2012 LLNL Nuclear Forensics Summer Program

Glenn T. Seaborg Institute
Lawrence Livermore National Laboratory
Physical and Life Sciences
Livermore, CA 94550, USA

Director: Annie Kersting (kersting1@llnl.gov)
Education Coordinator: Nancy Hutcheon
Administrator: Camille Vandermeer
Website  https://seaborg.llnl.gov/

Sponsors:
National Technical Nuclear Forensics Center, Domestic Nuclear Detection
Office, Department of Homeland Security
LLNL: Glenn T. Seaborg Institute, Physical and Life Sciences Directorate

LLNL-TR-604174
The Lawrence Livermore National Laboratory (LLNL) Nuclear Forensics Summer Program is designed to give both undergraduate and graduate students an opportunity to come to LLNL for 8-10 weeks during the summer for a hands-on research experience. Students conduct research under the supervision of a staff scientist, attend a weekly lecture series, interact with other students, and present their work in poster format at the end of the program. Students also have the opportunity to participate in LLNL facility tours (e.g. National Ignition Facility, Center for Accelerator Mass-spectrometry) to gain a better understanding of the multi-disciplinary science that is on-going at LLNL.

Currently called the Nuclear Forensics Summer Program, this program began 12 years ago as the Actinide Sciences Summer Program. The program is run within the Glenn T. Seaborg Institute in the Physical and Life Sciences Directorate at LLNL. The goal of the Nuclear Forensics Summer Program is to facilitate the training of the next generation of nuclear scientists and engineers to solve critical national security problems in the field of nuclear forensics and have the student experience conducting research at the Lab. We select students who are majoring in physics, chemistry, geochemistry, mathematics, nuclear engineering, chemical engineering and environmental sciences. Students engage in research projects in the disciplines of actinide and radiochemistry, isotopic analysis, computational analysis, radiation detection, and nuclear engineering in order to strengthen the ‘pipeline’ for future scientific disciplines critical to DHS (DNDO), NNSA.

This is a competitive program with over 100 applicants for the 8-10 slots available. Students come highly recommended from universities all over the country. For example, this year we hosted students from Clemson University, Massachusetts Institute of Technology, University of Nevada, Las Vegas, University of Minnesota, University of Cincinnati, Duke University, Pennsylvania State University, University of Missouri and University of California, Berkeley. (See Table 1). We advertise with email to physics, engineering, geochemistry and chemistry departments throughout the U.S. We also host students for a day at LLNL who are participating in the D.O.E. sponsored “Summer School in Radiochemistry” course held at San Jose State University and have recruited from this program. We also participate in the Nuclear Forensics Undergraduate Summer Program sponsored by DHS-DNDO (FY12 held at University of Missouri) and recruit potential students.

This year students conducted research on such diverse topics as: actinide (Np, U, Pu) isotopic fingerprinting, statistical modeling in nuclear forensics, actinide analysis for nuclear forensics, environmental radiochemistry, radiation detector materials development, coincidence counting methods, nuclear chemistry, and heavy element separations chemistry.

In addition to hands on training, students attend a weekly lecture series on topics applicable to the field of nuclear forensics (see Table 2). Speakers are experts from both within and external to LLNL. Speakers are able to discuss the importance of their work in the context of advances in the field of nuclear forensics.
Graduate students are invited to return for a second year at their mentor’s discretion. We encourage the continuation of research collaboration between graduate student, faculty advisor and laboratory scientists. Graduate and undergraduate students on fellowship such as the Nuclear Forensics Graduate Fellowship are invited into our summer program. This year we had three; two in the graduate program and one in the undergraduate program.

We use our summer program to create a successful pipeline of top quality students from universities across the U.S. Since 2002, 42 students have returned and/or conducted their graduate research at LLNL:

- 12 have become postdoctoral fellows,
- 2 have become postdoc positions at other national labs,
- 7 have been hired as career scientists at LLNL.
- 3 have hired at career scientists at other national labs, and
- 3 three are currently faculty in the area of nuclear forensics/radiochemistry.

A big factor in the success of this program is the dedication of the staff scientists who volunteer to mentor the summer students. In FY11, funding from the Nuclear Forensics Graduate Mentoring Program (sponsor: DNDO) helped to partially support the time staff took to teach the summer interns. Staff scientists we able to take the necessary time to develop an appropriate summer project, oversee the safety training and dedicate more time helping the interns maximize their productivity and scientific potential.
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<thead>
<tr>
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<td>Elizabeth DeRubeis</td>
<td>Geology</td>
<td>California State University, East Bay</td>
<td>Grad</td>
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<td>2</td>
<td>John Despotopulos</td>
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<td>3</td>
<td>Marc Fitzgerald***</td>
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<td>4</td>
<td>April Gillens**</td>
<td>Environmental Engineering &amp; Earth Sciences</td>
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<td>5</td>
<td>Mitchell Goshert</td>
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<td>Timothy Jacomb-Hood*</td>
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<td>Erin Kenney</td>
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<td>Lisa Meyers</td>
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<td>10</td>
<td>Grayson Rich</td>
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<td>Barbara Wang**</td>
<td>Nuclear Engineering</td>
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* = Nuclear Forensics Undergraduate Intern  
** = Nuclear Forensics Graduate Fellows  
*** = Has since became a Nuclear Forensics Graduate Fellow (9/12)
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<td>6/21/12</td>
<td>Dawn Shaughnessey</td>
<td>Present Day Superheavy Element Discovery at LLNL and FLNR</td>
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<td>7/2/12</td>
<td>Arthur Rodgers</td>
<td>Prompt Forensics with Speed-of-Sound Data</td>
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<td>Ben Jacobsen, LLNL</td>
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<td>Naomi Marks, LLNL</td>
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<td>Rich Gostic, LLNL</td>
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<td>7/19/12</td>
<td>Nick Scielzo</td>
<td>Beta-Delayed Neutron Spectroscopy Using Trapped Ions</td>
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<td>Annie Kersting</td>
<td>Actinides in the Environment</td>
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<td>8/1/12</td>
<td>Dr. Siegfried Hecker</td>
<td>An eye on nuclear North Korea: Looking from the inside and the outside.</td>
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<td>Elizabeth DeRubeis</td>
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<td>Using Rn-222 to estimate groundwater inflow to Martis Creek</td>
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<td>Lisa Meyers</td>
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<td>Grayson Rich</td>
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* = Nuclear Forensics Undergraduate Intern  
**= Nuclear Forensics Graduate Fellows

