LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-743114

2017 LLNL Nuclear Forensics Summer Internship Program

M. Zavarin

December 13, 2017

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

2017 LLNL NUCLEAR FORENSICS SUMMER INTERNSHIP PROGRAM

GLENN T. SEABORG INSTITUTE
LAWRENCE LIVERMORE NATIONAL LABORATORY
PHYSICAL AND LIFE SCIENCES DIRECTORATE

Glenn T. Seaborg Institute
Lawrence Livermore National Laboratory
Physical and Life Sciences Directorate
Livermore, CA 94550
https://seaborg.llnl.gov/

Director: Mavrik Zavarin (zavarin1@llnl.gov)
Administrator: Camille Vandermeer

Sponsors:
National Technical Nuclear Forensics Center
Domestic Nuclear Detection Office
Department of Homeland Security

Lawrence Livermore National Laboratory
Glenn T. Seaborg Institute
Physical and Life Sciences Directorate

LLNL-TR-743114

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA273.

The Lawrence Livermore National Laboratory (LLNL) Nuclear Forensics Summer Internship Program (NFSIP) is designed to give graduate students an opportunity to come to LLNL for 8–10 weeks of hands-on research. 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 can also meet staff scientists one-on-one, participate in LLNL facility tours (e.g., the National Ignition Facility and Center for Accelerator Mass Spectrometry), and gain a better understanding of the various science programs at LLNL.

The NFSIP began 20 years ago as the Actinide Sciences Summer Program (see LLNL Newsline article, Appendix A). The program is run by the Glenn T. Seaborg Institute in the Physical and Life Sciences Directorate at LLNL (see recently updated poster highlighting the summer program, Appendix B). The goal of the NFSIP is to facilitate training for next generation nuclear scientists and engineers to solve critical national security problems in the field of nuclear forensics. Students are selected from the fields of physics, chemistry, geology, mathematics, nuclear engineering, chemical engineering, and environmental sciences. Students engage in research projects in the disciplines of actinide chemistry, radiochemistry, isotopic analysis, computation, radiation detection, and nuclear engineering in order to strengthen the "pipeline" for future scientific disciplines critical to the Department of Homeland Security (DHS) Domestic Nuclear Detection Office (DNDO).

2017 Nuclear Forensics Summer Internship Program students met with NTNFC management on July 10, 2017. From left: Lindsay Strain (NTNFC), Elii Ronay (Vanderbilt University), Ellen Monzo (University of Minnesota, Duluth), Amalie Zeitoun (NTNFC manager), Ate Visser (LLNL mentor), Jeremy Osborn (Texas A&M, College Station), Aaron Tamashiro (Oregon State University, Corvallis), and Marissa Loustale (California State University, Sacramento).

The NFSIP is highly competitive with over 150 applicants for between 5–7 available slots. Additional students funded through paid internships and fellowships from NNSA, DHS, and DOE are invited to participate in the summer lecture series and poster symposium. This year, the NFSIP hosted students from 5 universities (See Table 1) across the US (Figure 1). The NFSIP students conducted research on such diverse topics as noble gas signature analysis of underground nuclear detonations, high precision measurement of Th and U decay constants for nuclear materials chronology, simulation of reactor fuel signatures, Sr and Mg isotopic signature determination using thermal ionization mass spectrometry and multicollector inductively coupled plasma mass spectrometry, and analysis of nuclear cross section data and gamma ray spectra for detector applications (see Table 2 for poster titles). Continuation of research collaboration between the graduate student, faculty advisor, and LLNL mentors is strongly encouraged. In many cases, NFSIP research evolves into a significant component of the students' graduate theses. For example, two graduates of the 2016 NFSIP (Jack Goodell and Katie Hoffman) joined LLNL through programmatic funding and a DOE Office of Science Graduate Student Research (SCGSR) Program fellowship to continue their graduate studies at LLNL in 2017.

In addition to hands-on training, students attend a weekly lecture series on topics applicable to the field of nuclear forensics (see Table 3). Selected speakers represent the breadth of expertise required for nuclear forensics research. Speakers discuss the importance of their work in the context of national and international nuclear forensics.

Graduate and undergraduate students on fellowships, such as the Nuclear Forensics Graduate Fellowship (NFGF), are invited to join the summer program. This year, LLNL hosted three NFGF program students (Table 1). In addition, 10 students funded by other nuclear science fellowships or programmatic funding participated in summer program activities.

As part of an effort to build a "pipeline" for next generation nuclear forensics scientists, LLNL hosts students who are participating in the DOE sponsored "Summer School in Radiochemistry" held at San Jose State University (SJSU). The SJSU summer students come to LLNL to meet onsite summer students, discuss nuclear forensics research opportunities at LLNL, and tour state-of-the-art facilities. The SJSU summer students are strongly encouraged to apply to the LLNL nuclear forensics program—SJSU summer student graduate Ellen Monzo participated in the 2017 NFSIP.

The LLNL summer program provides a nuclear forensics pipeline of top-quality students from universities across the U.S. Since 2002, 30–40% of former attendees have returned to conduct their graduate research at LLNL. In addition to those returning for graduate work:

- 18 became post-doctoral fellows at LLNL
- Six became post-doctoral fellows at other national labs
- 14 were hired as career scientists at LLNL
- Five were hired as career scientists at other national labs
- Four were hired as faculty in nuclear forensics/radiochemistry/nuclear science
- Four others were hired at additional government institutions

A big factor in the success of this program is the dedication of the staff scientists who volunteer to mentor the summer students. Three of those mentors are, in fact, past recipients of NTNFC fellowships, and are now helping to grow the next generation of nuclear forensics scientists. In 2017, funding from NTNFC's Graduate Mentor Assistance Program (GMAP) helped to support the time required to mentor NFSIP students as well as NFGF program students. The GMAP allows staff scientists to develop summer projects for their students, oversee necessary safety training, and dedicate time to helping the interns and students maximize their productivity and scientific potential. Posters summarizing each NFSIP student's research were presented at the Laboratory Student Poster Day and are included at the end of this report.

