Nuclear Forensic Analysis of Uranium - Rich Materials

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Environmental Isotope Geochemistry
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Overview

• Introduction to nuclear forensics
• Deposit type normalized REE signatures
  – Introduction
  – Methods
  – Results and Discussion
• Trace element and U isotope analysis of uranium ore and ore concentrate
  – Introduction
  – Methods
  – Trace Elements in U ore and UOC
  – U Isotopes in U ore and UOC
Nuclear Forensics

“Nuclear forensics is the technical means by which nuclear materials, whether intercepted intact or retrieved from post-explosion debris, are characterized (as to composition, physical condition, age, provenance, history) and interpreted.”

-Joint Working Group of the American Physical Society and the American Association for the Advancement of Science

Above Left: Vessel found to contain 4g of HEU (>20% $^{235}$U) Intercepted in Rousse, Bulgaria. 1999.
Above Right: Pu acquired by Dr. Emmett Brown for the purpose of temporal displacement.
Uraninite

- Uraninite is the most common and abundant form of uranium ore.
- Incorporates trace elements during crystallization.
- Can undergo post crystallization alteration.
- Trace element analysis reveals geologic and/or anthropogenic history.
U Deposit Types

Worldwide U Resources

- In 2014 ~56,000 tons of U were mined worldwide.
- U extracted from every continent except Antarctica.
- If material were intercepted, how can we determine its origin?
REE Signatures of U Deposits

- REE concentrations normalized to chondritic abundances
- Plotted on log scale
- Qualitatively compared as a function of deposit type

Methods

- 6 deposit types based on IAEA designations
  - Sandstone
  - Tabular Sandstone
  - Granite Related
  - Intrusive
  - Metamorphite
  - Unconformity
- 67 localities
- 532 individual datasets

Spano et al. A Novel Nuclear Forensic Tool Involving Deposit Type Normalized Rare Earth Element Signatures. Terra Nova, 2017, 29-5, 294-305
Methods

- Removes natural variations in abundance resulting from primordial earth distributions of REEs

- Ensures equal contribution of deposit signatures
- Negates variations in absolute concentrations

REE concentrations normalized to chondrite

CN-REE data normalized to total REE content

CN-REE data averaged for each deposit type

CN-REE data averaged for each locality

Locality Average

Deposit Type Average

Spano et al. A Novel Nuclear Forensic Tool Involving Deposit Type Normalized Rare Earth Element Signatures. Terra Nova, 2017, 29-5, 294-305
Results: DTA-CN-REE Signatures

Spano et al. A Novel Nuclear Forensic Tool Involving Deposit Type Normalized Rare Earth Element Signatures. Terra Nova, 2017, 29-5, 294-305
Intrusive

- LREE and HREE depletions
- Prominent negative Eu anomaly (source controlled)
- Crystallographically controlled REE pattern

- Related to partial melting and/or plutonic activity
  - Alaskite
  - Quartz-monzonite
  - Carbonatite
  - Peralkaline syenite
  - Pegmatite
- Quartz-pebble conglomerate deposits also included

Spano et al. *A Novel Nuclear Forensic Tool Involving Deposit Type Normalized Rare Earth Element Signatures.* Terra Nova, 2017, 29-5, 294-305
Granite Related

- U occurs within or adjacent to granitic bodies
  - Endogranitic
  - Perigranitic
- Includes some metamorphite, metasomatite, and polymetallic iron oxide breccia deposits

- LREE enrichment
- HREE depletion
- Negative Eu anomaly
- Influenced by REE availability

Monazite, LREE(PO₄)
Metamorphite

- Result from alteration of U-rich sediments and/or volcanic material
- Form at elevated T (350-500°C)
- Includes metasomatic and collapse-breccia pipe deposits
- Some granite-related deposits reclassified as metamorphite

- LREE and HREE depletions
- No Eu anomaly
- Crystallographically controlled REE pattern
Unconformity

- Above, below, or along unconformable contacts
- Alteration by lateritic weathering and/or hydrothermal activity
- Ore-forming fluids redistributed by tectonic activity

- LREE depletion
- Enriched in Tb and Dy
- Pattern may be influenced by cogenesis of LREE-Rich Al-P-S minerals (source controlled)
Sandstone

- Sedimentary hosted U
- Low temperature deposits
- Basal channel, roll-front, tectonic-lithologic, mafic dykes/sills

- LREE enrichment, flat HREE
- Negative Eu anomaly
- REE source controls shape of DTA pattern

Spano et al. A Novel Nuclear Forensic Tool Involving Deposit Type Normalized Rare Earth Element Signatures. Terra Nova, 2017, 29-5, 294-305
Sandstone - Tabular

