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DHS-Postdoc - FY13 - Mid- and year-end report - Brennecka

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Tasking

LLNL will deliver to DHS DNDO/NTNFC a mid-year activity report on the activities of LLNL's Post-Doctoral Fellow.

LLNL will deliver to DHS DNDO/NTNFC a year-end report on the activities of LLNL's Post-Doctoral Fellow.

Part I – Mid-year activities

The focus of my effort during the second half of FY13 was planning and performing experiments that enable the high precision isotopic measurement of the heavy rare earth elements (HREEs) gadolinium (Gd) and dysprosium (Dy). The isotopic compositions of these elements will be used as forensic signatures in a variety of nuclear materials.

The high-precision measurement of Gd and Dy isotopics requires the quantitative separation of each element from the sample matrix, and especially other HREEs that have direct isobaric interferences. As such, I developed a chemical procedure that isolates the element of interest (shown below in Fig. 1). This is the first such chemistry developed that separates these elements from one another, and will result in multiple methods publications which are currently in preparation.

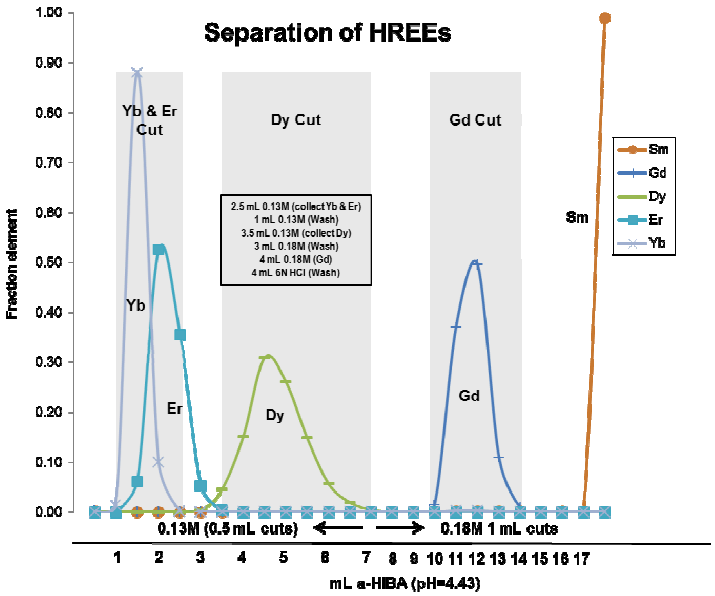

Figure 1. The chemical separation procedure developed for isolation of Gd and Dy from the other heavy rare earth elements. This procedure results in 95+% recovery of the element of interest and reduces the ratio of interfering element/element of interest to $<10^{-5}$.

As a proof of concept of this procedure's ability to detect isotopic variation, I isolated and analyzed Gd and Dy from refractory solids in meteorites predicted to have slight variation in both Gd and Dy isotopics. These samples proved to be distinct from terrestrial standards, and the results were presented at the Lunar and Planetary Science Conference in March of 2014. This was the first report of its kind for these elements, and has provided exciting insight into the isotopic composition of the early Solar System. At present, we are able to measure differences in Gd isotopics in samples at ~1 part in 10,000 for the isotopes of interest.

Following development of the mass spectrometry and chemical separation procedures for the measurement of Gd and Dy isotopics, the chemistry was transferred to a laboratory facility designed to handle higher levels of radioactivity, a requirement in order for the methods to be used on the materials of interest.

Part II – Year-end Activities

Continuing the Gd and Dy isotopics work, I submitted an abstract to the IAEA conference on Nuclear Forensics (July 7-10) on Gd isotopes in nuclear materials. My presentation at the meeting will focus on evolution of Gd isotopes as a function of neutron fluence. In short, the isotopes ^{155}Gd and ^{157}Gd both have very large neutron capture cross sections (likelihood they will capture a neutron). As such, when more neutrons interact with the sample, the isotopic composition evolves as a function of the time and exposure to neutrons, as shown in figure 2. The capture of neutrons on ^{155}Gd and ^{157}Gd causes corresponding deficits in those isotopes and a corresponding excess in ^{156}Gd and ^{158}Gd. This isotopic composition should act as a somewhat unique signature of nuclear material, and additionally allow the calculation of the neutron fluence the sample has experienced. This project represents the first use of Gd isotopes in nuclear material and will hopefully result in the development of a novel and robust signature.