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA2734
Using Rn-222 to estimate groundwater inflow to Martis Creek
Elizabeth DeRubeis, Richard Bibby, Bradley Esser, and Jean Moran

1 California State University East Bay, 2 Lawrence Livermore National Laboratory,
3 Lawrence Livermore National Laboratory Glenn T. Seaborg Institute

Abstract: The goal of this project is to find areas where groundwater is flowing into the streams in Martis Valley, located near Lake Tahoe, California, in order to determine the stream system's dependence upon groundwater. Using Rn-222, a daughter product of the U-238 (found in granitic rocks) decay series, it is possible to determine areas of groundwater inflow, since surface waters will be lower in radon activity than groundwater. As the population in the Lake Tahoe/Truckee region increases, there will be an increase in how much groundwater is pumped for human consumption, leaving less available for the stream system. While many of the downstream areas of Martis Creek have low radon activities, there are some areas of relatively high activity, which indicate possible groundwater inflow.

Introduction:
- Martis Valley is located just north of Lake Tahoe, California
- This may be a large recharge area due to snowfall/snowmelt
- The geology of the area is granite, metamorphic, volcanic, alluvial, and glacial deposition. Due to the large presence of granite, Rn-222 is present in the area from the decay of U-238
- Rn-222 is volatile, has a half life of 3.82 days, and can be used as a groundwater tracer, since it has higher activity levels in groundwater than in surface water
- Sediment in the streambed may also release Rn-222 into surface water
- With climate change, an increase in temperatures would cause shorter periods of precipitation, leading to earlier snowmelt. Groundwater inflow would be even more critical for streams to maintain their flows, but as population increases in the region, more demand will be placed on groundwater for human consumption.

Results:
There was only one area that showed a significant amount of Rn-222 activity. This was from a stagnant pool of water that still had not gone dry three weeks after the initial sampling, though sections of Middle Martis Creek had. There are several of these pools around the valley, which could be an indication that groundwater is flowing in.

Discussion:
The lack of Rn-222 activity in the stream could mean one of two things:
1) Groundwater has less of a role in the streams in Martis Valley than was previously thought, or 2) Groundwater is coming into the streams, but farther upstream, and is degassing before it reaches the areas that sampling took place in. It is likely the latter, as the pools of stagnant water have not gone dry, while other areas of the streams have become dry. Future sampling will occur in areas farther upstream to determine if this is the case.

Methods:
In the field, water samples were collected in 20mL glass vials filled with 10mL of scintillation cocktail. Using a hoolde syringe, 10mL of water was collected and injected beneath the cocktail, and the radon transferred from the water to the scintillation cocktail. The samples were then placed on a liquid scintillation counter to be analyzed for Rn-222 activity.

Future Work:
1) Continued sampling for Rn-222 farther upstream in Martis Creek
2) Flow measurements along areas where samples are taken
3) Tracer study using SF6 and Xe, similar to one successfully performed at Alameda County Water District

Comparisons between winter and summer radon activity in surface water show potential groundwater inflow areas.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
Extraction Chromatographic Studies of Flerovium (Element 114) and Element 115 Homologs

John Despotopoulos¹, Narek Gharibyan², Julie Gostici, Roger Henderson², Ken Moody², Dawn Shaughnessy², Ralf Sudowe¹, Evgeny Tereshatov²
¹University of Nevada – Las Vegas, ²Chemical Sciences Division – Lawrence Livermore National Laboratory

INTRODUCTION AND MOTIVATION
Recent studies of the chemical behavior of element 112 and 114 in the gas phase together with the discovery of isotopes with suitable half-lives have spurred a renewed interest in the development of suitable chemical systems to study the solution chemistry of elements with Z ≥ 114 [1,2]. Due to the short half-lives of the transactinide elements, fast and efficient separations are necessary so that the chemical properties of these elements can be compared to those of their lighter homologs. Separations based on extraction chromatography resins show promise for achieving the required short separation times, high yields and high separation factors that are required for transactinide studies. The adsorption of Pb and Sn, the lighter homologs of element 114, on Eichrom’s Pb extraction chromatographic resin has been investigated from various acid matrices to evaluate its suitability for the study of element 114. Similarly, Bi and Sb, the lighter homologs of element 115, have been used to evaluate this resin for the investigation of element 115.

