Meet the Presenter... **Dr. Lester R. Morss**

Lester R. Morss began his scientific career in inorganic chemistry and radiochemistry by carrying out research on the actinide elements uranium through californium under Professor Burris B. Cunningham, earning a PhD at University of California, Berkeley in 1969. After postdoctoral research on f element thermochemistry with James W. Cobble at Purdue University, he reached the rank of full professor of chemistry at Rutgers University, New Brunswick, NJ, doing research in synthetic inorganic chemistry and thermochemistry of transition elements. He joined the Chemistry Division of Argonne National Laboratory in 1980, where his primary research focus was the solid-state chemistry and thermochemistry of the transuranium elements. After reaching the rank of senior chemist at Argonne, he was elected a fellow of American Association for the Advancement of Science and spent six months as an Alexander von Humboldt senior research scientist at the University of Hannover, Germany in 1992. He retired from Argonne in 2002 and then served until 2010 as program manager for Heavy Element Chemistry in the Office of Basic Energy Sciences of US Department of Energy. He resides in Columbia, Maryland, where he is now an adjunct professor of chemistry at University of Maryland, College Park and a Visiting Scholar at George Washington University (where he teaches a special topics course each spring) and at the University of Notre Dame.

Professorial Lecturer, George Washington University
Email: lmorss@gwu.edu
Transplutonium elements: Ultramicrochemistry and atom-at-a-time chemistry

Dr. Lester R. Morss
Professorial Lecturer, George Washington University
The Actinide Challenge: Understanding 5f Electron Behavior

Actinide elements important in the closed nuclear fuel cycle
Outline

• What you will learn in “Transplutonium elements: Ultramicrochemistry and atom-at-a-time chemistry”
  – History of discovery
  – Methods of production of isotopes of Bk-Lr
  – Electronic structure and properties of atoms and ions
  – Stability of actinide ions (redox, complexing)
  – Ultramicrochemistry
  – Atom-at-a-time chemistry
Why study heavy actinides?

- **Reasons to study them ---**
  - Extend the Periodic Table
  - Unique properties of $5f$ electrons
  - Actinide systematics:
    - bonding in metals
    - bonding in compounds and solutions
  - Divalency of Fm-No
  - Possibility of other unusual oxidation states
    - Am(VII), Cm(VI), Md(I)
  - Uses for $^{252}$Cf as neutron source
  - Precursors of the transactinides (rutherfordium, etc.)

- **Reasons not to study them ---**
  - Properties are lanthanide-like beyond Am
  - Very short half lives make experiments difficult
  - Ultramicro or tracer scale
  - Expensive to synthesize
  - Not important part of nuclear fuel cycles
  - Not relevant for environmental radiochemical waste management
Production of heavy actinides by reactor irradiation

Fig. 15.1 Nuclear reaction sequence for production of transplutonium elements by intensive slow-neutron irradiation. The principal path is shown by heavy arrows (horizontal, neutron capture; vertical, beta decay). The sequence above $^{258}\text{Fm}$ is a prediction.
Production of heavy actinides by reactor irradiation

Fig. 15.1 Nuclear reaction sequence for production of transplutonium elements by intensive slow-neutron irradiation. The principal path is shown by heavy arrows (horizontal, neutron capture; vertical, beta decay). The sequence above $^{258}$Fm is a prediction.
Production of Cm-Fm at ORNL

- High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory has operated since 1966
  - Produced $^{248}\text{Cm}-^{257}\text{Fm}$ until 2004 for US researchers; some $^{248}\text{Cm}$ and $^{249}\text{Cf}$ still exist
  - Produced $^{249}\text{Bk}$ for one heavy element target in 2009
- Radiochemical Engineering Development Center (REDC) has separated heavy element from HFIR irradiated targets