- Slightly higher T metallogensis than other sandstone deposits
- Intermediate between other sandstone deposits and those that have been hydrothermally altered

- La depletion
- No Eu anomaly
- Relatively flat pattern $\rightarrow$ crystallographically controlled

Spano et al. A Novel Nuclear Forensic Tool Involving Deposit Type Normalized Rare Earth Element Signatures. Terra Nova, 2017, 29-5, 294-305
Method Validation

• REE data for UOC and uraninite from known localities (12) treated as unknowns

• Unknown REE data treated as those in database
  – Normalize to chondrite
  – Normalize to total REE content

• Scatter plot of DTA-CN-REE and unknown signatures

• Linear regression of data
  – $m$ and $R^2 \rightarrow 1$ when unknown matches deposit type

Deposit type positively identified for all “unknowns”
Method Validation

- UOC from Powder River Basin (roll front, WY, USA) deposit treated as unknown
Method Validation

- Correlates with sandstone and granite-related DTA signatures
- Slope is higher for sandstone DTA, better match

Spano et al. A Novel Nuclear Forensic Tool Involving Deposit Type Normalized Rare Earth Element Signatures. Terra Nova, 2017, 29-5, 294-305
Method Validation

- Slope is higher for sandstone DTA, better match
Conclusions

• A novel method for identifying the provenance of U-oxides of unknown origins has been developed and validated.
• Quantifies degree of similarity between an unknown material and known U deposit types.
• Can determine metallogenesis of U deposits with ambiguous origins.
Trace Element and U Isotope Analysis of Uraninite and Uranium Ore Concentrate

• Do REE and U isotope signatures change during early ore processing?
• Can signatures in UOC be related to the uraninite from which it originated?
• Can valuable forensic data be obtained via laser ablation analysis?
Powder River Basin Uranium

- **Upper Cretaceous - Tertiary** (~35-50 Ma) intermontane basins
- **Poorly sorted arkose sandstones**
- **U ore minerals**
  - Pitchblende \( (\text{UO}_2+x) \)
  - Coffinite \( (\text{USiO}_4) \)
- **Found as**
  - Grain coatings
  - Filling void spaces
  - Replacing organic matter
- **Associated minerals**
  - Pyrite
  - Marcasite
  - Hematite
  - Calcite
Methods

UOC Powder

~1 week

~1 day

Uraninite

-Trace elements Balboni et al.

-U isotopes- this study

Samples digested for solution-mode ICP-MS analysis

Prepared as epoxy mounts for laser ablation analysis

REE and trace elements removed, diluted to ~50 ppb

Bulk analysis

MC-ICP-MS for U isotope analysis

SM-ICP-MS for trace element analysis

• Element2

• Attom

LA-ICP-MS for trace element analysis

• Element2

• Attom


Experiment Design - Solution Mode Trace Element Analysis

S2  • Digested in triplicate - Each sample run as spiked and unspiked
S3  • Internal Standard - As, Rh, In, Re, Tl
S4  • Spike - Ba, Sc, V, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb, Mo, Sn, Sb, Cs, Ba, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th, U
S5  • External Standards
    • Standard A - Li, Be, Sc, V, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, Cs, Ba, La, Ce, Pr, Tb, Dy, Ho, Er, Tm, Yb, Pb, Bi, Th, U
    • Standard B - Cr, Ga, Rb, Cs, Ce, Nd, Sm, Eu, Gd, Lu, Hf, Ta, W, Th
Experiment Design - Laser Ablation

- EMP for internal standard (Ca or V)
- Standard bracketing with NIST 610 SRM (~500 ppm)
- Laser ablation
  - Element 2
  - Attom

\[ \text{conc}_{ni} = \frac{\text{cps}_{nij}}{\text{abundance}_j} / (\text{yield}_{ni}) \]

\[ \text{yield}_{ni} = \text{yield}_{ns} \times \text{Int}(\text{yield}_{ni} / \text{yield}_{ns})^{\text{std}} \]

~25 μm raster line
1 μm /s scan speed
2Hz
15μm beam
100% power
.013mJ
Fluence ~7.6 J/cm³
CN-REE Signatures in UOC

- Slight variations in concentration
- Identical REE signatures obtained with laser ablation and solution mode analyses
- Can obtain valuable forensic data with laser ablation!

Backscatter electron image of epoxy-mounted UOC. Inhomogeneity of grain size and composition is observed.