TRANSACTINIDE CHEMISTRY CHALLENGES
- Low production rates, with only a few atoms produced over the entire cycle.
- Short lifetimes, ranging from 10^2 seconds to a few hours.
- Chemical system must be reliable, robust, fast, and extremely efficient for ultra-trace applications (Automation required).

PROJECT GOALS
- Continue research aimed at the production of transactinide elements.
- Develop a chemical system for separating the homologs and pseudo-homologs of element 114 and 115 (Sn, Pb and Sb, Bi respectively).
- Separation schemes must give knowledge of the chemical form of the homologs and pseudo-homologs during the separation procedure, to allow extrapolation of the transactinide elements chemical properties.
- Chemical system must be automatable.

RESULTS
- Figure: The batch uptake of Pb (112, 114) as a function of hydrochloric acid and nitric acid using Pb as a tracer and with 1 hour equilibrium time.

ACKNOWLEDGEMENTS

REFERENCES
Forensic Signatures in Trinity Fallout Beads
Marc Fitzgerald, Richard Gostic, Greg Spriggs, Ian Hutchison
University of Nevada – Las Vegas

Abstract
Analysis of fallout particles from Trinity and other nuclear explosions is central to understanding
the fallout formation process. Insight into this process is important in order to quantify the
environmental consequences of aboveground nuclear testing. Historical studies have investigated
the average abundance and spatial distribution of radionuclides within fallout debris taken from near
ground zero, but none have characterized the perturbation of the stable elements as a consequence
of extreme heating. We show, through inductively coupled plasma mass spectrometry, that
substantial variation exists in yttrium, ytterbium and thulium with respect to other rare earth
elements (REE). This pattern is not completely explained by historical fallout models, and merits
further investigation. (3) We also find an overall abundance of copper, ruthenium, lead, and actinides in
the fallout beads, which were likely derived from the testing environment of the explosion.

Experimental Objective and Design
- Main Goal: Characterization of the elemental composition of glassy fallout bead relative to the
  local soil.
- Ten fallout beads, pictured above, and one soil sample were characterized by non-destructive
  LbGe gamma spectroscopy to estimate abundances of Am and Cs.
- These results guided the dilution procedure used for subsequent inductively coupled mass
  spectrometry (ICP-MS) analysis to survey major and trace element abundances.

One survey scanning 100 different isobars between masses 6 to 258 was performed. This was followed
by a more detailed scan between masses 230 to 260, to focus specifically on the actinide masses.

Equations Used
\[
\text{Sample} + \text{ACID} \rightarrow \text{Solution} + \text{Measure}\ (eq. 1)
\]

Results
- Measured CPS

Discussion and Future Work
Based on these analyses, we conclude that there is significant chemical excursions and
substantial isotopic variation in the fallout beads relative to the local soil, as a result of mixing with
the detonation debris. The elements copper, ruthenium, lead, as well as the actinides could only
have been derived from the test. REE depletions observed in T2, T3, T4, and T10 relative to soil, in
contrast with the other 4 beads (enriched in REE relative to soils) suggests variations in the fraction
behavior prior to bead solidification. The lanthanide enriched samples yield a REE pattern
consistent with the progression in melting point temperatures for the lanthanides. Samples T3,
T4, T7, and T10 appear to have a "sawtooth" depletion zones at cerium, gadolinium, erbia, and
ytterbium. Corresponding zones of enrichment are observed in samples T2, T6, and T8 despite their
overall depleted natures. This pattern suggests that, at least for cerium, gadolinium, and ytterbium,
a change in chemistry such as oxidation must be occurring prior to fallout formation. Yttrium,
which behaves similar to the lanthanides, also follows this "sawtooth" pattern for T7 and T9.
Investigation using EXAFS/XANES techniques could reveal the chemical characteristics of
the lanthanides and provide insight into fallout formation.

References

This work was performed under the auspices of the U.S. Department of Energy Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344, Lawrence Livermore National Security, LLC.
Development of a lithium-glass based composite neutron detector for $^3$He replacement

Grayson Rich, Nuclear Forensics Internship Program
Kareem Kazkaz, Physics Division, PLS Directorate

Motivated by the worldwide shortage of helium-3, we have fabricated a neutron detector based on a solid, composite material made of lithium-loaded scintillating glass cubes and scintillating acrylic, optimized both for neutron detection and gamma rejection. Monte Carlo simulations predict a 5" by 5" cylindrical detector of this type will have an intrinsic detection efficiency for unmoderated fission neutrons of 10%. A 2" diameter, 3" tall prototype, fabricated at LLNL this summer, is currently being experimentally characterized.

Physics of composite scintillator operation

Detectors are composed of grains of a scintillating material embedded throughout a supporting matrix.

Neutrons incident on the detector are absorbed in the acrylate and are then preferentially captured in the embedded neutron-sensitive scintillator grains. The resulting scintillation light travels through the transparent matrix and is detected by photomultiplier tubes mounted around the volume.

Neutron capture events in the grains result in ions with stopping ranges on the order of 10 μm, consequently, such events deposit energy almost exclusively in the grains. In contrast, electrons from gamma-ray events have ranges on the order of millimeters in the grains and centimeters in the plastic. Consequently, gamma-ray events are highly likely to deposit an appreciable amount of energy in the plastic matrix and can often be multiple, multi-material events.