### Table 15.1 Production of transcurium isotopes in USA.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{248}\text{Cm}$</td>
<td>$3.48 \times 10^5$ yr</td>
<td>150 mg(^b)</td>
<td>100 mg(^b)</td>
</tr>
<tr>
<td>$^{249}\text{Bk}$</td>
<td>330 d</td>
<td>50 mg</td>
<td>45 mg</td>
</tr>
<tr>
<td>$^{249}\text{Cf}$</td>
<td>351 yr</td>
<td>50 mg(^c)</td>
<td>&lt;45 mg(^c)</td>
</tr>
<tr>
<td>$^{252}\text{Cf}$</td>
<td>2.645 yr</td>
<td>500 mg</td>
<td>400 mg</td>
</tr>
<tr>
<td>$^{253}\text{Es}$</td>
<td>20.47 d</td>
<td>2 mg(^d)</td>
<td>1–2 mg(^d)</td>
</tr>
<tr>
<td>$^{254}\text{Es}$</td>
<td>275.7 d</td>
<td>3 µg</td>
<td>4 µg</td>
</tr>
<tr>
<td>$^{257}\text{Fm}$</td>
<td>100.5 d</td>
<td>1 pg</td>
<td>1 pg</td>
</tr>
</tbody>
</table>

\(^a\) One or two separation campaigns per year until about 1995; one campaign every 18–24 months from about 1995 to 2003.
\(^b\) From alpha decay of $^{252}\text{Cf}$.
\(^c\) From beta decay of $^{249}\text{Bk}$.
\(^d\) Mixed with 0.06–0.3% $^{254}\text{Es}$; chemical separation of $^{253}\text{Cf}$ followed by its beta decay can yield $\sim 200$ µg of isotopically pure $^{253}\text{Es}$.
High Flux Isotope Reactor (HFIR)

http://neutrons.ornl.gov/facilities/HFIR
Radiochemical Engineering Development Center (REDC)

- Opened in 1966, REDC has been the facility for processing transuranium isotopes produced by HFIR
History of Transcurium Elements

- Berkelium: discovered by Thompson, Ghiorso, Seaborg, 1949 by cyclotron bombardment
- Californium: discovered by Thompson, Street, Ghiorso, Seaborg, 1950 by cyclotron bombardment
- Einsteinium: discovered by Ghiorso et al., 1952 in thermonuclear test debris
- Fermium: discovered by Ghiorso et al., 1953 in test debris
- Mendelevium: discovered by Ghiorso et al., 1955 by cyclotron bombardment
- Nobelium: discovered by Ghiorso et al., 1958 by cyclotron bombardment
- Lawrencium: discovered by Ghiorso et al., 1961 by cyclotron bombardment
- Rutherfordium (discovered 1969) and heavier transactinide elements: specialized accelerators and atom-at-a-time chemistry
Al Ghiorsos Long and Happy Life


With a dozen elements to his credit, more even than his great friend, mentor, and colleague Glenn Seaborg, Albert Ghiorsos holds the world record for the discovery of transuranium elements -- and possibly for elements of any kind. Its an astonishing achievement for someone who found his true calling almost by accident.

Born July 15, 1915; died December 26, 2010
### Electronic Configurations

<table>
<thead>
<tr>
<th>Lanthanide series</th>
<th>Actinide series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Gaseous atom</td>
</tr>
<tr>
<td>La</td>
<td>5d6s(^2)</td>
</tr>
<tr>
<td>Ce</td>
<td>4f5d6s(^2)</td>
</tr>
<tr>
<td>Pr</td>
<td>4f(^6)s(^2)</td>
</tr>
<tr>
<td>Nd</td>
<td>4f(^6)s(^2)</td>
</tr>
<tr>
<td>Pm</td>
<td>4f(^6)s(^2)</td>
</tr>
<tr>
<td>Sm</td>
<td>4f(^6)s(^2)</td>
</tr>
<tr>
<td>Eu</td>
<td>4f(^7)s(^2)</td>
</tr>
<tr>
<td>Gd</td>
<td>4f(^5)d6s(^2)</td>
</tr>
<tr>
<td>Tb</td>
<td>4f(^7)s(^2)</td>
</tr>
<tr>
<td>Dy</td>
<td>4f(^10)s(^2)</td>
</tr>
<tr>
<td>Ho</td>
<td>4f(^11)s(^2)</td>
</tr>
<tr>
<td>Er</td>
<td>4f(^12)s(^2)</td>
</tr>
<tr>
<td>Tm</td>
<td>4f(^13)s(^2)</td>
</tr>
<tr>
<td>Yb</td>
<td>4f(^14)s(^2)</td>
</tr>
<tr>
<td>Lu</td>
<td>4f(^14)5d6s(^2)</td>
</tr>
</tbody>
</table>
## The oxidation states of the lanthanide elements