NUCLEAR FORENSICS SUMMER INTERNSHIP PROGRAM

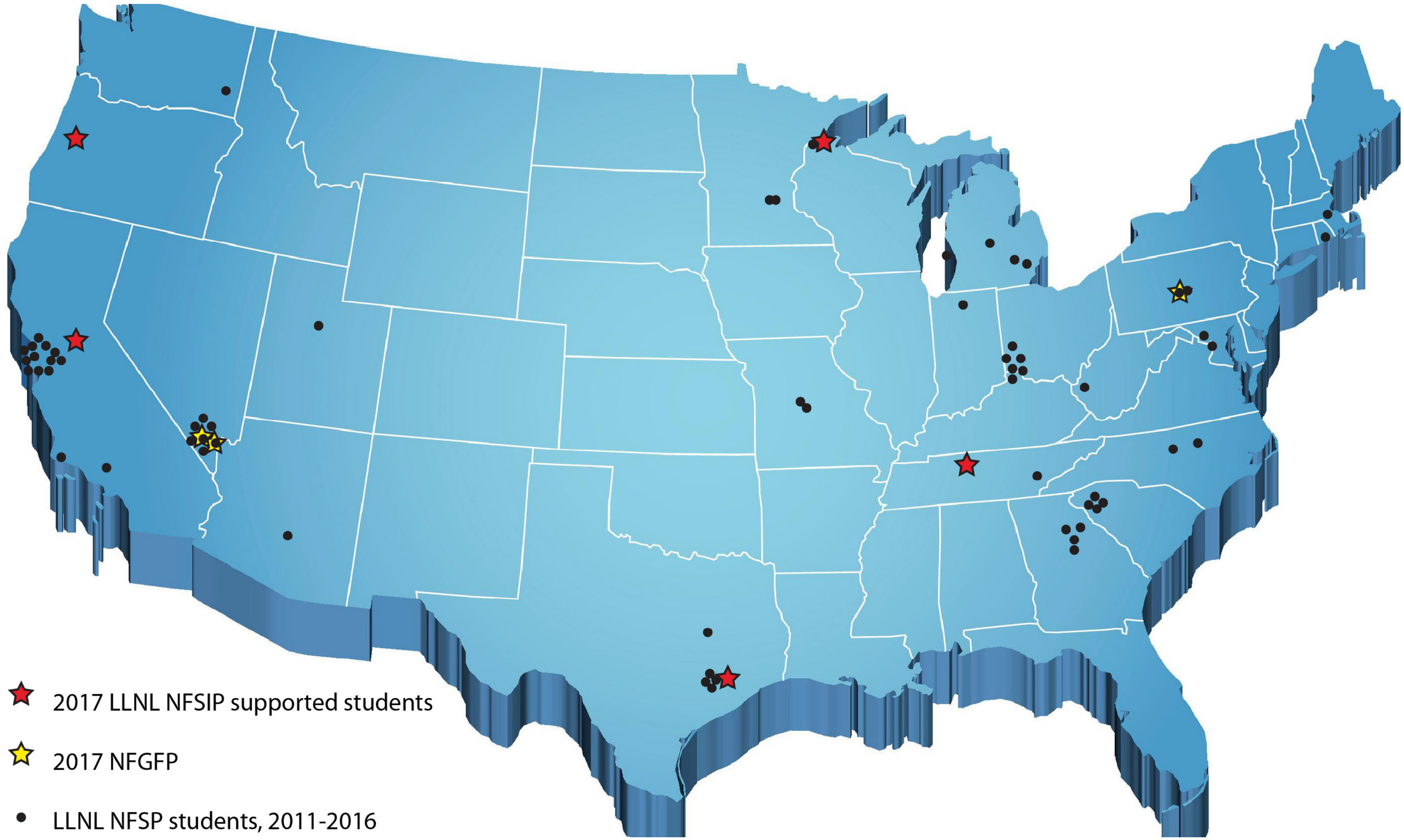


Figure 1. LLNL 2017 Nuclear Forensics Summer Internship Program (NFSIP) participants are selected from across the United States

NFSIP STUDENTS

Table 1. 2017 NFSIP Students

MARISSA LOUSTALE Graduate Student, Isotope Hydrology Sacramento State	**ELLEN MONZO** Undergraduate Student, Biochemistry Minnesota UMD Duluth	**JEREMY OSBORN** Graduate Student, Nuclear Engineering Texas A&M University	**ELLI RONAY** Graduate Student, Geochemistry Vanderbilt University	**AARON TAMASHIRO** Graduate Student, Nuclear Engineering Oregon State University
JOHN "JACK" GOODELL [a] Graduate Student, Chemistry University of Maryland 1856	**KATIE HOFFMAN** [a] Graduate Student, Chemistry University of Cincinnati	**CHAD DURRANT** [b] Graduate Student, Nuclear Engineering PennState	**JEFF ROLFES** [b] Graduate Student, Radiochemistry UNLV	**MARK FITZGERALD** [b] Graduate Student, Radiochemistry UNLV

[a] Returning 2016 NFSIP students funded through other grants and fellowships.

[b] Nuclear Forensics Graduate Fellow

NFSIP STUDENTS

Table 2. NFSIP Student Projects and Mentors

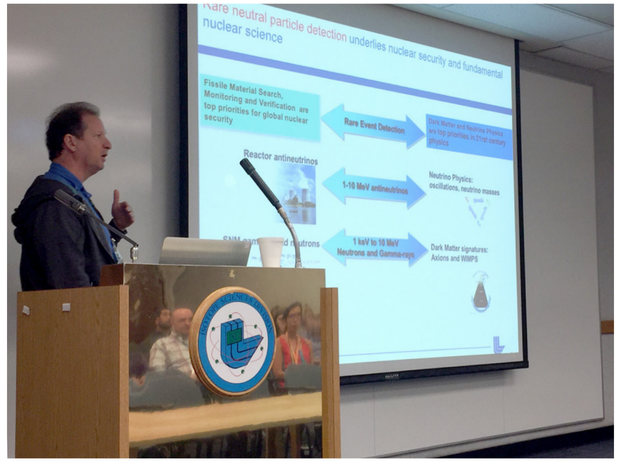
Student	Mentor	Project Poster Title
Marissa Loustale	Ate Visser, Carolyn Crow, and Bill Cassata	**Noble Gas Mass Spectrometry and Interpretation of Hydrogeologic Isotopic Signatures at the Nevada National Security Site**
Ellen Monzo	Tashi Parsons-Davis	**Alpha Spectroscopy Source Preparation for Radionuclide Metrology**
Jeremy Osborn	Martin Robel and Brett Isselhardt	**Samarium as a Thermal Reactor FluxMonitor For Used Fuel**
Elli Ronay	Naomi Marks	**($^{234}U/^{238}U$)i and $^{87}Sr/^{86}Sr$ in an Indian stalagmite: implications for monsoonrainfall proxycalibration**
Aaron Tamashiro	Jason Burke	**Evalution of U-238 Fission Product Yields**

Table 3. Nuclear Forensics Summer Program Seminar Schedule

Date	Speaker	Topic
6/15/17	David Weisz *Postdoc, Chemical and Isotopic Signatures Group, Nuclear and Chemical Sciences Division*	**Aerodynamic Fallout Glass and Fallout Formation Chemistry**
6/22/16	Ate Visser *Staff Scientist, Environmental Radiochemistry Group, Nuclear and Chemical Sciences Division*	**The Isotopic Fingerprints of Hydrological Processes**
6/29/16	Adam Bernstein *Group Leader, Rare Event Detection, Nuclear and Chemical Sciences Division*	**Rare Event Detection in Nuclear Science and Security**
7/6/16	Mona Dreicer *Deputy Director, Center for Global Security Research*	**Treaty Monitoring and Verification**
7/14/16	Sean Gates *Staff Scientist, Environmental Radiochemistry Group, Nuclear and Chemical Sciences Division* Roger Henderson *Staff Scientist, Nuclear and Radiochemistry Group, Nuclear and Chemical Sciences Division*	**Application of the U – He chronometer to the analysis of nuclear forensic materials** **A Renaissance of Plutonium Metal Production at the Gram Scale**
7/20/16	Naomi Marks *Staff Scientist, Chemical and Isotopic Signatures Group, Nuclear and Chemical Sciences Division*	**Case Studies in Nuclear Forensics: A primer on Comparative Analysis Techniques**
8/4/16	Mavrik Zavarin *Director, Glenn T. Seaborg Institute, Physical and Life Sciences Directorate*	**Closeout**

LECTURES AND TOURS

David Weisz (Hutcheon post-doctoral fellow)
describes the nature and chemistry of nuclear fallout



Adam Bernstein describes rare event
detection in nuclear security and basic nuclear science

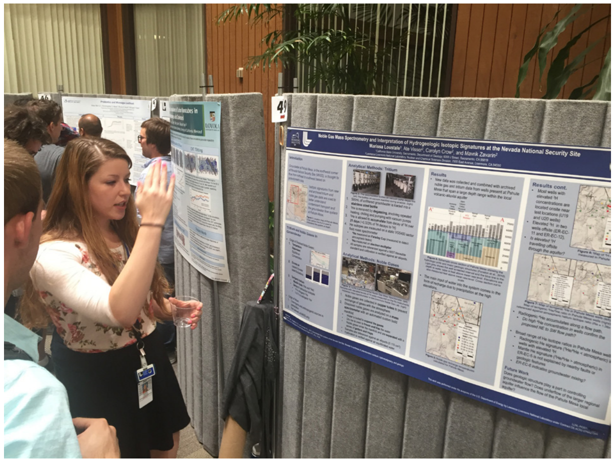
Roger Henderson describes the chemistry and
application of plutonium metal production at the gram scale

Mona Dreicer describes treaty monitoring
and verification in the context of nuclear science

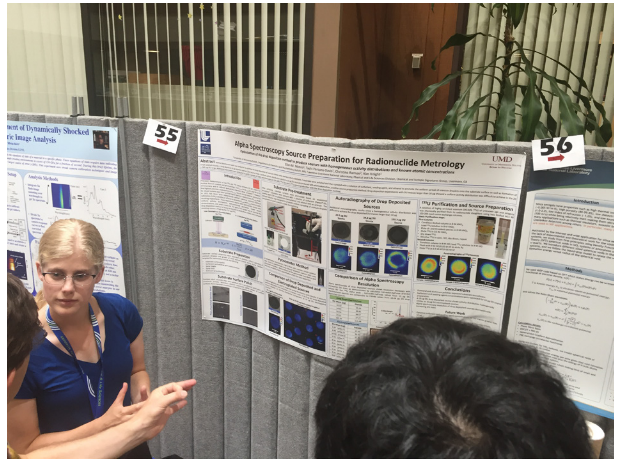
Sean Gates describes the use of noble gas
mass spectrometry in nuclear forensics chronometry

