



National Analytical Management Program (NAMP)  
U.S. Department of Energy Carlsbad Field Office

# Radiochemistry Webinars

## *Actinide Chemistry Series*

- *Transplutonium Actinides*

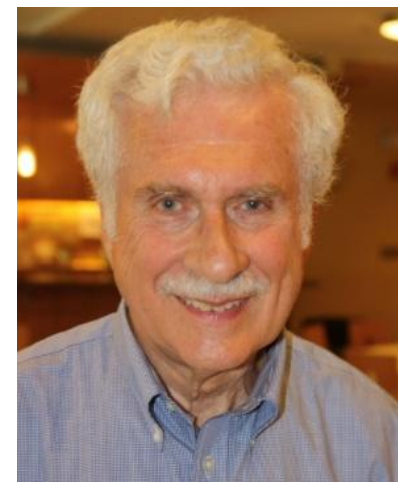


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# Meet the Presenter... *Dr. Lester R. Morss*

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.



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# Transplutonium elements: Ultramicrochemistry and atom-at-a-time chemistry

Dr. Lester R. Morss

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TRAINING AND EDUCATION SUBCOMMITTEE



# The Actinide Challenge: Understanding 5f Electron Behavior

1 H Hydrogen																	2 He Helium						
3 Li Lithium	4 Be Beryllium																	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium																	13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton						
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon						
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon						
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Ha Hahnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112	113	114	115	116								

Lanthanide series

58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
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Actinide series

90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium
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Actinide elements important in the closed nuclear fuel cycle