The use of pulse shape discrimination (PSD), the different timing characteristics of scintillation light from the grains and the plastic, allows for determination of the matter in which the energy deposition took place, allowing rejection of gamma-ray events with minimal reduction of accepted neutron events.

Fabrication of prototype detectors

Initial steps of fabrication procedures were carried out using inexpensive glass cubes of a specific type to our final cubes and PVT without scintillating dye. The photo at left shows the results of some early tests, with different layers clearly visible. Each layer was cured for different times and at different temperatures to determine optimal curing parameters. Several methods of integrating bubble formation were also explored.

The images on the right are of the 2” x 3” prototype composite of lithium-glass cubes and dye-loaded PVT; both photos look along the length of the detector. The top image demonstrates the transmission of the scintillating acrylic through the volume while the bottom image shows fluorescence under UV excitation.

Compared to commonly available LBG-based detectors our prototype has much improved optical quality and a more even distribution of scintillator grains along its length.

Areas for improvement over earlier efforts

Several groups have recently explored composite detectors featuring lithium gadolinium borate (LiGB) as the embedded scintillator and it was found that only captures on Li were reliably separable from gamma-ray contamination. In the PSD plot shown below, obtained with an LBG detector, the island centered around 2.5 MeV is attributed to captures on Li, while the island at about 0.8 MeV corresponds to $^3$He captures from (N,He) reactions. This motivates the selection of an alternative embedded scintillator without isotopes with competitive neutron capture cross sections.

Numerous candidate embedded scintillator materials were considered, subject to criteria aimed at optimizing Li capture efficiency and rejection of the resulting scintillation light in addition to maintaining high gamma rejection capabilities. KG2-type lithium glass was chosen for its high number of lithium nuclei per mole, its desirable scintillation time constant, and its closely matched index of refraction with the PVT matrix.

Following selection of a scintillator material, its dimensions can be optimized to maximize the neutron detection by the matrix resulting from a neutron capture reaction. Following simulations to determine the mean penetration depth before capture of neutrino incident on lithium glass, we utilized a 1.0 analytical model developed by Kazkaz et al. to determine an optimal grain dimension of 1.5 mm [Kazkaz].

Simulations of Li-glass composite detectors

- Monte Carlo simulations using GEANT4 were conducted to determine efficiency for detection of unmoderated fission neutrons from $^{238}$U and to estimate sensitivity to gamma-rays.
- The neutron peak region of interest (NPR) was defined by a 3σ window of a Gaussian fit to the peak in energy deposition in the cubes occurring at around 1.8 MeV corresponding to captures on Li in the glass (shaded in the plot below) [F901].
- In the PCH4 source simulation illustrated in the upper plot, the scintropic source was located 16.2 cm from the circular face of the detector, generating 10μm primary events. Counts inside the NPR were considered detected neutrons.
- For the monoenergetic gamma-ray sources, with 1μm primary events directed towards the center of the circular face of the detector, counts inside the NPR represent potential contamination of the neutron counts by gamma-ray backgrounds.
- Our simulations do not consider the impact of PSD on gamma-ray backgrounds, which has been shown previously to reduce sensitivity to gamma-backgrounds to the penultimate level for LiBG detectors [Kazkaz].

The results of extensive Monte Carlo simulations of our detectors predict an intrinsic detection efficiency for unmoderated fusion reactions from $^{238}$U of 1% for the 2” diameter, 3” tall detector and 10% for the 5” by 5” detector.

Pulse shape analysis

Pulses in the new composite detector show distinguishable decay characteristics (upper plot) of two example waveforms acquired using the 2” x 3” prototype with a 5 GS/s oscilloscope.

Our data acquisition system utilizes a 200 MHz digital with motorized firmware that facilitates pulse shape analysis on 8 individually denser regions of integration. Different configurations and combinations of these gates facilitates effective and flexible PSD.

Adapting a tail start time of 40 ns was selected to maximize the separation of the $\lambda_{n,\gamma}$-retro for the pulses shown at top (center plot).

The lower plot shows examples of both neutron and gamma induced events as captured by the digitizer. Shown at left are two integration gates selected to afford flexibility in analysis through making available several different bin start times.

Preliminary results

- Preliminary PSD plots
- PCH4 source 2” x 3” detector
- Neutron event visible around 1300 MeV and 1750 MeV
- Future optimization of analysis and PSD techniques could further distinguish neutron events
- This suggests >10% sensitivity detection efficiency

Bibliography and acknowledgments

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-PUB-817142

The authors would like to acknowledge extreme gratitude for the assistance offered by Peter Thiede, H Paul Middaugh, Michelle A. Faust, and Lindsey E. Grassreed, all of whom have a refreshing generosity, kindness, and dedication to science without which this project could not have proceeded.
Carbon stable isotope signatures of TBP

April R. Gillens\textsuperscript{1}, Michael Singleton\textsuperscript{2}, and Brian A. Powell\textsuperscript{3}; \textsuperscript{1}Environmental Engineering and Earth Sciences, Clemson University, Clemson, SC
\textsuperscript{2}Environmental Radiochemistry Group, Chemical Sciences Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA

Abstract

Tri-n-octyl phosphine oxide (TBP) is the primary component of the Plutonium Uranium Reduction Extraction (PUREX) process. Its degradation products are dibutyl phosphate (DBP), monobutyl phosphate (MBP), butanol, and phosphoric acid. Many have agreed that in the case of phosphate esters such as TBP, acid hydrolysis will cleave the C-O bond whereas alkaline hydrolysis will attack the P-O bond. The examination of carbon stable isotopes of TBP under reprocessing-like conditions may determine if TBP has a unique signature in nuclear reprocessing. This work aims to determine whether there is a carbon stable isotope fractionation of TBP as it is subjected to high acid and basic conditions. Further work will involve characterizing TBP degradation under the same conditions as this study using a developed FTR-ATR technique for the estimation of the amount of DBP produced in these reactions.