2017 NFSIP students received a copy of Scott Berkun's
Confessions of a Public Speaker highlighting the
importance of effective presentation of scientific research

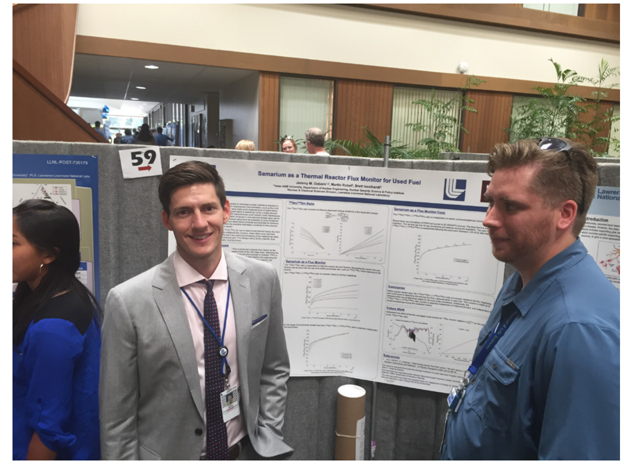
LLNL SUMMER POSTER SESSION



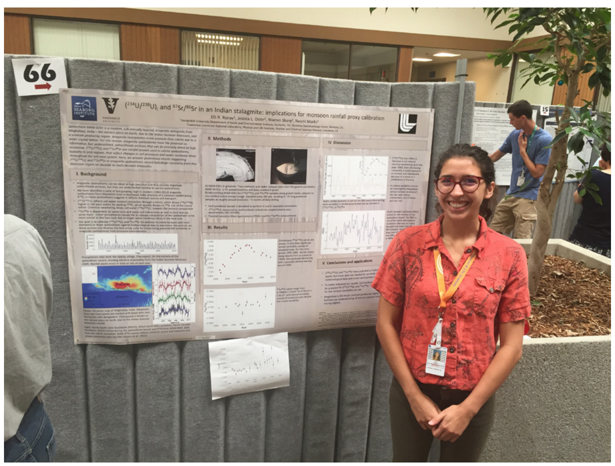
Marissa Loustale discusses her poster "Noble Gas Mass Spectrometry and Interpretation of Hydrogeologic Isotopic Signatures at the Nevada National Security Site" at the LLNL summer student poster session



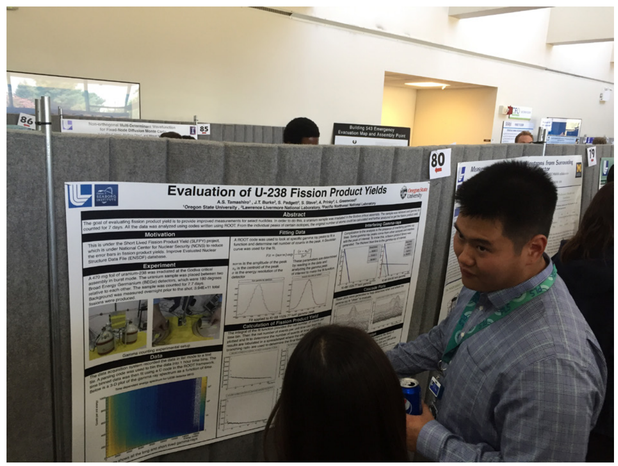
Ellen Monzo explains her poster "Alpha Spectroscopy Source Preparation for Radionuclide Metrology" at the LLNL summer student poster session



Jeremy Osborne (left) discusses "Samarium as a Thermal Reactor Flux Monitor for Used Fuel" with Jack Goodell (2016 NFSIP student) at the LLNL summer student poster session



Elii Ronay presents her poster "Uranium and Strontium Isotopic Signatures in an Indian Stalagmite" at the LLNL summer student poster session



Aaron Tamashiro presents his poster "Evaluation of U-238 Fission Product Yields" at the LLNL summer student poster session

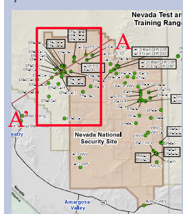
NUCLEAR FORENSICS SUMMER PROGRAM POSTERS

Noble Gas Mass Spectrometry and Interpretation of Hydrogeologic Isotopic Signatures at the Nevada National Security Site

Marissa Loustale[1], Ate Visser[2], Carolyn Crow[2], and Mavrik Zavarin[2]
[1]California State University, Sacramento, Department of Geology, 6000 J Street, Sacramento, CA 95819
[2]Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, 7000 East Avenue, Livermore, CA 94550

Introduction

Groundwater at Pahute Mesa, in the northwest corner of Nevada National Security Site (NNSS), is thought to flow from northeast to southwest based on potentiometric data.

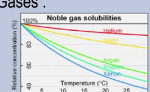


Isotopic signatures from new and archived tritium and noble gas data are used to better understand contaminant transport and the groundwater flow system at Pahute Mesa.

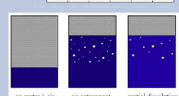
Figure 1: Location map of Pahute Mesa. Cross section line A-A' is used to understand the system at depth.

Tritium and Noble Gases in Groundwater

- Origin of Dissolved Noble Gases :
  1. **Temperature Dependent** Equilibrium Concentration



  2. **Excess air** caused by water table fluctuations



  3. **Terrigenic helium**
     - **Mantle fluids** (^{3}He and ^{4}He)
     - **Decay** of radioactive isotopes
       - ^{3}H to tritiogenic ^{3}He
       - U & Th to radiogenic ^{4}He
- Origin of tritium:
  1. Cosmogenic and anthropogenic sources in precipitation
  2. Test derived, at NNSS only

Analytical Methods: Tritium

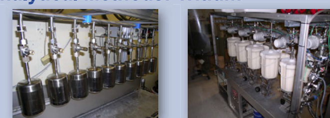


Figure 2 : ^{3}He accumulation bottles on vacuum pump degas line. (left) ^{3}He bottles on vacuum manifold during analysis. (right)

1. 500mL of unfiltered groundwater is loaded into a **stainless steel bottle**
2. ^{3}He is removed by **degassing**, involving repeated heating, chilling and pumping with vacuum pumps
3. ^{3}He is allowed to **accumulate** from decay of ^{3}H over **21 days** (~0.323% of ^{3}H decays to ^{3}H)
4. He isotopes are measured on a static VG5400 sector field mass spectrometer
   - **^{4}He** measured on **Faraday Cup** (measured to detect atmospheric leaks)
   - **^{3}He** measured on **electron multiplier**
   - All samples are referenced against a NIST-traceable standard and calibration is verified against air aliquots.

Analytical Methods: Noble Gases

Figure 3 : LLNL's environmental Noble Gas Mass Spectrometer. (left) Samples with elevated levels of ^{3}H were measured on the Nu Instruments Noblesse mass spectrometer in the Livermore Noble Gas Lab. (right)

1. Noble gases are collected in **copper tubes** to prevent exchange of gases with the atmosphere.
2. Dissolved noble gases are analyzed on a **mass spectrometer** with an automated custom build manifold.
   - Water is boiled to **expand the gases**
   - Dry ice is used to **freeze and trap** the water
   - Noble gases enter the manifold and are **separated** with a series of **getters and traps**
   - Samples are referenced against air aliquots (0.115 cm^3).
   - Calibration is verified against air equilibrated water.

Results

- New data was collected and combined with archived noble gas and tritium data from wells present at Pahute Mesa that span a large depth range within the local volcanic-alluvial aquifer

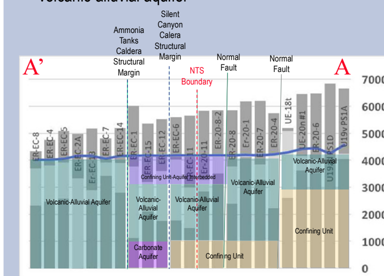


Figure 4: Schematic cross section of Pahute Mesa showing the hydrologic units and major geologic structures (Fenelon et al., 2010). Light grey shows the well screened interval and the blue line is the depth to water table in feet above mean sea level. Elevations are also measured feet above mean sea level. Cross section not to scale.

- The main input of water into the system comes in the form of recharge due to precipitation at the high elevations.