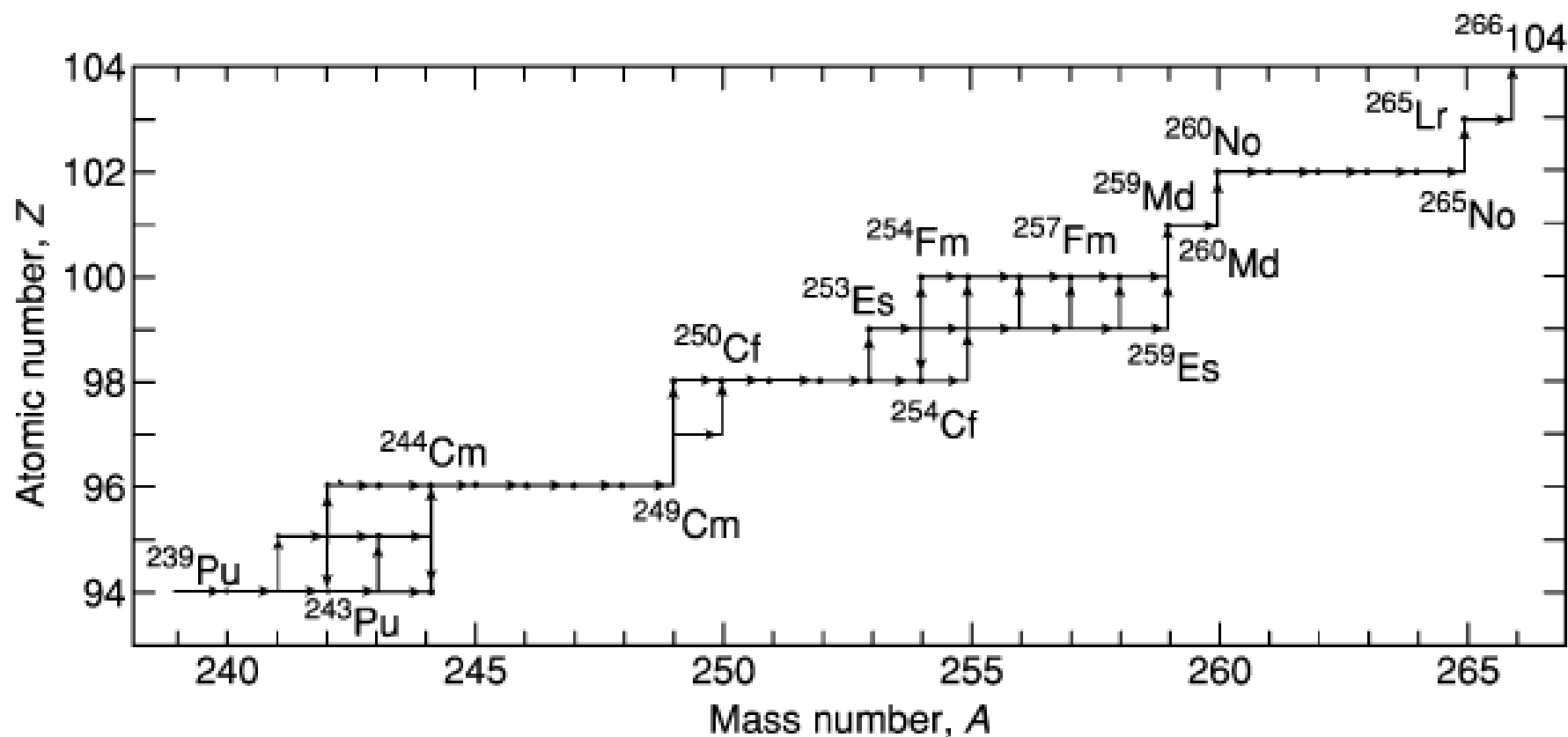
# Outline

- 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?

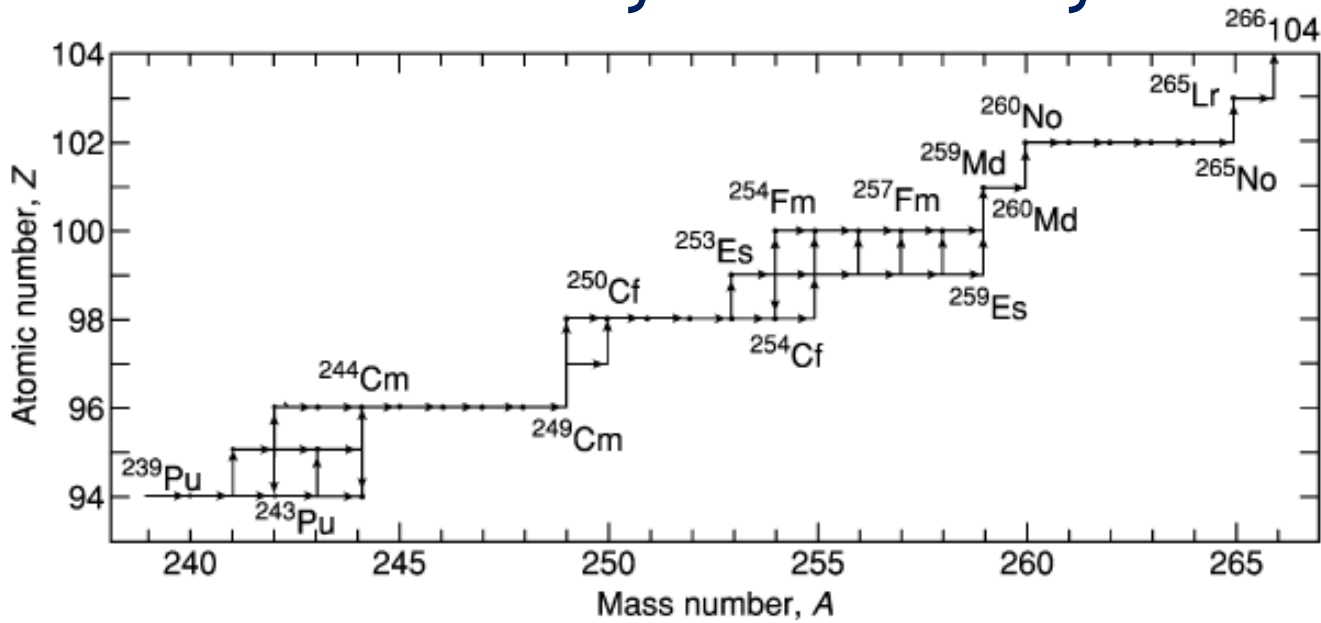
- Reasons to study them ---
  - Extend the Periodic Table
  - Unique properties of  $5f$  electrons
  - Actinide systematics:
    - bonding in metals
    - bonding in compounds and solutions
  - Divalency of Fm-No
  - Possibility of other unusual oxidation states
    - Am(VII), Cm(VI), Md(I)
  - Uses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