<table>
<thead>
<tr>
<th>Atomic No.</th>
<th>Element</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>La</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation states</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2)</td>
<td>2</td>
<td>2</td>
<td>(2)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

**Bold type = most stable; ( ) = least stable.**

Most electronic transitions are “forbidden” … colors represent ions that absorb in the visible spectrum.
The oxidation states of the actinide elements

<table>
<thead>
<tr>
<th>Atomic No. Element</th>
<th>89 Ac</th>
<th>90 Th</th>
<th>91 Pa</th>
<th>92 U</th>
<th>93 Np</th>
<th>94 Pu</th>
<th>95 Am</th>
<th>96 Cm</th>
<th>97 Bk</th>
<th>98 Cf</th>
<th>99 Es</th>
<th>100 Fm</th>
<th>101 Md</th>
<th>102 No</th>
<th>103 Lr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation states</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) (2) 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 (3) 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 4 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 5 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 6 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 7 7?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Bold type = most stable; ( ) = unstable but exists under some conditions; ? = claimed but not substantiated. Colors describe ions in aqueous solution.**
### Ionic Radii of Lanthanides and Actinides (Coordination Number 6) (Shannon, 1976)

<table>
<thead>
<tr>
<th>No. of 4f or 5f electrons</th>
<th>Lanthanide series</th>
<th>Actinide series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2+</td>
<td>3+</td>
</tr>
<tr>
<td>0</td>
<td>La$^{3+}$</td>
<td>1.032</td>
</tr>
<tr>
<td>1</td>
<td>Ce$^{3+}$</td>
<td>1.01</td>
</tr>
<tr>
<td>2</td>
<td>Pr$^{3+}$</td>
<td>0.99</td>
</tr>
<tr>
<td>3</td>
<td>Nd$^{3+}$</td>
<td>0.983</td>
</tr>
<tr>
<td>4</td>
<td>Nd$^{2+}$</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>Sm$^{3+}$</td>
<td>0.958</td>
</tr>
<tr>
<td>6</td>
<td>Sm$^{2+}$</td>
<td>1.18</td>
</tr>
<tr>
<td>7</td>
<td>Eu$^{2+}$</td>
<td>1.17</td>
</tr>
<tr>
<td>8</td>
<td>Tb$^{3+}$</td>
<td>0.923</td>
</tr>
<tr>
<td>9</td>
<td>Dy$^{3+}$</td>
<td>0.912</td>
</tr>
<tr>
<td>10</td>
<td>Dy$^{2+}$</td>
<td>1.07</td>
</tr>
<tr>
<td>11</td>
<td>Er$^{3+}$</td>
<td>0.890</td>
</tr>
<tr>
<td>12</td>
<td>Tm$^{3+}$</td>
<td>0.880</td>
</tr>
<tr>
<td>13</td>
<td>Tm$^{2+}$</td>
<td>1.03</td>
</tr>
<tr>
<td>14</td>
<td>Yb$^{2+}$</td>
<td>1.02</td>
</tr>
</tbody>
</table>

1 Corrected to coordination number 6. Values for Fm-Lr ions are estimates (CATE Chapter 13)
Lanthanide contraction


Most recent papers of many on this topic:
D’Angelo et al., *Inorg Chem* 50, 4572 (2011) (EXAFS data, abstract graphic below)

Fig. 1. The tetrad and octad effects seen in the ionic radii of $\text{VI}^3$ and $\text{VIII}^3$, respectively. Ionic radii by Shannon (1976) are plotted against the atomic number.
Actinide contraction

Fig. 4. Contraction of ionic radii of the heavy lanthanides(III) and actinides(III). The radii of Fm$^{3+}$ and Md$^{3+}$ are calculated from $R_{\text{max}}$ by extrapolation procedure.