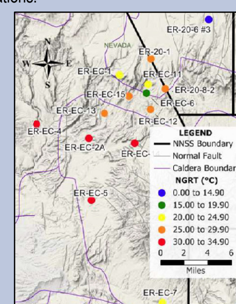


Figure 5: Noble gas recharge temperatures calculated for Pahute Mesa.

Results cont.

- Most wells with elevated ^{3}H concentrations are located onsite near test locations (U19 and U20 wells)
- Elevated ^{3}H in two wells offsite (ER-EC-11 and ER-EC-12).
- *Is elevated ^{3}H travelling offsite through the aquifer?*

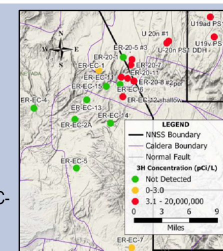


Figure 6: Map of ^{3}H concentration measured in Pahute Mesa wells.

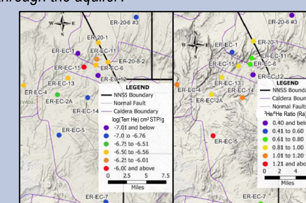


Figure 7: Map of terrigenic ^{4}He in Pahute Mesa wells (left). Map of terrigenic ^{3}He/^{4}He ratio in Pahute Mesa wells (right), referenced against atmospheric helium isotope ratio (Ra = 1.38x10^{-6}).

- Radiogenic ^{4}He accumulates along a flow path.
  - *Do high ^{4}He concentration in wells confirm the proposed NE to SW flow path?*
- Broad range of He isotope ratios in Pahute Mesa wells
  - Radiogenic He signature (^{3}He/^{4}He < atmospheric) in wells with elevated ^{3}H
  - Mantle He signature (^{3}He/^{4}He > atmospheric) in ER-EC-5 is not explained by nearby faults or geologic features
  - *ER-EC-6 indicates groundwater mixing?*

Future Work

Does geologic structure play a part in controlling groundwater flow? Does underflow of the larger regional aquifer influence the flow of the Pahute Mesa local aquifer?

References:
Fenelon, J.M., Sweetkind, D.S., and Laczniak, R.J., 2010, Groundwater flow systems at the Nevada Test Site, Nevada: A synthesis of potentiometric contours, hydrostratigraphy, and geologic structures: U.S. Geological Survey Professional Paper 1771, 54 p., 6 pls.

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

LLNL-POST-735972

Alpha Spectroscopy Source Preparation for Radionuclide Metrology

Optimization of the drop deposition method to produce sources with homogeneous activity distributions and known atomic concentrations

Ellen M. Monzo[1], Tashi Parsons-Davis[2], Christina Ramon[2], Kim Knight[2]

[1]University of Minnesota Duluth, Department of Chemistry and Biochemistry, Duluth, MN, [2]Lawrence Livermore National Laboratory, Physical and Life Sciences Division, Chemical and Isotopic Signatures Group, Livermore, CA

UMD University of Minnesota Duluth Driven to Discover

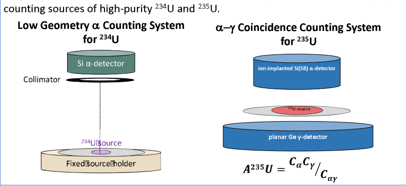
Abstract Method development work was conducted to optimize the drop deposition of uranium nitrate onto stainless steel substrates. Substrates were polished and then sprayed with a solution of surfactant, seeding agent, and ethanol to promote the uniform spread of uranium droplets onto the substrate surface as well as formation of small uranium crystals. A drop deposited 10 μg depleted uranium (DU) source shows a uniform activity distribution similar to 10 μg DU sources produced with electrodeposition, another source production method. Drop deposition experiments with DU masses larger than 10 μg showed a uniform activity distribution was difficult to achieve in the 20 – 300 μg DU range. Additional experiments were conducted to purify a sample of highly enriched uranium (99.94% ^{235}U) for use in ^{235}U source production with the drop deposition method.

Introduction

^{234}U 2.455X10^5 y

^{235}U 7.04 x 10^8 y

Precision measurements of the ^{234}U and ^{235}U decay constants (λ) are critical for nuclear forensic analysis and geochronology. The $\lambda_{U\text{-}234}$ and $\lambda_{U\text{-}235}$ are used for U-Pb chronometry and to calibrate geologically important decay constants.[1,2] However, the highest precision measurements of $\lambda_{U\text{-}234}$ rely on natural materials assumed to be closed systems over time[3] and the highest precision measurement of $\lambda_{U\text{-}235}$ made in 1971 has never been independently verified.[4] Lawrence Livermore National Laboratory (LLNL) is leading an effort to re-determine $\lambda_{U\text{-}234}$ and $\lambda_{U\text{-}235}$ via direct alpha counting experiments. These experiments require alpha spectroscopy sources with uniform activity distributions, well-constrained geometries, known atomic concentrations, and small crystal size. The goal of the project was to optimize the drop deposition method of source production to satisfy these criteria and to prepare counting sources of high-purity ^{234}U and ^{235}U.



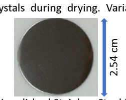
$$A^{235}U = \frac{C_\alpha C_\gamma}{C_{\alpha\gamma}}$$

$$N = N_o e^{-\lambda t} \quad \lambda = \frac{\ln(2)}{t_{1/2}} \quad A = \lambda N$$

Substrate Preparation

Substrate surface properties were optimized to promote uniform spreading of uranium droplets and growth of small uranium crystals during drying. Variables targeted for optimization include the following:

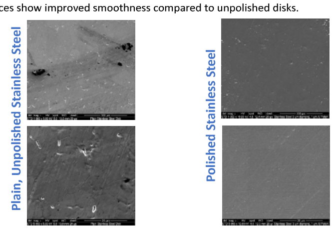
- Substrate surface polish
- Surfactant and seeding agent concentrations
- Spray height
- Spray time
- Airbrush spray diameter



Plain, Unpolished Stainless Steel Disk

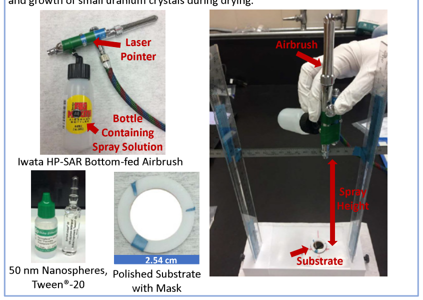
Substrate Surface Polish

Stainless steel substrate disks were polished with 3 μm diamond polish and 1 μm aluminum powder. Secondary electron microscopy (SEM) images of polished surfaces show improved smoothness compared to unpolished disks.



Substrate Pre-treatment

After polishing, substrate surfaces were pre-treated based on established procedure.[5] Substrates were sprayed with a solution of surfactant (Tween®-20), seeding agent (50 nm polystyrene nanospheres), and ethanol with an airbrush . The sprayed solution was designed to promote uniform spreading of uranium droplets and growth of small uranium crystals during drying.



Iwata HP-SAR Bottom-fed Airbrush

50 nm Nanospheres, Tween®-20

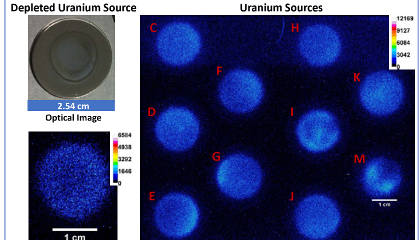
Polished Substrate with Mask

Pycnometer Method

A polyethylene pycnometer (right) filled with uranium nitrate solution was used to quantitatively drop deposit depleted uranium (DU) onto prepared substrates. Measurement of the pycnometer mass before and after use enabled precise quantification of the DU mass deposited.

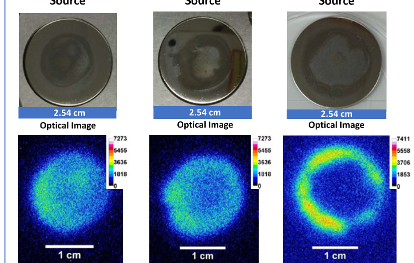
Comparison of Drop Deposited and Electroplated Sources

Autoradiography was used to image the spatial distribution and intensity of uranium activity deposited onto substrates in arbitrary units. A 10.3 μg DU drop deposited source displays an activity distribution comparable to 10 μg DU electroplated sources.[6]



Autoradiography of Drop Deposited Sources

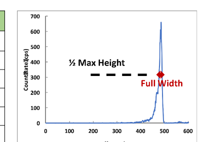
Additional autoradiography results show a homogeneous activity distribution was difficult to achieve for drop deposited DU masses larger than 10 μg.