Experimental

Five milliliters of pure TBP (EMD Chemical, Inc.) was reacted with 5 ml of 50% wt NaOH in a 40 ml bottle. Another 5 ml of TBP was reacted with 5 ml of 8M HNO\textsubscript{3} (Fisher Scientific). The organic and aqueous phases were continuously agitated using a stir bar. Samples were taken in variable time increments. The last samples were analyzed using GC-FID (Agilent 6890) to determine the concentration of TBP remaining and the amount of degradation products produced. All samples were evaluated using GC-C-RIMS for carbon stable isotope analysis. TBP and DBP standards were also analyzed on the EA-IRMS.

Results

The basic reaction was terminated after 4 days due to a crystal formation in the organic phase (Figure 1). Another basic reaction was reproducible but no stir bar was added for agitation. There was no crystal formation after six days in this reaction. The acidic reaction continued without issue until termination on day 6 (Figure 1). Based on the measured Table 1. Carbon stable isotope (\delta\textsuperscript{13}C) data of TBP in acid and basic reactions

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Table 2. 8\textsuperscript{13}C of pure TBP & DBP

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<tbody>
<tr>
<td>TBP</td>
<td>-30.80</td>
<td>-27.30</td>
</tr>
<tr>
<td>DBP</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Acknowledgements

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References

Unraveling Environmental Contributions to Fallout Formation

Timothy Jacomb-Hood\textsuperscript{1}, Gary Eppich\textsuperscript{2}, Kim Knight\textsuperscript{2}, Gregory Spriggs\textsuperscript{2}, Richard Gostic\textsuperscript{2}, Michael Kristo\textsuperscript{2}, and Ian Hutchene\textsuperscript{2}

\textsuperscript{1}The Pennsylvania State University
\textsuperscript{2}Lawrence Livermore National Lab

**Overview**

Following a near surface nuclear detonation, fallout is formed containing a mixture of the device, radioactivity released by the explosion, and the near ground zero environment. The precise mechanisms of fallout formation remain poorly understood. The current model of fallout formation is that the nuclear explosion evaporates the surrounding material, including the device. This material forms glasses that trap elements from the detonation and surrounding environment. Mixing and fractionation behavior may be a function of the different saturated vapor pressures at a given temperature and pressure [1].

For this study, we examined nine surface soil samples and six glassy fallout beads from the National Nuclear Security Site (NNSS). We measured major and trace element composition, mineralogy, U and Th concentration and isotopic composition of the soils, and U and Th concentration and isotopic composition of the glassy beads. We compare the isotopic information from the soils to that of the fallout glass in the context of chemical and mineralogical composition of NNSS soils. Soil samples were selected to be representative of three pits within the test site, and were believed to be minimally contaminated by historical testing.

**Method**

**Isotopic Composition**

Glass-based 137Cs is similar, in contrast with the soils, which display much larger variations. After correcting for soil U, 137Cs/129I of the glassy beads is lower by a factor of 5 than uncorrected values. Using an average U concentration from the soils of 2.25 mg/kg and assuming an equal mass contribution, we show a simple subtraction to correct U isotopic compositions in the fallout for the environmental contribution (green data). This results in fallout glass enrichments of approximately 0.8% 137Cs.

**Model “Age”**

In the uranium decay series, 238U decays to 234U, which decays to 230Th. By measuring the ratio of 238U to 232Th, a model age can be calculated, assuming no initial daughter (230Th) and no addition or removal of 230Th and 234U after bead formation.

Using this method, we calculate model ages that varied from 163-213 years before present. These ages cannot be correct as dew-grazed testing was limited to the years 1945-1962. Thus, there is excess 230Th relative to 234U. To explain this, chemical fractionation between uranium and thorium may have occurred during the formation of the glassy fallout beads. It is unclear whether 231Pa was added to 230Th or lost during this process.

**Conclusions**

After performing the analyses we found that two of our soil samples contained non-natural uranium isotopic signatures. One looks like it was contaminated by a test with characteristics similar to the investigated glassy fallout beads, the other looks to be contamination of a slightly different composition.

Both analysis of the glass beads showed, somewhat surprisingly, that they cluster in their isotopic compositions for uranium and thorium. Among the soils, there are large variations in the thorium concentrations.

From these experiments we can deduce that when the fallout forms the HEU combines with the natural soil, creating a mixture of the two components which can be explained through a simple two component mixing model. There may be Th contribution from the device or during the formation of fallout glass Th and U are chemically fractionated from one another.