Bilewicz, “Ionic radii of heavy actinides,” Radiochim Acta 92, 69, 2004
Elution of tripositive lanthanide and actinide ions on Dowex 50 cation-exchange resin and AHIB (ammonium α-hydroxyisobutyrate) eluant. \( \text{Lr}^{3+} \) band (dashed line) was predicted.
Coordination of Ln$^{3+}$ and An$^{3+}$ aquo ions

Hydration numbers $h$ are shown with open circles and left axis. Coordination numbers in first hydration sphere $N_{\text{H}_2\text{O}}$ are shown with filled circles and right axis. References: F David papers and CATE Chapter 23, from classical conductance measurements, X-ray and neutron scattering, inference from solid hydrates, etc. Hydration numbers $h$ refer to total hydration (all water molecules that feel the effect of a cation over several concentric hydration spheres); coordination numbers refer to first sphere, i.e. primary hydration (i.e. the water molecules directly coordinated to the cation).
Coordination of Ln$^{3+}$ and An$^{3+}$ aquo ions

Fig. 1 First hydration shell CN in the Ln(III), circles, and An(III), diamonds, series as obtained from refs. [17,25], respectively.

Hydrolysis: acid-base reaction

- $\text{M}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{MOH} (\text{aq}) + \text{H}^+(\text{aq})$
  - no reaction, e.g. $\text{K}^+$
- $\text{M}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{M(OH)}^+(\text{aq}) + \text{H}^+(\text{aq})$
  - slight reaction, e.g. $\text{Ca}^{2+}$
- $\text{M}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{M(OH)}^{2+}(\text{aq}) + \text{H}^+(\text{aq})$
  - significant hydrolysis; can proceed to additional steps
  - For $\text{Bk}^{3+}$, $\log \beta_{11} = \log \beta_{11} - 14 = -5.66$
- $\text{M}^{4+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{M(OH)}^{3+}(\text{aq}) + \text{H}^+(\text{aq})$
  - predominant hydrolysis
  - For $\text{Bk}^{4+}$, $\log \beta_{11}$ unknown but for $\text{Pu}^{4+}$, $\log \beta_{11} = 0.6$
  - will proceed to additional steps, for example
  - $\text{MOH}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{M(OH)}_2^{2+} + \text{H}^+(\text{aq})$
Complexation stability constants (log $\beta_{11}$)

- Formation complex with cation (metal ion) in solution
  - $ML_{q-1} + L \rightleftharpoons ML_q \quad K_q = K_{1q} = [ML_q]/([ML_{q-1}][L])$
  - $M + qL \rightleftharpoons ML_q \quad \beta_q = \beta_{1q} = [ML_q]/([M][L]^q)$
  - Example: $\text{Bk}^{3+} + \text{Cl}^- = \text{BkCl}^{2+} \quad \beta_{11} = K_{11} = [\text{BkCl}^{2+}]/\{[\text{Bk}^{3+}][\text{Cl}^-]\}$

- Complexation reactions with ligand deprotonation: $^*K_q$ and $^*\beta_q$
  - Example: $\text{Pu}^{4+} + \text{OH}^- = \text{Pu(OH)}^{3+} \quad \beta_{11} = [\text{Pu(OH)}^{3+}]/\{[\text{Pu}^{4+}][\text{OH}^-]\}$$
  \text{Pu}^{4+} + \text{H}_2\text{O} = \text{Pu(OH)}^{3+} + \text{H}^+ \quad ^*\beta_{11} = [\text{Pu(OH)}^{3+}][\text{H}^+]/[\text{Pu}^{4+}] = \beta_{11} \cdot K_w$

<table>
<thead>
<tr>
<th></th>
<th>Cm$^{3+}$</th>
<th>Bk$^{3+}$</th>
<th>Cf$^{3+}$</th>
<th>Es$^{3+}$</th>
<th>Fm$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^-$</td>
<td>8.08</td>
<td>8.34</td>
<td>8.38</td>
<td>8.86</td>
<td>10.2</td>
</tr>
<tr>
<td>F$^-$</td>
<td></td>
<td>2.89</td>
<td>3.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td></td>
<td>-0.18</td>
<td></td>
<td>-0.18</td>
<td></td>
</tr>
<tr>
<td>glycolate</td>
<td></td>
<td>2.85</td>
<td>2.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>acetate</td>
<td></td>
<td>2.05</td>
<td>2.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data from CATE Chapters 10, 11, 12, 23
### Lanthanide and Actinide Oxides