CN-REE Signatures in UOC and Uraninite

- Signatures normalized to total REE content
- Identical REE patterns for uraniumite and UOC!
CN-REE Signatures in UOC and Uraninite

- Signatures normalized to total REE content
- Identical REE patterns for uraniuminite and UOC!
- UOC and uraninite from WY have signatures unique from other roll front deposits!
REE Partitioning in Uraninite and UOC

- Uraninite structure expands at high temperatures (>350°C).
  - Can accommodate all REE regardless of size.
- At lower temperatures, mid-heavy REE are preferred (ionic radii constraints).
- REE incorporation also influenced by elemental availability, fluid salinity, etc.

U Isotopes as a Forensic Indicator

$^{238}\text{U}/^{235}\text{U}$
- Nuclear field shift
- Info about redox state of deposit

$^{235}\text{U}/^{234}\text{U}$
- $\alpha$-recoil damage
- Leaching and aqueous alteration

Each U deposit should have characteristic signatures resulting from geochemical differences.

Do these signatures change during early ore processing?

$^{238}\text{U}/^{235}\text{U}$

- $^{238}\text{U}$ Preferentially reduced, caused by nuclear field shift.
- Heavy isotope concentrated in reduced phase.
- Can indicate redox history of ores.
- Mass independent fractionation
- Results from difference in shape and size of isotopes.
  - Nuclear charge distribution changes

Fujii et al., *Chemical Geology*, 267 (2009), p. 139-156
Bigeleisen-Mayer Theory of Mass Dependent Fractionation

\[ \varepsilon = \frac{1}{24} \left( \frac{\hbar}{kT} \right)^2 \frac{\delta m}{mm'} \left( M_Y v_Y^2 n_Y - M_x v_x^2 n_x \right) \]

\( \varepsilon \) = isotope enrichment factor
\( \hbar, k, T \) = Plank, Boltzmann constants, temp.
\( m, m' \) = isotope masses
\( M \) = mass of coordinating ligand
\( v \) = vibrational frequency of molecule (with m center)
\( n \) = number of coordinating ligands

Fujii et al., Chemical Geology, 267 (2009), p. 139-156
Bigeleisen-Mayer Theory of Mass Dependent Fractionation

• Born-Oppenheimer approximation
  – Nucleus much heavier than e-
  – Assumed to be stationary
  – In light nuclides this falls apart
  – Nucleus contributes kinetic momentum to orbital e-
  – Momentum contribution depends on mass

Mass Dependent Isotopic Fractionation

Fujii et al., *Chemical Geology*, 267 (2009), p. 139-156
Nuclear Field Shift

• Atomic energy depends on size and shape of electric charge distribution of nucleus

• For light elements:
  – Field shift $\ll$ mass shift

• For heavy elements:
  – Field shift $\gg$ mass shift
  – Larger nuclear charge distribution = lower binding potential

Fujii et al., Chemical Geology, 267 (2009), p. 139-156
Nuclear Field Shift

\[ \varepsilon_{fs} = \pi |\psi(0)|^2 \frac{a_0^3}{Z} f(Z) \delta < r^2 > \]

- \( |\psi(0)|^2 \) = electron density at the nucleus
- \( a_0 \) = Bohr radius
- \( F(Z) \) = known function for element of atomic number \( Z \)
- \( < r^2 > \) = isotopic difference in charge radius

In neutron-rich even numbered isotopes \( \rightarrow \) shape of nuclei is more important than size in causing fractionation.

Fujii et al., Chemical Geology, 267 (2009), p. 139-156
Nuclear Field Shift

- Heavy isotope preferentially concentrated in reduced phase during redox reactions.
  - Related to ability of nuclei to attract e-
  - Impacted by rigidity of bonding (results from charge density of nucleus)

235U/234U

- α-recoil damage to crystal structure, 234U preferentially removed during alteration.
- Depletion of 234U can indicate leaching and aqueous alteration of U ores.
- Ore interaction with groundwater results in:
  - Excess 234U: deposition is ongoing
  - Depleted 234U: deposition has stopped
α-Recoil Induced Fractionation

Experiment Design: U Isotope Analysis

- REE and trace elements stripped via ion exchange columns
- Diluted to ~50 ppb U
- Analyzed using MC-ICP-MS
- Samples bracketed with CRM 112-A (New Brunswick Laboratory) for mass-bias correction.
- Repeated analyses on consecutive days

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U Isotopes in Uraninite and UOC

No isotopic fractionation during conversion from uraninite to UOC.


Conclusions

• Data are reproducible across techniques
  – Quicker access to data!
• REE signatures do not change during conversion to UOC
• Unique REE signature for Powder River Basin UOC
• U isotope signatures persist during early ore processing