The fallout beads were all similar in their bulk isotopic compositions. Performing a simple correlation for the environmental contributions making simple assumptions, we calculate a starting isotopic composition for the fallout of 92% 234U, consistent with what might be expected. The correctness of our assumption, however, cannot be verified with the present data.
**Improved Geolocation of Uranium Ore Concentrate through Geochemical Insights**

Erin Kenney¹, Martin Robel², Naomi Marks², Ian Hutchence²
1. Massachusetts Institute of Technology
2. Lawrence Livermore National Laboratory, Chemical Sciences Division

**Abstract:** Using the values of the rare earth element (REE) concentrations in UOC samples from six known sources, a series of univariate and multivariate analysis methods were compared to determine their effectiveness in identifying and correlating the REE concentrations with the geochemical properties of the ores. Various preprocessing methods were applied to the data to see which methods yielded the most consistent results. The evaluated data were then used to construct a refined model for the geochemical properties of the ores.

**Introduction:**

- The Uranium Resource Quantification involves the analysis of rare earth element (REE) concentrations in UOC samples from six known sources, and the correlation of these concentrations with the geochemical properties of the ores.
- The geochemical properties of the ores were compared for each of the six known sources in order to determine the effectiveness of the various preprocessing methods.
- The evaluated data were then used to construct a refined model for the geochemical properties of the ores.

**Data Preprocessing Experiment:**

- **Uranium Ore Concentrate Rare Earth Element Concentrations:**
  - **Normalization:**
    - Standard Beta distribution
    - Inverse Gaussian distribution
    - Beta distribution
    - Exponential distribution
  - **Normalization:**
    - Inverse gamma distribution
    - Exponential distribution
    - Normal distribution
    - Gamma distribution
  - **Normalization:**
    - Inverse gamma distribution
    - Exponential distribution
    - Normal distribution
    - Gamma distribution
  - **Normalization:**
    - Inverse gamma distribution
    - Exponential distribution
    - Normal distribution
    - Gamma distribution
  - **Normalization:**
    - Inverse gamma distribution
    - Exponential distribution
    - Normal distribution
    - Gamma distribution

**Results:**

- **Classification error:**
  - Using advanced (log_{10}) and SIV preprocessing reduced the classification error substantially by minimizing the influence of variable scale, improving correlation.
  - Additional diverse and sophisticated preprocessing techniques further reduced the classification error.

**Conclusions:**

- Using advanced (log_{10}) and SIV preprocessing reduced the classification error substantially by minimizing the influence of variable scale, improving correlation.
- Additional diverse and sophisticated preprocessing techniques further reduced the classification error.

- Using calculated geochemical ratios did not produce the lowest error, but could be more robust due to its underlying geochemical basis (as compared to a purely empirical model).
Frozen in Time
Anna Lindquist1, Kim Knight1, Zurong Dai2, Rick Ryerson3, Ian Hutcheon4, Greg Spriggs2
1 University of Minnesota, Department of Earth Sciences, Minneapolis, MN
2 Lawrence Livermore National Laboratory, Physical and Life Sciences, Chemical Sciences Division, Livermore, CA

Crystrallinity and composition help to constrain the cooling environment of fallout.

Abstract
This poster looks at spheroidal glassy fallout beads from several near surface nuclear tests using transmission electron microscopy (TEM) and electron microprobe (EMP) analyses to investigate the crystallinity and distribution of elements within fallout. Fallout forms during near-surface nuclear tests as a result of superheated material rapidly cooling and falling to the ground. Preliminary studies (Gostic, 2011; Lindquist, 2013) have shown that most residual radioactivity is contained in glassy aerodynamic components which can be separated from fallout soils. These materials form within seconds after a detonation and often contain complicated major element and activity distributions. Our study characterizes compositional and structural variations to provide constraints on the environment and cloud conditions at the time of fallout formation. This continued work assists a more complete understanding of the conditions under which these materials form, thus aiding interpretation of the information preserved in these glasses.

Crystallinity
Transmission electron microscopy (TEM) creates images similarly to optical microscopy, but uses a beam of electrons instead of light. TEMs can collect information about morphology, structure, and chemical composition from very small (down to nanoscale) regions. In this study we used diffraction patterns, which illustrate the structure of the sample, and bright-field images, which show the morphology of a sample.

Composition
Electron microprobe (EMP) analysis was used to collect compositional data from polished glassy fallout beads. An EMP uses a beam of electrons to excite atoms from the sample surface. As the atoms return to lower energy states, X-rays with characteristic wavelengths are emitted and detected by the EMP to determine the composition of the sample.

We collected qualitative compositional maps (below) and quantitative spot analyses (above). In the backscattered electron (BSE) image above bright areas represent higher average atomic number, and darker areas lower average atomic number. Yellow spots indicate quantitative EMP spot analyses and correlate to the graph (above right). This bead is fairly typical of the average composition and compositional variation within the fallout beads we studied. Composition data can be used to approximate the solidification temperature via known oxide melting points.

Weibull analysis (below) shows little evidence for the presence of discrete mineral grains within beads, though relic or partially melted grains (based on sharp compositional boundaries and a-D morphology) may be present in rare cases.