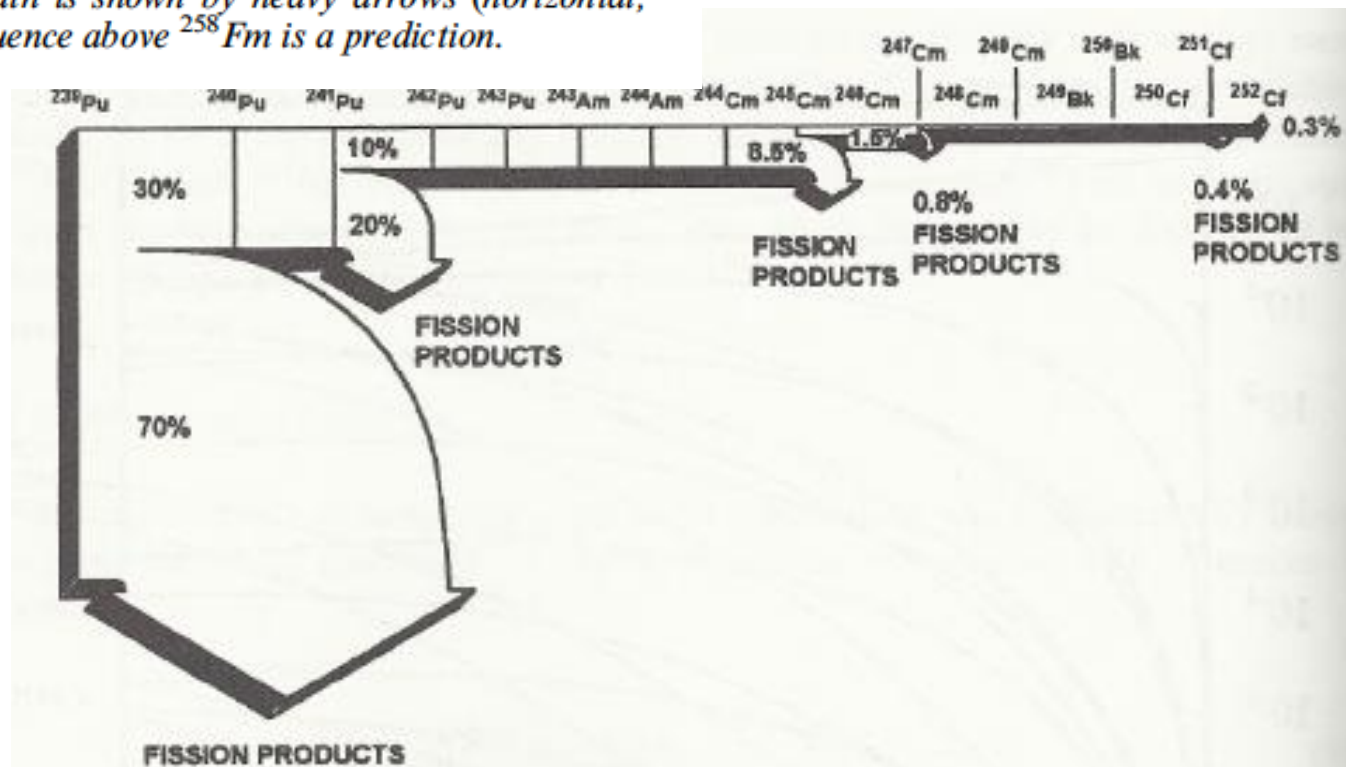


**Fig. 15.1** Nuclear reaction sequence for production of transplutonium elements by intensive slow-neutron irradiation. The principal path is shown by heavy arrows (horizontal, neutron capture; vertical, beta decay). The sequence above  $^{258}\text{Fm}$  is a prediction.

# 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  $^{258}\text{Fm}$  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.*<sup>a</sup>

<i>Isotope</i>	<i>Half-life</i>	<i>Amount/year (1983)</i>	<i>Amount/campaign (2004)</i>
$^{248}\text{Cm}$	$3.48 \times 10^5$ yr	150 mg <sup>b</sup>	100 mg <sup>b</sup>
$^{249}\text{Bk}$	330 d	50 mg	45 mg
$^{249}\text{Cf}$	351 yr	50 mg <sup>c</sup>	<45 mg <sup>c</sup>
$^{252}\text{Cf}$	2.645 yr	500 mg	400 mg
$^{253}\text{Es}$	20.47 d	2 mg <sup>d</sup>	1–2 mg <sup>d</sup>
$^{254}\text{Es}$	275.7 d	3 $\mu\text{g}$	4 $\mu\text{g}$
$^{257}\text{Fm}$	100.5 d	1 pg	1 pg