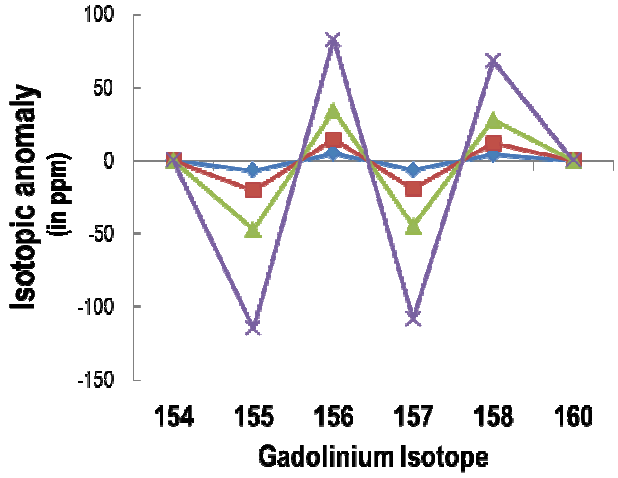

Figure 2.The predicted Gd isotope character of samples that have experience different neutron fluences. The size of the anomalies are a direct result of the neutron fluence experience and thus will allow calculation of the neutron environment in which the sample was located.

Additional nuclear forensic projects:

In addition to the work on Gd and Dy isotopes, I have begun work investigating historical filter collected samples of fallout. Small particles trapped in cronisol filters from historical tests exist that have not yet been investigated. The ultimate goal is to remove the particles from the filters they are contained in, and study the particles using non-destructive techniques such as scanning electron microscope and ion microprobe. Thus far, my work has focused on establishing a protocol to remove the filter material by oxidizing the filter in an oxygen rich atmosphere. This is to minimize the temperature that the particles experience, and thus maximizing the original characteristics of the historical fallout material. As displayed in figure 3a/b, the filter sample is placed in a quartz vial inside a furnace with an oxygen bleed system. The furnace is ramped over a series of hours with a small amount of additional oxygen to slowly eliminate the filter material. The leftover particles can then be removed and studied using *in situ* techniques described above.

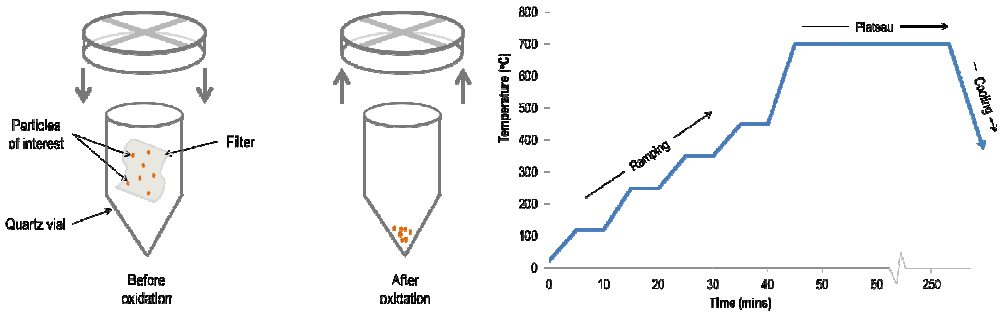

Figure 3A/B. A) Cartoon of the historical filter paper before and after ashing has occurred. B) Optimal ramping protocol for the lowest possible temperature to eliminate the filter material.

Work Products This Past Year:

Presentations Delivered:

IAEA - International Conference on Advances in Nuclear Forensics, Vienna, Austria July 2014, "*Gadolinium Isotopic Signatures in Nuclear Material*" **G.A. Brennecka**, L.E. Borg, M. Kristo, I.D. Hutcheon. **To be delivered in July**

LPSC Annual Meeting, The Woodlands, TX, March 2014, "*The gadolinium and dysprosium isotopic composition of a supernova injection inferred from Allende CAIs*", **G.A. Brennecka**, L.E. Borg, M. Wadhwa.

