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Title: Postdoc Proposal

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Background: Within this proposal are ideas and research goals a project which will study stable isotope fractionation of light elements (i.e. H, N, C, O) through chemical systems relevant to the nuclear fuel cycle, including nuclear fuel fabrication and reprocessing; specifically those that involve CO_x, CH_4, NO_x, H_2O, and U_xO_y. The main interest is to understand why chemically similar isotopes separate into different phases during relevant chemical processes (i.e. fractionation). With a better understanding of how light isotopes separate during different chemical treatments comes the ability to track how and where interdicted nuclear materials were produced. The data from these studies are important for forensic interests as well as fundamental science. Fractionation of light isotopes has not been well studied – few reports since the 1960s have been published[1,2] – and more experimental investigations are needed. The concepts from these studies could then be applied to plutonium-containing systems. The main challenge in this project stems from synthesizing and characterizing a number of materials, and identifying the fractionation of specific isotopes.
Proposed Research: The goal of this project is to determine whether variables such as the molarity of nitric acid (HNO_3), temperature, and surface characteristics of uranium materials have an effect on the fractionation of ^{15}N between the solution and vapor phases. A number of studies and characterizations can be performed to identify stable isotope fractionation in uranium containing systems. The surfaces of uranium oxide (UO_2), U_3O_8, clean uranium metal, and uranium metal with a surface oxide layer will be characterized via powder X-ray diffraction, scanning electron microscope imaging, time-of-flight mass spectrometry, X-ray absorption fine spectroscopy, and other similar methods. These characterization tools will allow for surface characterization, including morphology, and oxide layer depth. Studies of particle size will also be included, to determine whether surface area contributes significantly to light isotope fractionation. These materials can then be dissolved in HNO_3, and the fractionation of ^{15}N can be determined via distillation. The headspace (e.g. the vapors from the mixture) will be analyzed using isotope ratio mass spectrometry. Differences in fractionation of ^{15}N between the solution and vapor phases will be compared between the experiments to determine which of these variables can affect fractionation. Very small (2.66 μm diameter on average) UO_2 particles can be easily synthesized using hydrothermal methods (whereby the reaction vessel is at temperatures above 100 °C and at pressures above 1 atmosphere), and can be used to determine if particle size is a variable of interest. After this concept has been proven using uranium, similar mission-relevant experiments will be done using plutonium. Another avenue of interest is using radiation source exposure to determine if radiation damage within the material can effect stable isotope fractionation. Nitric acid will be exposed to gamma, alpha, or neutron irradiation using benchtop sources such as ^{251}Cf and ^{60}Co. The formation of gases, such as NO_x, over time will be monitored, and the resulting fractionation of ^{15}N over time can be measured by analyzing the headspace of the reaction using gas chromatography mass spectrometry; the data will show whether radiation damage has any effect.
Impact: Results from the stable isotope project are anticipated to show how light isotopes are separated depending on the chemical process to give an idea of what unknown materials could look like based on how, or where they were produced. Understanding the preparation, storage conditions (i.e. duration, chemical form) or movement of materials is beneficial in aiding in the identification of interdicted materials by the nuclear forensics community, as well as government agencies. If interdicted material can be identified and properly assigned, the country as a whole will be protected.
References: (1)Mills, T. R. *Separation Science and Technology* **1990**, *25*, 335-345. (2)Walters, W. W.; Michalski, G. *Geochimica et Cosmochimica Acta* **2016**, *191*, 89-101.

I confirm that I wrote this proposal and will perform this research during my postdoctoral appointment. Dr. Jacquelyn M. Dorhout, Ph.D.