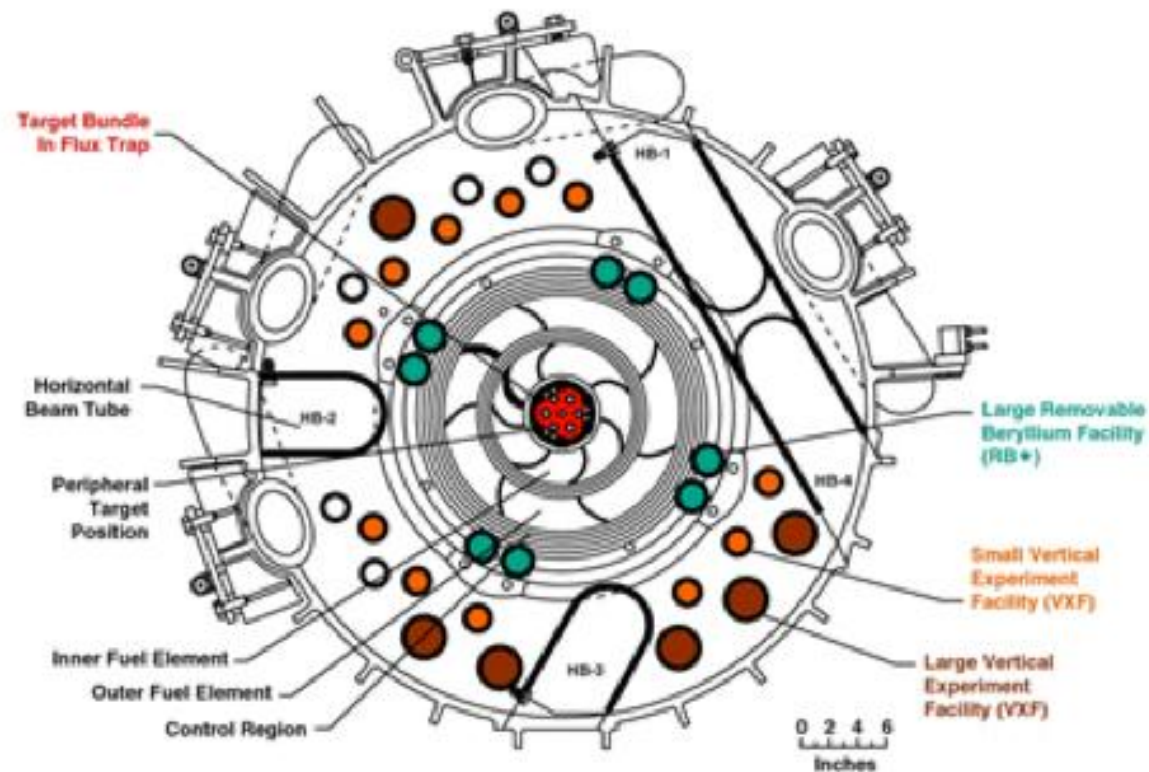
<sup>a</sup> One or two separation campaigns per year until about 1995; one campaign every 18–24 months from about 1995 to 2003.

<sup>b</sup> From alpha decay of  $^{252}\text{Cf}$ .

<sup>c</sup> From beta decay of  $^{249}\text{Bk}$ .

<sup>d</sup> Mixed with 0.06–0.3%  $^{254}\text{Es}$ ; chemical separation of  $^{253}\text{Cf}$  followed by its beta decay can yield  $\sim 200$   $\mu\text{g}$  of isotopically pure  $^{253}\text{Es}$ .