Presentation to LLNL summer student interns, July 2013, "*Geolocation of Nuclear Materials for Forensic Applications*", LLNL-PRES-558153.

Goldschmidt Geochemistry annual meeting, Florence, Italy, August 2013, "*Evidence for supernova injection into the solar nebula and the decoupling of r-process nucleosynthesis*" **G.A. Brennecka**, L.E. Borg, M. Wadhwa.

Publications during FY2013-14:

G.A. Brennecka, L.E. Borg, M. Kristo, I.D. Hutcheon. Gadolinium Isotopic Signatures in Nuclear Material. *IAEA - International Conference on Advances in Nuclear Forensics*, Vienna, Austria July 2014

G.A. Brennecka, L.E. Borg, M. Wadhwa (2014) The gadolinium and dysprosium isotopic composition of a supernova injection inferred from Allende CAIs. *Lunar and Planetary Science Conference*, 2014, The Woodlands, TX, USA.

P. Mane, **G.A. Brennecka**, S.J. Romaniello, M. Wadhwa (2014) Mg and U isotopic systematics in Allende CAIs: Implications for the origin of uranium isotopic variation in refractory inclusions. *Lunar and Planetary Science Conference*, 2014, The Woodlands, TX, USA.

L.E. Borg, **G.A. Brennecka,** N. Marks, S. Symes (2014) Neodymium isotopic evolution of the Solar System inferred from isochron studies of planetary materials. *Lunar and Planetary Science Conference*, 2014, The Woodlands, TX, USA.

S.J.K. Symes, L.E. Borg, **G.A. Brennecka** (2014) A young differentiation age for Mars deduced from high-precision ^{142}Nd analyses of martian meteorites. *Lunar and Planetary Science Conference*, 2014, The Woodlands, TX, USA.

G.A. Brennecka, L.E. Borg, M. Wadhwa. (2013) Evidence for supernova injection into the solar nebula and the decoupling of *r*-process nucleosynthesis *Proceedings of the National Academy of Sciences* **110** p. 17241-17246.

G.A. Brennecka, L.E. Borg, M. Wadhwa (2013) Evidence for supernova injection into the solar nebula and the decoupling of r-process nucleosynthesis. *Goldschmidt Geochemistry Conference*, 2013, Florence, Italy.

A. Goldmann, **G. Brennecka**, J. Noordmann, S. Weyer, M. Wadhwa (2013) The ^{238}U/^{235}U of the Earth and the Solar System. *Goldschmidt Geochemistry Conference*, 2013, Florence, Italy.

G.A. Brennecka, L.E. Borg, M. Wadhwa. (*in press*) Insights into the Martian Mantle: The Age and Isotopics of the Meteorite Fall Tissint. *Meteoritics & Planetary Science*

S. Romaniello, **G.A. Brennecka**, A.D. Anbar (*Submitted*) Fractionation of ^{238}U/^{235}U in the water column of the Black Sea. *Geology*

L.E. Borg, S.J.K. Symes, **G.A. Brennecka** (*in review*) Prolonged Accretion of the Terrestrial Planets Deduced from Isotopic Systematics of Martian Meteorites. *Nature*

A. Goldmann, **G.A. Brennecka**, J. Noordmann, S. Weyer, M. Wadhwa (*in revision*) The uranium isotopic composition of the Earth and the Solar System. *Geochimica Cosmochimica Acta*

L.J. Spivak-Birndorf, A. Bouvier, M. Wadhwa, P.A. Bland, P. Spurný, M.C. Towner, G. Benedix, S. Hammond, N. Rogers, K. Howard, **G.A. Brennecka** *(in revision)* Trace element geochemistry and chronology of Bunburra Rockhole, a unique asteroidal basalt. *Meteoritics & Planetary Science*

G.A. Brennecka, L.E. Borg. (*in preparation*) Quantitative Separation of Individual Heavy Rare Earth Elements for Mass Spectrometric Analysis. *International Journal of Mass Spectrometry*.