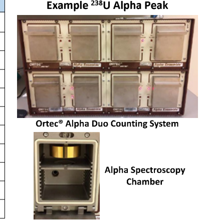
Comparison of Alpha Spectroscopy Resolution

Alpha spectroscopy of drop deposited sources shows resolution decreases with increasing DU mass as demonstrated by calculated full-width-half-max (FWHM) values for the ^{238}U alpha peak . Full-width-half-max values from 10 μg DU electroplated sources are comparable to FWHM values from 10-24 μg DU drop deposited sources.

Drop Deposited Sources	
DU Mass (μg)	**FWHM**
10.32	32.26
14.43	39.86
20.54	38.57
24.32	37.27
195.33	113.44
Electroplated Sources	
DU Mass (μg)	**FWHM**
9.97 (plate C)	25.35
9.98 (plate D)	39.50
10.02 (plate E)	27.30
9.92 (plate F)	32.99
9.98 (plate G)	29.50
9.95 (plate H)	30.32
9.94 (plate I)	32.85
9.95 (plate J)	30.57
9.93 (plate K)	28.75
9.89 (plate M)	66.27



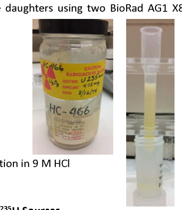
Example ^{238}U Alpha Peak


Ortec® Alpha Duo Counting System

Alpha Spectroscopy Chamber

^{235}U Purification and Source Preparation

A solution of highly enriched uranium (99.94% ^{235}U) of unknown age and progeny was chemically purified from its radionuclide daughters using two BioRad AG1 X8 100-200 mesh anion exchange columns.



Basic Purification steps:

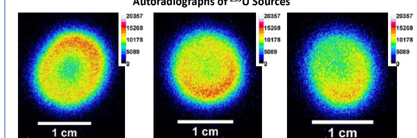
First Column

- Condition BioRad column in 8 M HNO_3
- Load ^{235}U solution in 8 M HNO_3
- Elute di- and tri-valent species in 8 M HNO_3
- Elute ^{235}U in 0.5 M HNO_3
- Dry down ^{235}U
- Dissolve ^{235}U in conc. HCl, dry down, repeat

Second Column

- Condition column in 9 M HCl, load ^{235}U solution in 9 M HCl
- Flush with 9 M HCl/0.05 M HF to elute Pa
- Elute ^{235}U in 0.5 M HCl/0.05 M HF

Autoradiographs of ^{235}U Sources



Sample 1 Autoradiograph Sample 2 Autoradiograph Sample 3 Autoradiograph

Conclusions

- Diamond and aluminum polishes improved substrate smoothness
- Surfactant and seeding agent concentrations were optimized for 10 μg DU source preparation
- A 10 μg DU drop deposited source shows activity distribution homogeneity similar to 10 μg DU electroplated sources
- Alpha spectroscopy resolution of drop deposited sources decreases with increasing DU mass

Future Work

- Optimize surfactant and seeding agent concentrations for DU masses greater than 10 μg
- Analyze drop deposited ^{235}U sources in an α–γ coincidence counting system
- Calculate $\lambda_{U\text{-}235}$ from coincidence counting data
- Analyze drop deposited ^{234}U sources in a low geometry α counting system
- Calculate $\lambda_{U\text{-}234}$ from low geometry counting data

References

1. Moody, K.; Hutcheon, I.; Grant, P. *Nuclear Forensic Analysis*. 2nd ed. CRC Press: Boca Raton, FL, 2015.
2. T.M. Harrison et al., (2015) It's About Time: Opportunities and Challenges for U.S. Geological Survey. Institute of Geophysics and Planetary Physics Publication 6539, University of California, Los Angeles.
3. Cheng, H.; Edwards, R. L.; Hoff, J.; Gallup, C. D.; Richards, D. A.; Asmerom, Y. The half-lives of uranium-234 and thorium-230. *Chem. Geol.* **2000**, *169*, 17-33.
4. Jaffey, A. H.; Flynn, K. F.; Glendenin, L. E.; Bentley, W. T.; Essling, A. M. Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U. *Physical Review C* **1971**, *4*, 1889.
5. Van Ammel, R., Eykens, S., Eykens, R., & Pommé, S. Preparation of drop-deposited quantitative uranium sources with low self-absorption. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* **2011**, *652*, 76-78.
6. Monzo, E., et al. *Optimization of Uranium Molecular Deposition for Alpha-Counting Sources*. No. LLNL-TR-714439. Lawrence Livermore National Laboratory (LLNL), Livermore, CA, 2016.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. This internship was supported by the National Technical Nuclear Forensics Center, Domestic Nuclear Detection Office, Department of Homeland Security. We would also like to thank the LLNL Laboratory Directed Research and Development (LDRD) program, project 16-LW-053 for financial support. One of the authors (T P-M) acknowledges the support of the Department of Homeland Security through a National Technical Nuclear Forensic Center Post-doctoral Fellowship. LLNL-POST-735501

LLNL-POST-735501

Samarium as a Thermal Reactor Flux Monitor for Used Fuel

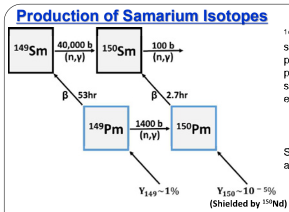
Jeremy M. Osborn[1,2], Martin Robel[2], Brett Isselhardt[2]
[1]Texas A&M University, Department of Nuclear Engineering, Nuclear Security Science & Policy Institute
[2]Nuclear & Chemical Sciences Division, Lawrence Livermore National Laboratory

Introduction

The ability to determine reactor flux from a used fuel sample or interdicted nuclear material is important in developing nuclear forensics analyses. Improvements in measurement instrumentation, such as the LLNL LION resonance ionization mass spectrometer (RIMS), have made quick measurements of stable fission product abundances possible. RIMS uses wavelength-tuned lasers to selectively ionize a single element before being sent to the mass analyzer. As a result, RIMS measurements avoid isobaric mass interferences. With respect to interdicted nuclear material, the information contained in intra-element isotope ratios will be insensitive to any chemical separation. Intra-element isotope ratios have the possibility to avoid limitations imposed by using only concentrations of radioactive and stable fission products and actinides for forensics analysis, however research must be done to interpret the available information contained in intra-element isotope ratios relating to the operating details of a reactor.

Previous studies have identified $^{136}Xe/^{134}Xe$ and $^{137}Cs/^{135}Cs$, for use in determining thermal reactor flux from used fuel.[1] In addition to the robustness gained by additional flux monitors, these ratios come with their challenges. Xenon is a noble gas, and thus will be lost if any chemical processing of the material has taken place. The cesium ratio is sensitive to reactor shutdowns and ^{137}Cs decays with a 30.08 y half-life, thus information on the reactor operating history, ideally, must be known.

Production of Samarium Isotopes

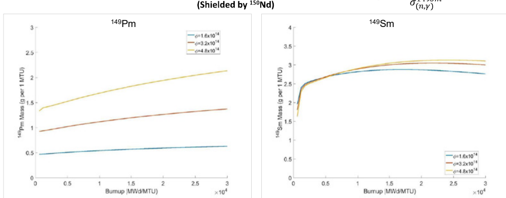


^{149}Sm is produced indirectly from fission as the stable nuclei of the 149 mass chain. Assuming the precursors are short enough to consider ^{149}Pm is produced directly from fission and neglecting the small amount of ^{149}Pm neutron capture, the equilibrium value of ^{149}Pm is as follows:

$$^{149}Pm(eq) = \frac{\Sigma_f^{fuel} * \phi * Y_{149}}{\lambda_{149Pm}}$$

Solving for the equilibrium concentration of ^{149}Sm and substituting ^{149}Pm yields the following:

$$^{149}Sm(eq) = \frac{\Sigma_f^{fuel} * Y_{149}}{\sigma_{(n,\gamma)}^{149Sm}}$$



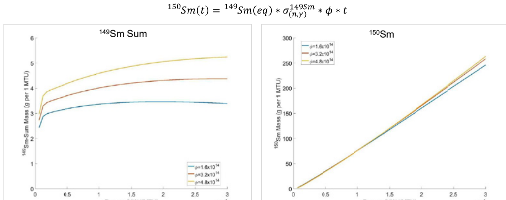
Concentrations of ^{149}Pm (left) and ^{149}Sm (right) within a PWR fuel burned at three different flux levels, using SCALE 6.2.