<table>
<thead>
<tr>
<th></th>
<th>CeO$_2$</th>
<th>Pr$<em>6$O$</em>{11}$</th>
<th>Nd$_2$O$_3$</th>
<th>Nb$_2$O$_3$</th>
<th>Sm$_2$O$_3$</th>
<th>Eu$_2$O$_3$</th>
<th>Gd$_2$O$_3$</th>
<th>Tb$_2$O$_3$</th>
<th>Dy$_2$O$_3$</th>
<th>Ho$_2$O$_3$</th>
<th>Er$_2$O$_3$</th>
<th>Tm$_2$O$_3$</th>
<th>Yb$_2$O$_3$</th>
<th>Lu$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$O$_3$</td>
<td>Ce$_2$O$_3$</td>
<td>Pr$_2$O$_3$</td>
<td>Nd$_3$O$_3$</td>
<td>Pr$_2$O$_3$</td>
<td>Sm$_2$O$_3$</td>
<td>EuO</td>
<td>Tb$_4$O$_7$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NdO</td>
<td>SmO</td>
<td>EuO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Not all oxides are shown! No Fm-Lr compounds are known because $t_{1/2}$ of all isotopes are too short.

UO$_3$

Pa$_2$O$_5$  U$_2$O$_5$  Np$_2$O$_5$

|            | ThO$_2$ | PaO$_2$ | UO$_2$ | NpO$_2$ | PuO$_2$ | AmO$_2$ | CmO$_2$ | BkO$_2$ | CfO$_2$ | Ac$_2$O$_3$ | Pu$_2$O$_3$ | Am$_2$O$_3$ | Cm$_2$O$_3$ | Bk$_2$O$_3$ | Cf$_2$O$_3$ | Es$_2$O$_3$ |
|------------|---------|---------|--------|---------|---------|---------|---------|---------|---------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
## Stoichiometric Chlorides of f Elements

<table>
<thead>
<tr>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl$_3$</td>
<td>CeCl$_3$</td>
<td>PrCl$_3$</td>
<td>NdCl$_3$</td>
<td>PmCl$_3$</td>
<td>SmCl$_3$</td>
<td>EuCl$_3$</td>
<td>GdCl$_3$</td>
<td>TbCl$_3$</td>
<td>DyCl$_3$</td>
</tr>
<tr>
<td>NdCl$_2$</td>
<td>SmCl$_2$</td>
<td>EuCl$_2$</td>
<td>Gd$_2$Cl$_3$</td>
<td>Tb$_2$Cl$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ac</td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
</tr>
<tr>
<td>AcCl$_3$</td>
<td>PaCl$_5$</td>
<td>ThCl$_4$</td>
<td>UCl$_6$</td>
<td>UCl$_5$</td>
<td>UCl$_4$</td>
<td>NpCl$_4$</td>
<td>AmCl$_3$</td>
<td>CmCl$_3$</td>
<td>BkCl$_3$</td>
</tr>
</tbody>
</table>

Note: Solid reduced Es halides (samples believed to be EsCl$_2$ and EsBr$_2$) were made at ORNL in the 1970s and their spectra were reported: Fellows et al., *Inorg. Nucl. Chem. Lett.* 11, 737 (1975); Symposium Commemorating the 25th Anniversary of Elements 99 and 100, LBNL-7701; Young et al., *Inorg Chem* 20, 3979 (1981). However, the samples were not sufficiently crystalline to yield X-ray diffraction results.
Berkelium

- Discovered by Thompson, Ghiorso, Seaborg, 1949 by cyclotron bombardment
  - $^{241}\text{Am} + \alpha \rightarrow ^{243}\text{Bk} + 4n$