# High Flux Isotope Reactor (HFIR)

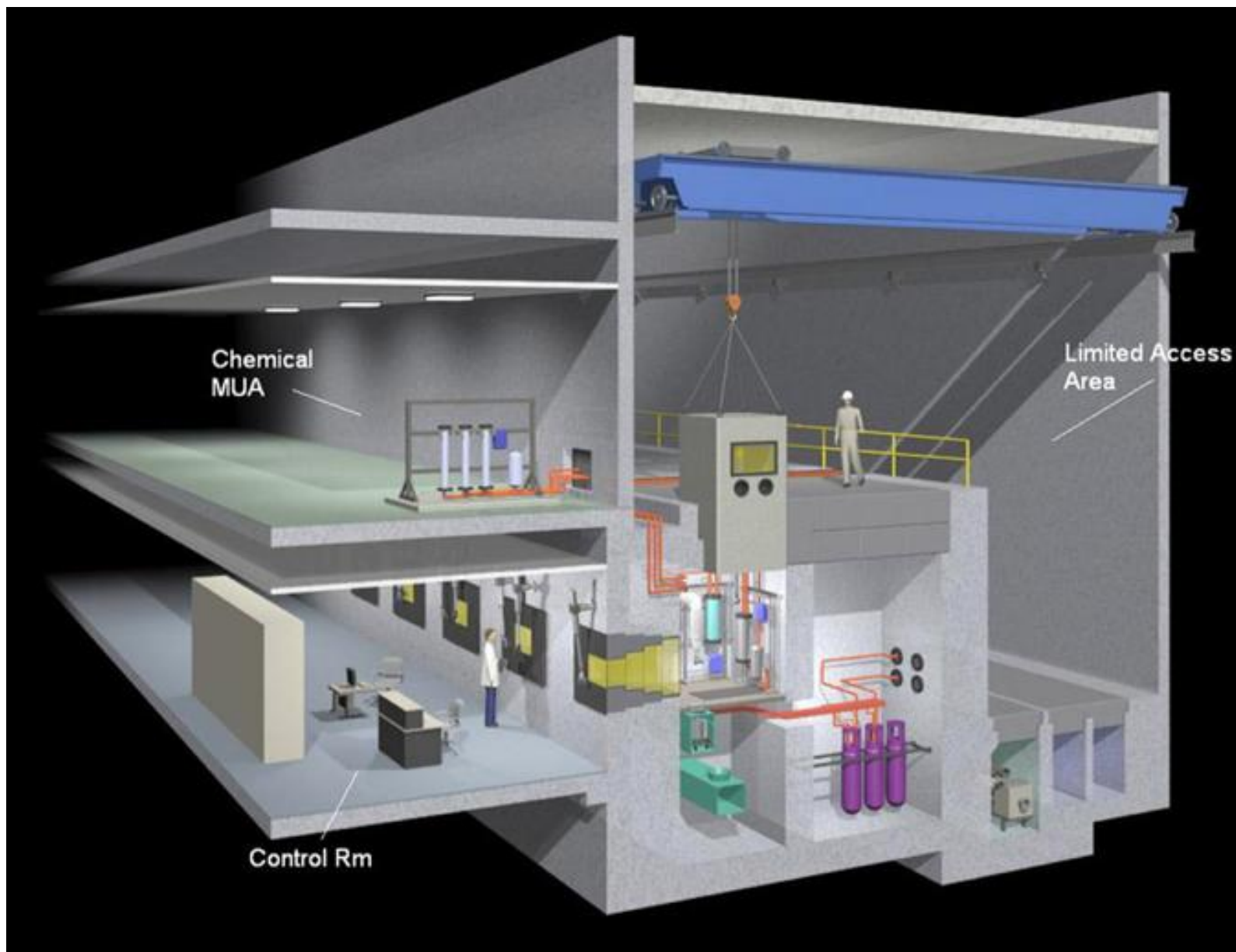


<http://neutrons.ornl.gov/facilities/HFIR>

/

# Radiochemical Engineering Development Center (REDC)

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



[http://www.ornl.gov/sci/nsed/group\\_fcid\\_nmp.shtml](http://www.ornl.gov/sci/nsed/group_fcid_nmp.shtml)

# 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

# History of Transplutonium Elements

## Al Ghiorso's Long and Happy Life

<http://www.lbl.gov/today/2005/Jul/11-Mon/ghiobio-jump.html>

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

Born July 15, 1915; died December 26, 2010



## Electronic configurations of 4f and 5f atoms and free ions.

Actinide configurations are built upon Rn core [1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>4s<sup>2</sup>3d<sup>10</sup>4p<sup>6</sup>5s<sup>2</sup>4d<sup>10</sup>5p<sup>6</sup>6s<sup>2</sup>4f<sup>14</sup>5d<sup>10</sup>6p<sup>6</sup>]. Predicted configurations are in parentheses.