Cooling Environment

Conclusions
• The fireball from a 0.01–100 Kt weapon cools to ~2500°C within seconds (Spriggs, 2001).
• Temperatures at which oxide species transition from liquid to solid (right) can be used to understand the cooling regime of fallout.
• Most bead material is amorphous, suggesting very rapid quenching of the silicate liquid.
• Glassy material is feldspathic in composition, consistent with the dominant source material for the silicate melts being surrounding dirt and soil (Jacobson-Hood, 2012).
• Crystalline regions are observed, but generally as discrete phases, separated from the bulk of the matrix.
• Crystalline diffraction patterns often match common rock-forming mineral phases.
• Crystalline materials are likely included grains from the dust and debris of the surrounding environment, not phases that crystallized during quenching of the silicate melts or unmelted device components.

References
1) Gostic, Richard et al. (2011), LLNL-POST-492905
2) Jacobson-Hood, Timothy et al. (2012), LLNL-POST-570154
3) Lindquist, Anna et al. (2011), Foilin, hot, hot, hot!, LLNL-POST-492773
4) Spriggs (2001), Thermal pulse from a nuclear detonation, LLNL-PRES-406971
5) webelmets.com, accessed July 31, 2015
LLNL-POST-569061
Introduction

Nuclear forensics is a multidisciplinary science that uses a variety of analytical methods and tools to explore the physical, chemical, elemental, and isotopic characteristics of nuclear and radiological material. These signatures may allow determination of the materials provenance and the method of manufacture. The uranium isotopic composition reveals whether the uranium is natural, depleted, or enriched and whether the material has ever been subjected to neutron irradiation and subsequently reprocessed. The radionuclides (i.e., age dating) presented here determine the time since purification of a uranium-bearing material based upon the ingrowth of 239Pu toward its parent 240Pu in a non-disturbed environment. The uranium decay series and the position of 235U and 234U in the sequence of decay products is shown in Figure 1. In this work, a variety of uranium bearing materials are analyzed to determine the nuclear forensics signatures in each sample.

Experimental

Sample Preparation:

- The uranium metal samples were digested with nitric acid. The soil samples were digested with nitric and hydrofluoric acid. Sample aliquots were spiked with 231U, 237Th, or 239Pu and processed through several separation and purification steps shown in Figure 2.

Instrumentation:

- Samples were analyzed using the following type of instrumentation:
  - MC-ICP-MS
  - SEM/EDS
  - Quadrupole-MS

Table 1: Uranium Isotopic Composition and Uranium Concentrations for Each Sample.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>U-238 %</th>
<th>U-235 %</th>
<th>U-234 %</th>
<th>U-233 %</th>
<th>U-236 %</th>
<th>U-237 %</th>
<th>U-239Pu %</th>
<th>U-240Pu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.005</td>
<td>0.004</td>
<td>0.006</td>
<td>0.001</td>
<td>0.002</td>
<td>0.003</td>
<td>0.004</td>
<td>0.006</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.007</td>
<td>0.006</td>
<td>0.008</td>
<td>0.002</td>
<td>0.003</td>
<td>0.005</td>
<td>0.004</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table 2: Uranium Concentrations for Each Metal Sample.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>U-238 ppm</th>
<th>U-235 ppm</th>
<th>U-234 ppm</th>
<th>U-233 ppm</th>
<th>U-236 ppm</th>
<th>U-237 ppm</th>
<th>U-239Pu ppm</th>
<th>U-240Pu ppm</th>
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</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>0.005</td>
<td>0.004</td>
<td>0.006</td>
<td>0.001</td>
<td>0.002</td>
<td>0.003</td>
<td>0.004</td>
<td>0.006</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.007</td>
<td>0.006</td>
<td>0.008</td>
<td>0.002</td>
<td>0.003</td>
<td>0.005</td>
<td>0.004</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Comparison of Uranium Metals

Four uranium metal samples were analyzed for nuclear forensic signatures. The fuel rod and fuel rod shaving samples have a significant amount of 239Pu and the model ages are older than their expected age. The 240Pu signature indicates that these samples may contain a component of recycled irradiated uranium. The model age of the metal samples appears older than the expected age due to excess initial 239Pu.

Figure 4: A) Uranium ratio comparison plot for each metal sample. (Error bars represent k = 1.) B) Age dating comparison for each metal sample. (Error bars represent k = 1.)

Future Work

- Analysis of uranium ore samples for signatures.
- Analyze ore and metal samples for RP4 signatures.

Conclusions

- Analyzing both uranium metal and soil samples from a metal rolling facility for nuclear forensic signatures can tell two sides of a story.
- The uranium metal is better suited for forensic analysis, as it may be a closed-system.
- Soil samples are mixtures of natural (old), and anthropogenic (young) material.
- Radiochemistry is an important tool in determining the provenance of nuclear or radiological material, but has its limitations.

References

First Principles Study of AnO₂(NO₃)₂(H₂O)₂ (An=U, Pu) VI to V Reduction Potential

2Mitchell Goshert, 1Patrick Huang, and 2Justin Walensky
Physical and Life Sciences Directorate and Glenn T. Seaborg Institute
1Lawrence Livermore National Laboratory
2University of Missouri

INTRODUCTION
• Aqueous uranyl and plutonyl dinitrates are common by-products of nuclear fuel reprocessing.
• What is their long-term mobility and fate?
• Oxidation state determines solubility and consequently the mobility in the environment.
• What are the thermodynamic parameters characterizing the transformation between oxidation states?
• Activites in solution exhibit a large variation in oxidation state and coordination number.
• Contributions due to variations in actinide speciation as to disentangle experimentally.
• Calculations of reduction potential can provide useful insight on the energy required to reduce these actinide species.