- $\text{Bk}^{3+}(\text{aq})$ stable; $\text{Bk}^{4+}(\text{aq})$ strong oxidant, similar to $\text{Ce}^{4+}(\text{aq})$
  - Basis of separation from neighboring elements: cation exchange followed by bis(2-ethylhexyl)phosphoric acid (HDEHP) extraction

- First chemical compound: $\text{BkO}_2$ (stoichiometric, $\text{Bk}^{4+}$, 5f$^7$)
  - 50 ng, identified by fcc powder diffraction film
  - Almost all other compounds $\text{Bk}^{3+}$

- Metal prepared 1969
  - $\text{BkF}_3 + 3\text{Li} = \text{Bk} + 3\ \text{LiF}$
  - dhcp, similar to most lanthanides, “trivalent”
  - solution calorimetry to yield $\Delta_f^o H^o(\text{Bk}^{3+},\text{aq})$
Ultramicroscale synthesis of trans-Cm compounds

Pioneering work of B B Cunningham, Univ of Calif Berkeley and Lawrence Radiation Laboratory (now LBNL), 1960-1970
Californium

- Discovered by Thompson, Street, Ghiorso, Seaborg, 1950 by cyclotron bombardment
- Lowest-Z actinide with accessible +2 state
  - Even accessible by polarography in aqueous solution
  - Am$^{2+}$ has been claimed in nonaqueous solution and halides
- $^{252}$Cf has fission branch that makes it an intense neutron source
- Metal prepared 1969, 1982
  - CfF$_3$ + 3Li $\rightarrow$ Cf + 3 LiF; or CfO$_2$ + Th or La
  - dhcp, fcc above ~ 600 °C; “trivalent”
  - melting point lower than lighter actinides
  - solution calorimetry to yield $\Delta_f H^o$(Cf$^{3+}$,aq)
Einsteinium

– Discovered by Ghiorso et al., 1952 in thermonuclear test debris
– Chemical effects of short $t_{1/2}$:

\[ ^{253}\text{Es} \rightarrow ^{249}\text{Bk} \rightarrow ^{249}\text{Cf} \rightarrow ^{245}\text{Cm} \]

• Young et al., *Inorg. Chem.* 20, 3979 (1981) found that +3 oxidation state is maintained, despite $\beta^-$ (electron) being emitted

\[ ^{253}\text{EsCl}_3 \rightarrow ^{249}\text{BkCl}_3 \rightarrow ^{249}\text{CfCl}_3, \text{ but} \]

\[ ^{253}\text{EsCl}_2 \rightarrow ^{249}\text{BkCl}_3 \rightarrow ^{249}\text{CfCl}_2 \] (Es$^{2+}$ and Cf$^{2+}$ are relatively stable, but BkCl$_2$ is unstable)

**Metal prepared 1971, 1979**

$\text{Es}_2\text{O}_3 + \text{La} (\text{Es more volatile than La})$

fcc, m. p. ~860 °C
Chemical identification of Es

Es$^{3+}$ absorption spectra

J. R. Peterson, Symposium Commemorating the 25th Anniversary of Elements 99 and 100, LBL-7701, pp 55-60
Es$^{3+}$ (aq) absorption spectrum

Fig. 2. Photograph of a light-pipe, microabsorption cell.

Fig. 5. Photomicrograph of light-pipe gap loaded with ~60 µl of solution.

J. R. Peterson, Symposium Commemorating the 25th Anniversary of Elements 99 and 100, LBL-7701, pp 55-60
Crystallography of Es compounds

Electron diffraction patterns:

\[ \text{Gd}_2\text{O}_3 \quad \text{Es}_2\text{O}_3 \]

Fermium

- Discovered by Ghiorso et al., 1953 in thermonuclear test debris
- Metal
  - Pure metal has not been prepared
  - Alloys of Fm and Es (10^{-5} to 10^{-7} atom % in Sm and Yb) were used to determine enthalpy of sublimation (Haire, 1989)
Melting points of f element metals

Fig. 11. The melting point of the lanthanide (●) and actinide (○) metals. The estimated values are indicated by ○.

Stability of f element metals

Fig. 11. The melting point of the lanthanide (●) and actinide (○) metals. The estimated values are indicated by ○.

