 345, 150–159. <https://doi.org/10.1016/j.crte.2013.01.004>
- NOMURA, M., HIGUCHI, N., FUJII, Y. (1996) Mass Dependence of Uranium Isotope Effects in the U(IV)–U(VI) Exchange Reaction. *Journal of the American Chemical Society* 118, 9127–9130. <https://doi.org/10.1021/ja954075s>
- SATO, A., BERNIER-LATMANI, R., HADA, M., ABE, M. (2021) *Ab initio* and steady-state models for uranium isotope fractionation in multi-step biotic and abiotic reduction. *Geochimica et Cosmochimica Acta* 307, 212–227. <https://doi.org/10.1016/j.gca.2021.05.044>
- SCHAUBLE, E.A. (2007) Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. *Geochimica et Cosmochimica Acta* 71, 2170–2189. <https://doi.org/10.1016/j.gca.2007.02.004>
- STIRLING, C.H., ANDERSEN, M.B., WARTHMAN, R., HALLIDAY, A.N. (2015) Isotope fractionation of ^{238}U and ^{235}U during biologically-mediated uranium reduction. *Geochimica et Cosmochimica Acta* 163, 200–218. <https://doi.org/10.1016/j.gca.2015.03.017>
- STYLO, M., NEUBERT, N., WANG, Y., MONGA, N., ROMANIELLO, S.J., WEYER, S., BERNIER-LATMANI, R. (2015) Uranium isotopes fingerprint biotic reduction. *Proceedings of the National Academy of Sciences* 112, 5619–5624. <https://doi.org/10.1073/pnas.1421841112>
- WALL, J.D., KRUMHOLZ, L.R. (2006) Uranium Reduction. *Annual Review of Microbiology* 60, 149–166. <https://doi.org/10.1146/annurev.micro.59.030804.121357>
- WANG, X., JOHNSON, T.M., LUNDSTROM, C.C. (2015) Low temperature equilibrium isotope fractionation and isotope exchange kinetics between U(IV) and U(VI). *Geochimica et Cosmochimica Acta* 158, 262–275. <https://doi.org/10.1016/j.gca.2015.03.006>
- YANG, S., LIU, Y. (2016) Nuclear field shift effects on stable isotope fractionation: a review. *Acta Geochimica* 35, 227–239. <https://doi.org/10.1007/s11631-016-0109-3>
- ZHENG, W., HINTELMANN, H. (2010) Nuclear Field Shift Effect in Isotope Fractionation of Mercury during Abiotic Reduction in the Absence of Light. *The Journal of Physical Chemistry A* 114, 4238–4245. <https://doi.org/10.1021/jp910353y>