SOLVENT MODEL
Conductor-like Polarizable Continuum Model (CPCM)
• Solvent effects are an important influence on reduction potentials.
• Model solvent as a continuum dielectric.
• Need to assume a conductor-like cavity containing solute.
• CPCM well-established for polar solvents (e.g., water).

For large, aspherical complexes, shape-adapted cavities are necessary.

THEORETICAL METHODOLOGY
Hartree-Fock (HF)
\[
\left[ \frac{-\hbar^2}{2m} \nabla^2 + V_{ext}(\mathbf{r}) \right] \psi_\alpha(\mathbf{r}) = \varepsilon_\alpha \psi_\alpha(\mathbf{r})
\]
• Mean field approximation: Each electron feels the same averaged, effective potential due to the remaining electrons.
• Does not include electron-electron correlation \( \Rightarrow \) qualitative, but not quantitatively accurate.
• Useful as starting point for higher-level theories.

Density Functional Theory (DFT)
• Mean-field theory (like Hartree-Fock).
• Approximate inclusion of electron correlation via model exchange-correlation functional \( \rho_{ex} \).
• We employ the B3LYP approximation for \( \rho_{ex} \): 1. Generally improves bond energies and lengths over HF.
2. Better suited for localized d- or f-electrons (minimizes self-interaction error).

OPTIMIZATION OF BOTH U(VI) AND U(V) SPECIES
• Both the HF and the DFT-B3LYP level of theory were employed.
• The structures of the UO₂(NO₃)₂(H₂O)₂ complex in both U(VI) and U(V) oxidation states were optimized.
• Vibrational analysis was employed to verify the stability of optimized structures.

The optimized structures of U(VI) (left) and U(V) (right).

STRAIGHTENED CAVITY

Spherical cavity

Reduction Potentials
• Inclusion of solvent effects yields a \( \gtrsim 4.9 \text{ eV} \) improvement over the gas phase model.
• Discrepancy between AG solv and exp.

CONSOLUTIONS
• Benchmark studies have been done on the UO₂(NO₃)₂(H₂O)₂ VI and V compounds.
• Our model involves an explicit representation of the first coordination sphere plus a continuum dielectric for the solvent environment.
• Solvation effects are essential for description of reduction potentials.

FREQUENCIES

UO₂(NO₃)₂(H₂O)₂ - Frequencies

UO₂ (cm⁻¹)
Hf (exp) B3LYP (gas) B3LYP (solv) Exp.
1062.0 894.5 880.9
1129.0 979.6 943.2

Hf yields shorter, stiffer bonds.
• Inclusion of solvent slightly red-shifts frequencies.

FUTURE WORK
• Secondary coordination sphere in the solvent model still need to be included for further improvement in reduction potential values.
• Spin-orbit correction.
• Improved treatment of electron correlation (second order perturbation theory, MP2).
• Plutonyl calculations.

ACKNOWLEDGMENTS
• M.G. gratefully thanks the Glenn T. Seaborg Institute for their financial support.
Cosmogenic Activation in the Neutrinoless Double-beta Decay Experiment CUORE

Barbara S. Wang1, Eric B. Norman1, Nicholas D. Sicilione2, Marisa Pedretti2, Stephen A. Wender2, Alan R. Smith1, Keenan J. Thomas1,4, Yuen-Dat Chan4

University of California, Berkeley; 2Lawrence Livermore National Laboratory; 3Los Alamos National Laboratory; 4Lawrence Berkeley National Laboratory

Abstract: CUORE (Cryogenic Underground Observatory for Rare Events) is an experiment that will search for neutrinoless double-beta (0νββ) decay. The CUORE detector is an array of 988 high-resolution, low-background TeO2 bolometers operated at cryogenic temperatures. All sources of background that can obscure the 0νββ decay signature must be well-understood. One of these sources is cosmogenic activation of the bolometers. A reliable estimation of this background is essential but difficult to obtain because of the lack of cross-section data. Thus, cross-section measurements have been carried out at LANSCE (Los Alamos Neutron Science Center).

Introduction

Background Events
- An event that is not 0νββ decay and can obscure the 0νββ decay peak is considered background.
- Need extremely low background in region around 2527 MeV
- CUORE’s goal is background at 2527 MeV: 0.001 MeV/year
- All sources of background must be well-understood
- Background due to cosmogenic activation of the TeO2 bolometers: highly uncharacterized

Cosmogenic Activation in CUORE
- Interactions with cosmic rays produce radionuclides in materials.
  - Explosive transportation
  - Each crystal spends 4 months above ground at sea-level
  - Long-lived radionuclides produced in TeO2 contribute background at 0νββ decay peak

Example: Beta decay of Co-60 (T1/2 = 5.27 y)

Methods and Results

LANSCE Neutron Spectrum (compared with cosmic ray neutron spectrum at sea-level)

Cross-section Measurement Information

To obtain the absolute peak efficiency, must be measured.

Cosmic ray neutron efficiency measured on same setup as in LANSCE.

Gamma Measurement Following Irradiation

Gamma rays from the radionuclides produced in TeO2 are measured after the neutron exposure.

Methods and Results (cont.)

Gamma rays from the radionuclides produced in TeO2 are measured after the neutron exposure.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.