Assuming the ^{149}Pm will fully decay prior to measurement or separation, the measured ^{149}Sm sum:

$$^{149}_{Sum}Sm(eq) = \frac{\Sigma_f^{fuel} * Y_{149}}{\sigma_{(n,\gamma)}^{149Sm}} + \frac{\Sigma_f^{fuel} * \phi * Y_{149}}{\lambda_{149Pm}}$$

Assuming an equilibrium concentration of ^{149}Sm and neglecting the ^{150}Sm neutron capture:

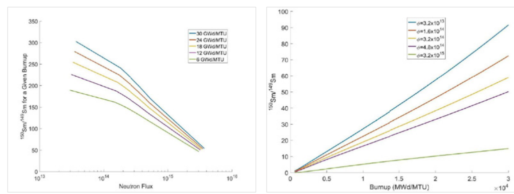
$$^{150}Sm(t) = {}^{149}Sm(eq) * \sigma_{(n,\gamma)}^{149Sm} * \phi * t$$



$^{150}Sm/^{149}Sm$ Ratio

The $^{150}Sm/^{149}Sm$ ratio consists of a fluence dependent isotope divided by a flux dependent isotope:

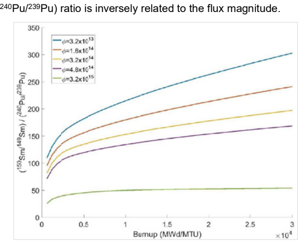
$$\frac{^{150}Sm}{^{149}_{Sum}Sm}(t) = \frac{\sigma_{(n,\gamma)}^{149Sm}\phi * t}{1 + \frac{\sigma_{(n,\gamma)}^{149Sm}\phi}{\lambda_{149Pm}}}$$



Samarium as a Flux Monitor

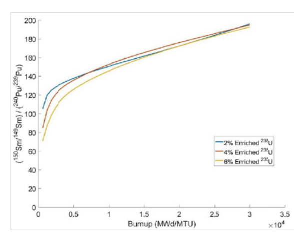
The $^{150}Sm/^{149}Sm$ ratio is dependent on both the neutron flux and fluence. Decoupling the neutron flux and fluence can be done with the use of an additional isotope ratio, such as $^{240}Pu/^{239}Pu$, which depends on the fluence.

The ($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio is inversely related to the flux magnitude.



($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio in PWR fuel burned at five flux levels, using SCALE 6.2.

Over the range of enrichments studied here the ($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio is relatively independent of fuel enrichment.

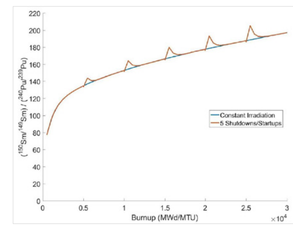


($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio in PWR fuel burned for three different fuel enrichments at the same flux level, using SCALE 6.2.

Samarium as a Flux Monitor Cont.

The ($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio is independent of reactor shutdowns/startups during irradiation.

Shown below are simulations of PWR fuel burned to 30 GWd/MTU burnup. The blue line is a constant irradiation. The red line has five 30-day shutdowns and startups during the irradiation. The ratio of ($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) re-establishes following the short-term transient (~25-40 d) after startups.



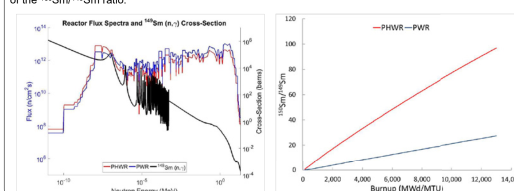
($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio in PWR fuel burned to 30 GWd/MTU with and without shutdowns/startups, using SCALE 6.2.

Conclusion

Within a given reactor-type, the ($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio is inversely related to the flux magnitude, and could serve to determine the thermal flux from measurements in used fuel. This monitor is made up of isotopes which are all effectively stable for the time scale considered. Additionally, the ($^{150}Sm/^{149}Sm$) / ($^{240}Pu/^{239}Pu$) ratio monitor is relatively independent of initial enrichment, and independent of shutdowns/startups during the irradiation history.

Future Work

Understand the effect of the flux-averaged cross-section for ^{149}Sm neutron capture ($\sigma_{(n,\gamma)}^{149Sm}$) on the behavior of the $^{150}Sm/^{149}Sm$ ratio.



References

1. A.C. HAYES, G. Jungman, Determining reactor flux from xenon-136 and cesium-135 in spent fuel, Nuclear Instruments and Methods in Physics Research A 690 (2012) 68-74.

This research was performed under the Nuclear Forensics Summer Internship Program, administered by the Glenn T. Seaborg Institute.

This internship was supported by the National Technical Nuclear Forensics Center, Domestic Nuclear Detection Office, Department of Homeland Security.

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

LLNL-POST-735473

$(^{234}U/^{238}U)_i$ and $^{87}Sr/^{86}Sr$ in an Indian stalagmite: implications for monsoon rainfall proxy calibration

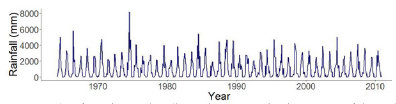
Elli R. Ronay[1*], Jessica L. Oster[1], Warren Sharp[2], Naomi Marks[3]

[1]Vanderbilt University Department of Earth and Environmental Sciences, Nashville, TN; [2]Berkeley Geochronology Center, Berkeley, CA;
[3]Lawrence Livermore National Laboratory, Physical and Life Sciences, Nuclear and Chemical Sciences Division, Livermore, CA

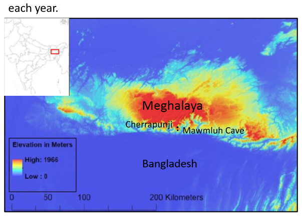
Speleothem MAW-0201 is a modern, sub-annually layered, aragonite stalagmite from Meghalaya, India – the rainiest place on Earth. Aragonite incorporates more uranium than calcite due to a wider crystal lattice. For this reason, aragonite speleothems have the potential as informative, but underutilized, paleoclimate archives that can be precisely dated at high resolution. $(^{234}U/^{238}U)_i$ and $^{87}Sr/^{86}Sr$ are rainfall proxies used in calcite speleothems, typically in arid regions, that reflect changes in soil processes and water residence times throughout the soil-cave system. Here, we present preliminary results suggesting $(^{234}U/^{238}U)_i$ and $^{87}Sr/^{86}Sr$ in aragonite speleothems record hydrologic variability from this monsoon region on decadal to multi-decadal timescales.

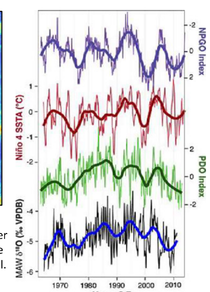
I. Background

- Aragonite speleothems can be dated at high precision and thus provide important paleoclimate archives, but they are understudied relative to calcite speleothems.
- We have identified a suite of fast-growing, high U, modern (1960-2012) aragonite speleothems from Mawmluh Cave in Northeast India. Analysis of a common rainfall proxy, $\delta^{18}O$, in these speleothems suggests it reflects moisture source and transport.
- $(^{234}U/^{238}U)_i$ reflects soil water-mineral interaction through α-recoil, which drives $(^{234}U/^{238}U)_i$ higher in soil pore waters by ejecting ^{234}Th, which quickly decays to ^{234}U, out of the crystal lattice. Chemical weathering drives soil water $(^{234}U/^{238}U)_i$ towards the mineral composition
- $^{87}Sr/^{86}Sr$ is dependent on water-rock and water-soil interactions as well as dust and sea spray input. Lower precipitation causes the Sr isotope composition of the speleothem to be more similar to the host rock due to longer water residence times in the host rock
- Our goal is to calibrate $(^{234}U/^{238}U)_i$ and $^{87}Sr/^{86}Sr$ (in addition to stable isotopes and trace elements) in these speleothems against meteorological data to determine the controls on these proxies and develop the best proxy suite for determining paleorainfall variability in aragonite speleothems from monsoonal environments.



Precipitation data from the nearby village, Cherrapunji, for the entirety of the speleothem record, showing extreme seasonality from the ISM. Rainfall peaks occur in June or July of each year.