Fig. 14. The sublimation enthalpy at $T=298.15$ K of the lanthanide (●) and actinide (○) metals. The estimated values are indicated by ○.
Atomic radii: Bonding of 5f metals compared to 3d, 5d, and 4f metals.

Wigner-Seitz radius: radius of a sphere that represents atomic volume in condensed system.
Mendelevium

- Discovered by Ghiorso, Choppin, et al., 1955 by cyclotron bombardment
  - First “atom-at-a-time” production

- Hulet et al. (1967) reduced Md$^{3+}$(aq) to Md$^{2+}$(aq) with Zn dust to show that Md$^{2+}$(aq) exists
  - First evidence of an An$^{2+}$(aq) ion

- David et al. (1981) used radiopolarography to establish electrochemical properties of the redox process
  \[ \text{Md}^{3+}(aq) + e^- = \text{Md}^{2+}(aq) \]

- Mikheev (1972 and later) claimed Md$^+(aq)$ repeatedly but Hulet et al. (1979) refuted this claim
Nobelium

• First reported by international team at Nobel Institute in Stockholm, 1957
  \[ ^{244}\text{Cm} + ^{13}\text{C} \rightarrow ^{253}\text{No} \text{ or } ^{255}\text{No} \text{ (but poor chemical evidence)} \]

• \(^{254}\text{No}\) discovered by Ghiorso et al., 1958 and by Flerov et al., 1958

• Maly et al. (1968), Silva et al. (1969, 1974) and Toyoshima et al. (2009) used \(^{255}\text{No}\) to determine redox properties by coprecipitation, ion exchange, and electrochemistry
  – the stable aqueous ion is \(\text{No}^{2+}\), not \(\text{No}^{3+}\)
Lawrencium

- Discovered by Ghiorso et al., 1961 by cyclotron bombardment
- \( \text{Lr}^{3+}(\text{aq}) \) was confirmed as the only stable oxidation state; its ionic radius was estimated by cation exchange
  - Scherrer, Hoffman papers in 1988
  - No evidence for \( \text{Lr}^{2+} \)
Ternary Halides and Oxides

- $\text{Cs}_2\text{CeCl}_6$, $\text{Cs}_2\text{PuCl}_6$, and $\text{Cs}_2\text{BkCl}_6$
  - Stable $\text{M(IV)}$ salts where $\text{MCl}_4(s)$ is unknown

- Ternary and quaternary f-element oxides also!
  - Heptavalent Np and Pu in $\text{Li}_5\text{NpO}_6$, $\text{Na}_5\text{PuO}_6$, etc.
  - There are NO binary compounds of Np(VII), Pu(VII)

Ultramicrotitration of Cs$_2$BkCl$_6$

Source: L. R. Morss PhD thesis, UCRL-18951
New developments in gas-phase actinide ion chemistry

- New mass spectrometric techniques
  - Laser ablation with prompt reaction and detection (LAPRD)
  - Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS)
  - Quadrupole ion trap mass spectrometry (QIT/MS)

- Properties measured
  - Bond dissociation energies of AnO⁺ [i.e., An⁺O(g)], AnO₂⁺, and AnO₂²⁺
  - Ionization energies of AnO, AnO⁺, AnO₂, and AnO₂⁺

- Order of reactivities in gas phase
  - Th⁺ ≥ Pa⁺ ≥ U⁺ ≡ Np⁺ > Cm⁺ ≧ Pu⁺ > Bk⁺ > Am⁺ ≡ Cf⁺ ≥ Es⁺

Transplutonium Actinides -- References

- Morss et al., *The Chemistry of the Actinide and Transactinide Elements*, 3rd or 4th ed., chapters 8-15
- David Pogue PBS “Hunting the Elements”, 2012
- PBS 2013: The Mystery of Matter: Search for the Elements
Upcoming NAMP Radiochemistry Webinars

- Radium Chemistry (April 25, 2013)
- Environmental/Bioassay Radiochemistry Series

For more information and to access recorded webinars, visit the NAMP website at [www.inl.gov/namp](http://www.inl.gov/namp)