Lanthanide series				Actinide series						
Element	Gaseous atom	M <sup>3+</sup> (g)	M <sup>3+</sup> (aq)	Element	Gaseous atom	M <sup>+</sup> (g)	M <sup>2+</sup> (g)	M <sup>3+</sup> (g)	M <sup>3+</sup> (aq)	M <sup>4+</sup> (g)
La	5d6s <sup>2</sup>			Ac	6d7s <sup>2</sup>	7s <sup>2</sup>	7s			
Ce	4f5d6s <sup>2</sup>	4f	4f	Th	6d <sup>2</sup> 7s <sup>2</sup>	6d7s <sup>2</sup>	5f6d	5f		
Pr	4f <sup>3</sup> 6s <sup>2</sup>	4f <sup>2</sup>	4f <sup>2</sup>	Pa	5f <sup>2</sup> 6d7s <sup>2</sup>	5f <sup>2</sup> 7s <sup>2</sup>	5f <sup>2</sup> 6d	5f <sup>2</sup>		(5f)
Nd	4f <sup>4</sup> 6s <sup>2</sup>	4f <sup>3</sup>	4f <sup>3</sup>	U	5f <sup>3</sup> 6d7s <sup>2</sup>	5f <sup>3</sup> 7s <sup>2</sup>		5f <sup>3</sup>	5f <sup>3</sup>	5f <sup>2</sup>
Pm	4f <sup>5</sup> 6s <sup>2</sup>	4f <sup>4</sup>	4f <sup>4</sup>	Np	5f <sup>4</sup> 6d7s <sup>2</sup>			5f <sup>4</sup>	5f <sup>4</sup>	(5f <sup>3</sup> )
Sm	4f <sup>6</sup> 6s <sup>2</sup>	4f <sup>5</sup>	4f <sup>5</sup>	Pu	5f <sup>6</sup> 7s <sup>2</sup>	5f <sup>6</sup> 7s	5f <sup>6</sup>	5f <sup>5</sup>	5f <sup>5</sup>	(5f <sup>4</sup> )
Eu	4f <sup>7</sup> 6s <sup>2</sup>	4f <sup>6</sup>	4f <sup>6</sup>	Am	5f <sup>7</sup> 7s <sup>2</sup>	5f <sup>7</sup> 7s	5f <sup>7</sup>	5f <sup>6</sup>	5f <sup>6</sup>	5f <sup>5</sup> )
Gd	4f <sup>7</sup> 5d6s <sup>2</sup>	4f <sup>7</sup>	4f <sup>7</sup>	Cm	5f <sup>7</sup> 6d7s <sup>2</sup>	5f <sup>7</sup> 7s <sup>2</sup>	5f <sup>8</sup>	5f <sup>7</sup>	5f <sup>7</sup>	(5f <sup>6</sup> )
Tb	4f <sup>9</sup> 6s <sup>2</sup>	4f <sup>8</sup>	4f <sup>8</sup>	Bk	5f <sup>9</sup> 7s <sup>2</sup>	5f <sup>9</sup> 7s	5f <sup>9</sup>	5f <sup>8</sup>	5f <sup>8</sup>	(5f <sup>7</sup> )
Dy	4f <sup>10</sup> 6s <sup>2</sup>	4f <sup>9</sup>	4f <sup>9</sup>	Cf	5f <sup>10</sup> 7s <sup>2</sup>	5f <sup>10</sup> 7s	5f <sup>10</sup>	5f <sup>9</sup>	5f <sup>9</sup>	(5f <sup>8</sup> )
Ho	4f <sup>11</sup> 6s <sup>2</sup>	4f <sup>10</sup>	4f <sup>10</sup>	Es	5f <sup>11</sup> 7s <sup>2</sup>	5f <sup>11</sup> 7s	5f <sup>11</sup>	5f <sup>10</sup>	5f <sup>10</sup>	(5f <sup>9</sup> )
Er	4f <sup>12</sup> 6s <sup>2</sup>	4f <sup>11</sup>	4f <sup>11</sup>	Fm	5f <sup>12</sup> 7s <sup>2</sup>			5f <sup>11</sup>	5f <sup>11</sup>	(5f <sup>10</sup> )
Tm	4f <sup>13</sup> 6s <sup>2</sup>	4f <sup>12</sup>	4f <sup>12</sup>	Md	5f <sup>13</sup> 7s <sup>2</sup>			5f <sup>12</sup>	5f <sup>12</sup>	(5f <sup>11</sup> )
Yb	4f <sup>14</sup> 6s <sup>2</sup>	4f <sup>13</sup>	4f <sup>13</sup>	No	5f <sup>14</sup> 7s <sup>2</sup>		(5f <sup>14</sup> )	5f <sup>13</sup>	5f <sup>13</sup>	(5f <sup>12</sup> )
Lu	4f <sup>14</sup> 5d6s <sup>2</sup>	4f <sup>14</sup>	4f <sup>14</sup>	Lr	(5f <sup>14</sup> 6d7s <sup>2</sup> or 5f <sup>14</sup> 7s <sup>2</sup> 7p)			5f <sup>14</sup>	5f <sup>14</sup>	(5f <sup>13</sup> )