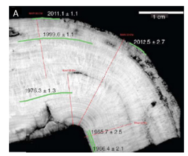


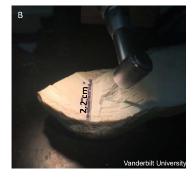


Above: Elevation map of Meghalaya, India. Mawmluh Cave and Cherrapunji are marked with black dots near the border with Bangladesh. Cherrapunji is known as the rainiest place on Earth, due to the Indian Summer Monsoon (ISM) rainfall. Inset map: D-maps

Right: NPGO, Niño4, PDO indices during the speleothem record, and $\delta^{18}O$ from MAW-0201. Bold lines are LOESS smoothed. MAW $\delta^{18}O$ mainly reflects moisture source and transport and shows similarities with the PDO (Myers et al., 2015)

II. Methods

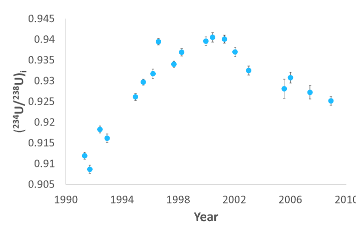




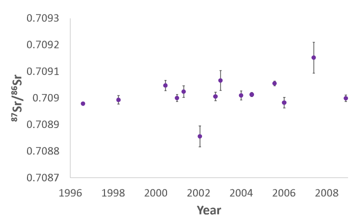
A) MAW-0201 in greyscale. Trace elements and stable isotopes taken from the growth axis labeled MAW 02-01a. U-Th sample locations and dates marked in green.
B) Micromilling MAW-0201 for $(^{234}U/^{238}U)_i$ and $^{87}Sr/^{86}Sr$ samples along growth bands, adjacent to micromilled stable isotope trough. Sampled every 200 μm, resulting in ~70 5mg powdered samples at roughly annual resolution. ~2 months of daily drilling

- Each powdered sample is dissolved to perform U and Sr separation procedures
- $(^{234}U/^{238}U)_i$ measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS)
- Thermal Ionization Mass Spectrometry (TIMS) used for $^{87}Sr/^{86}Sr$ measurements

III. Results

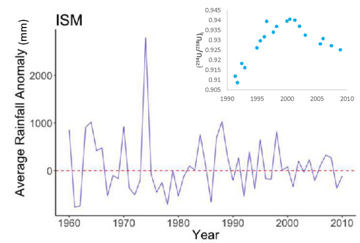


Preliminary $(^{234}U/^{238}U)_i$ values are always <1 and show significant annual variability outside of analytical error. For this time period, 1991-2009, we see values rising steadily from to a peak at ~2000, then gradually decreasing with a potential plateau starting around 2005.



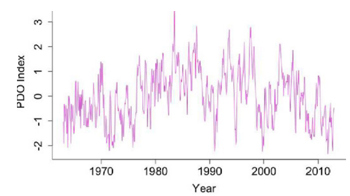
$^{87}Sr/^{86}Sr$ values range from 0.708856 ± $3.9x10^{-5}$ to 0.709152 ± $5.8x10^{-5}$, with annual variability outside of analytical error despite low overall variability

IV. Discussion



Yearly rainfall anomalies in mm for the ISM season showing long term variability in rainfall amounts that may be recorded in $(^{234}U/^{238}U)_i$

- $(^{234}U/^{238}U)_i$ may reflect a decrease in soil mineral chemical weathering up to the peak ~2000, then decreasing. Conversely, it could represent an increase and subsequent decrease in α-recoil or a combination of the two.
- Sr isotope variability cannot be meaningfully interpreted without isotopic analysis of the two main mixing endmembers, soil minerals and host rock.



Pacific Decadal Oscillation (PDO) indices for the entirety of the speleothem record. The PDO is one of the ocean-atmosphere oscillations that acts on multi-decadal time scales and affects ISM strength. The PDO and other large scale climate oscillations may affect isotopic abundances in MAW-0201.

V. Conclusions and applications

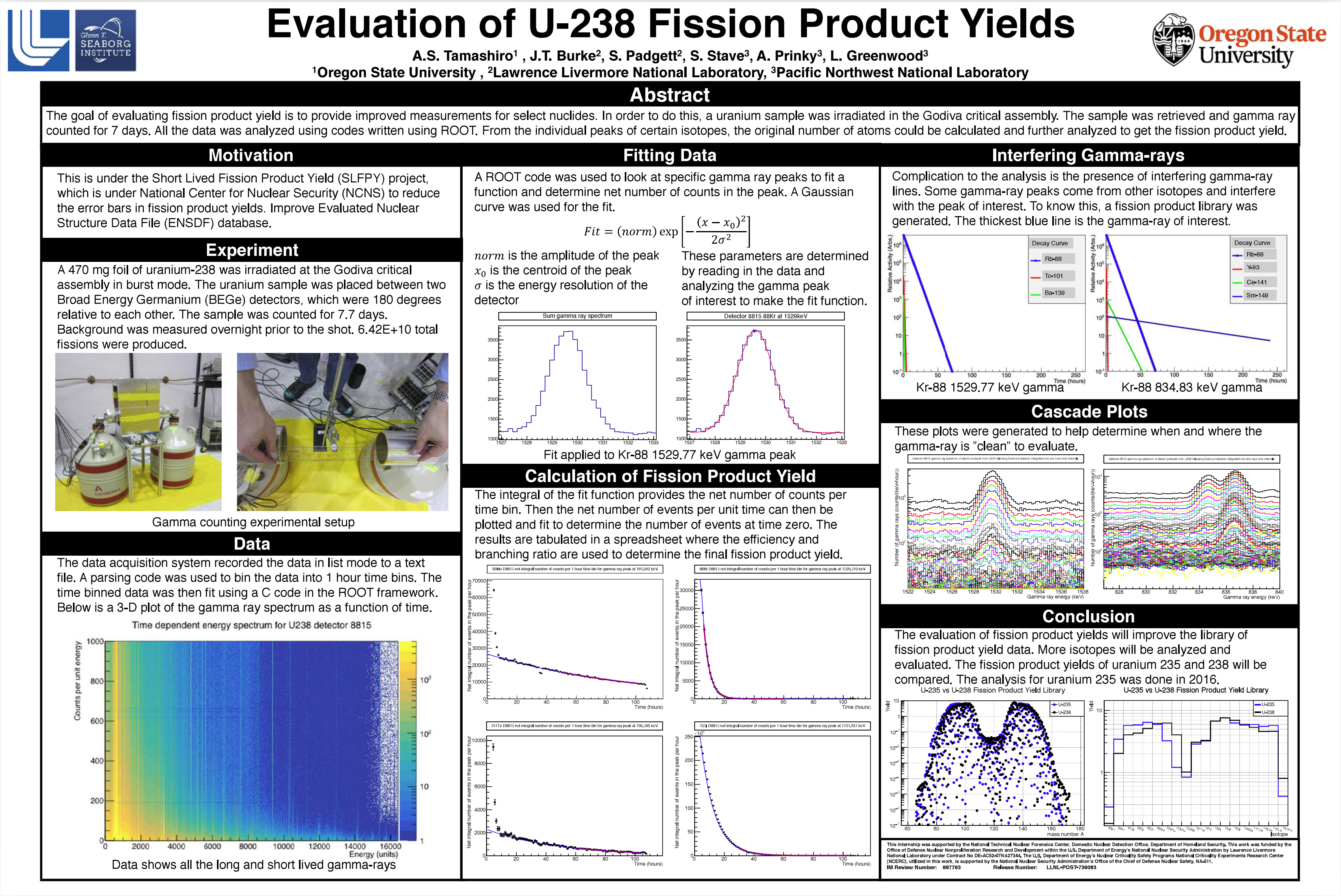
- $(^{234}U/^{238}U)_i$ and $^{87}Sr/^{86}Sr$ have potential as hydrologic proxies on various time scales, but more data are needed to correlate their behavior with meteorological data and ocean-atmosphere oscillation indices
- To better interpret our results, soil leachates and the dolomite host rock must be analyzed for $(^{234}U/^{238}U)_i$ and $^{87}Sr/^{86}Sr$. This way we can place endmembers for the isotopic variability we see.

References:
Myers, C. G., Oster, J. L., Sharp, W. D., Bennartz, R., Kelley, N. P., Covey, A. K., & Breitenbach, S. F. M. (2015). Northeast Indian stalagmite records Pacific decadal climate change: Implications for moisture transport and drought in India. *Geophysical Research Letters*, *42*(10), 4124–4132. doi.org/10.1002/2015GL063826
Wortham, B.E., Wong, C.I., Silva, L.C.R., McGee, D., Montañez, I.P., Rasbury, E.T., Cooper, K.M., Sharp, W.D., Glessner, J.J.G., Santos, R.V. (2017) Assessing response of local moisture conditions in central Brazil to variability in regional monsoon intensity using speleothem 87Sr/86Sr values. Earth and Planetary Science Letters, Vol. 463, p. 310-322. doi.org/10.1016/j.epsl.2017.01.034.
Oster, J.L., Ibarra, D.L., Harris, C.H., and Maher, K. (2012). Influence of eolian deposition and rainfall amounts on the U-isotopic composition of soil water and soil minerals. Geochimica et Cosmochimica Acta, v. 88, p. 146 – 166. doi.org/10.1016/j.gca.2012.04.004

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
IM Review and Release number here

LLNL-POST-735269

LLNL-POST-735269



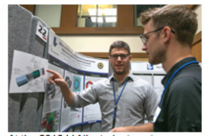
LLNL-POST-736083

APPENDIX

Twenty Summers of Nuclear Forensics and Actinide Science

In 1998, the Actinide Sciences Summer Program began training the next generation of actinide scientists (those who study elements 89 through 103 in an effort to identify the origin and behavior of nuclear materials). On Aug. 5, this longstanding program, renamed the Nuclear Forensics Summer Internship Program (NFSIP) in 2008, bid farewell to its 20th class.

As a component of the Lawrence Livermore National Laboratory branch of the Glenn T. Seaborg Institute, NFSIP is focused on inviting a small number of students-graduate and senior undergraduate-to work closely with LLNL scientists on nuclear forensics, environmental radiochemistry, and heavy element discovery topics. Each student conducts mentored research and produces a poster while attending NFSIP; many go on to apply the research to their own graduate Ph.D. theses. Over the past 16 years, 30-40 percent of NFSIP alumni have returned to Livermore in some capacity. Thirteen have been hired as career scientists, and at least 15 have been hired as postdoctoral staff.



At the 2016 LLNL student poster symposium, Austin Carter of the University of Michigan presents his Nuclear Forensics Summer Internship Program (NFSIP) research poster, "Monte Carlo Modeling of Vast Area Detection for Experimental Radiochemistry (VADER) NIF Diagnostic Instrument."

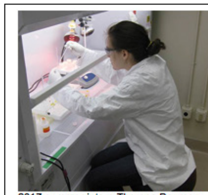
The original Actinide Sciences Summer Program was founded in response to a crisis. In the 1990s, American higher education was not producing enough nuclear science Ph.D.s to keep up with national security needs. Seaborg Institute founding director Darleane Hoffman and her colleagues raised awareness of the shortage, and in 1998, they succeeded in securing funding to begin the summer program. Over the past 20 years, the GTSI has hosted hundreds of students from over 70 colleges and universities.

During a conference at Argonne National Laboratories in 2014, former-NFSIP Director Annie Kersting was joined by many former NFSIP students now working in a variety of national security careers. Bottom row, from left: Jewel Wrighton, now working in the nuclear policy arena in Washington; Justin Walensky, a professor at the University of Missouri; Lindsay Shuller-Nickles, a professor at Clemson University; April Gillens, NNSA Fellow; Kersting; and Connor Hilton, a graduate student at the University of Maryland. Top row, from left: Brett Isselhardt, a staff scientist in forensics at LLNL; Chad Durrant, a Ph.D. student at the University of Pennsylvania; Greg Brennecka, faculty at the University of Meunster; and David Meier, a staff scientist at Pacific Northwest National Laboratory.

Mark Sutton, now deputy division leader for operations for NACS, was a member of that first Actinide Sciences Summer Program. "The summer program was my first taste of LLNL, and there I realized that LLNL was for me," he says. He returned in 2000 as a postdoctoral researcher.

Kerri Blobaum was in the 2000 class. Under the direction of Adam Schwartz -- now director of the Ames Laboratory in Iowa -- Blobaum was able to apply her materials science background to nuclear forensics. She credits her summer program experience as a "tryout" that eventually helped land her dream job. Today, she leads a team of LLNL materials characterization experts.

"Hearing from former students that being a summer student in nuclear forensics and environmental radiochemistry made a significant difference in their careers is a great feeling," says Annie Kersting, the previous director of the Seaborg Institute and the current head of University Relations for the Laboratory. Students seem to particularly value the one-on-one mentoring and the lecture series. Speakers have included "giants in the field of actinides," according to Blobaum. Glenn Seaborg himself paid a visit to the inaugural class.



2017 summer intern Theresa Baumer performs actinide separations in preparation for an analysis of plutonium from hydrothermally altered nuclear melt glass.

"I remember at the time being amazed that these highly respected scientists -- whose journal articles I had read and admired as a grad student -- were willing to spend the day with us," says Sutton.

"The whole summer was very fast-paced and full of firsts," says Teresa Baumer, a member of the 2017 class. "A major highlight was being able to complete a research project that involved carrying out experiments, analyzing data and putting it all together in a poster -- all over the course of one short summer. I learned many new techniques, including separation chemistry and modeling, that I can apply to my dissertation work back at my home university."

The direct interaction between Lab scientists and visiting students is central to NFSIP's success. "This kind of mentoring is invaluable to the students," said current Seaborg Institute and NFSIP director Mavrik Zavarin, "but I also see that the mentors benefit from the experience."

"The relationships formed during the summer institute formed the basis of my early connections to researchers," says Sutton, "from experimentalists working with me at the bench to mentors who, 19 years later, are still trusted advisors."

As students come through NFSIP, they help to strengthen the pipeline between LLNL and academic institutions. Kersting adds that some of the Seaborg Institute's capabilities (like the high-resolution secondary ion mass spectrometer, Transmission Electron Microscopy or Nano Secondary Ion Mass Spectrometry) are especially attractive to the university community.

"People recognize the success of the program externally, so they want to send their students here," she says. And over time, NFSIP and its predecessor program have helped to increase the number of Ph.D.s granted by university chemistry and earth science departments in the area of nuclear forensics, environmental radiochemistry and actinide chemistry -- all critical areas of scholarship needed for the national laboratories.

Based on the success of NFSIP, the Seaborg Institute is looking to expand opportunities for the next generation of nuclear scientists that come to Livermore, including potentially offering both long-term and short-term nuclear science student internships throughout the year. "The summer institute is a foundational part of the Seaborg Institute," Zavarin says. "We are now looking for new ways to host students and expand our education mission at LLNL."

The 2017 NFSIP class continued the legacy of its 19 predecessors: talented, committed students pairing up with Lab scientists to characterize nuclear materials, determine the behavior of radionuclides in the environment and study the fundamental properties of transactinide elements. Challenging careers await.

-Ben Kennedy

CLICK TO READ FULL ARTICLE

Appendix A. Newsline article highlighting the 20th year of the Nuclear Forensics Summer Internship Program and Actinide Science Summer Programs

THE GLENN T. SEABORG INSTITUTE NUCLEAR FORENSICS SUMMER INTERNSHIP PROGRAM

Livermore's Glenn T. Seaborg Institute runs an 8- to 10-week summer internship program for graduate students interested in nuclear forensics. Students conduct research under the supervision of a staff scientist, attend a weekly lecture series, and participate in a wide range of student activities across the LLNL campus.

Since its founding in 1998, the GTSI summer internship program has hosted students from over 70 colleges and universities.

Founded in 1998, the GTSI summer internship program focuses on training the next generation of nuclear scientists and engineers. Students majoring in physics, chemistry, geology, mathematics, nuclear engineering, chemical engineering, and environmental sciences from across the U.S. are invited to participate. They engage in research projects in actinide chemistry, radiochemisty, isotopic analysis, computation, and radiation detection. The ultimate goal of the program is to strengthen the workforce pipeline for nuclear forensics, radiochemistry, and super heavy element research.

Professor Glenn T. Seaborg poses with college students participating in the first GTSI summer internship session in 1998.

Sponsor: National Technical Nuclear Forensics Center, Domestic Nuclear Detection Office, Department of Homeland Security.

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

Lawrence Livermore National Laboratory

Glenn T. Seaborg Institute

PLS

Appendix B. Recently updated poster highlighting LLNL's NFSIP

SEABORG.LLNL.GOV