## The oxidation states of the lanthanide elements

Atomic No. Element	57 La	Ce	Pr	N d	Pm	S m	Eu	G d	T b	Dy	Ho	Er	Tm	Yb	Lu
Oxidation states															
				(2)		2	2			(2)	(2)	2		2	
	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>
		4	4	4					4						
	<p><b>Bold type = most stable;</b> ( ) = least stable.            Most electronic transitions are “forbidden” ... colors            represent ions that absorb in the visible spectrum.</p>														

# The oxidation states of the actinide elements

Atomic No. Element	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
Oxidation states															
													1?		
		(2)					2?			(2)	(2)	2		<b>2</b>	
	<b>3</b>	(3)	(3)	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	3	<b>3</b>
		<b>4</b>	4	<b>4</b>	4	<b>4</b>	4	4	<b>4</b>	4	4?				
			<b>5</b>	5	<b>5</b>	5	5	5?		5?					
				<b>6</b>	6	6	6	6?							
					<b>7</b>	<b>7</b>	7?								
						8?									

**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)

No. of 4f or 5f elec- trons	Lanthanide series						Actinide series					
	2+ ion	Radius (Å)	3+ ion	Radius (Å)	4+ ion	Radius (Å)	2+ ion	Radius (Å)	3+ ion	Radius (Å)	4+ ion	Radius (Å)
0			La <sup>3+</sup>	1.032	Ce <sup>4+</sup>	0.87			Ac <sup>3+</sup>	1.12	Th <sup>4+</sup>	0.94
1			Ce <sup>3+</sup>	1.01	Pr <sup>4+</sup>	0.85			Th <sup>3+</sup>		Pa <sup>4+</sup>	0.90
2			Pr <sup>3+</sup>	0.99					Pa <sup>3+</sup>	1.04	U <sup>4+</sup>	0.89
3			Nd <sup>3+</sup>	0.983					U <sup>3+</sup>	1.025	Np <sup>4+</sup>	0.87
4	Nd <sup>2+</sup>	1.20 <sup>1</sup>	Pm <sup>3+</sup>	0.97					Np <sup>3+</sup>	1.01	Pu <sup>4+</sup>	0.86
5			Sm <sup>3+</sup>	0.958					Pu <sup>3+</sup>	1.00	Am <sup>4+</sup>	0.85
6	Sm <sup>2+</sup>	1.18 <sup>1</sup>	Eu <sup>3+</sup>	0.947					Am <sup>3+</sup>	0.975	Cm <sup>4+</sup>	0.84
7	Eu <sup>2+</sup>	1.17	Gd <sup>3+</sup>	0.938	Tb <sup>4+</sup>	0.76	Am <sup>2+</sup>	1.16 <sup>1</sup>	Cm <sup>3+</sup>	0.97	Bk <sup>4+</sup>	0.83
8			Tb <sup>3+</sup>	0.923					Bk <sup>3+</sup>	0.96	Cf <sup>4+</sup>	0.821
9			Dy <sup>3+</sup>	0.912					Cf <sup>3+</sup>	0.95	Es <sup>4+</sup>	0.81
10	Dy <sup>2+</sup>	1.07	Ho <sup>3+</sup>	0.901			Cf <sup>2+</sup>	1.14	Es <sup>3+</sup>	0.93		
11			Er <sup>3+</sup>	0.890					Fm <sup>3+</sup>	0.92		
12			Tm <sup>3+</sup>	0.880				1.11	Md <sup>3+</sup>	0.91		
13	Tm <sup>2+</sup>	1.03	Yb <sup>3+</sup>	0.868				1.10	No <sup>3+</sup>	0.90		
14	Yb <sup>2+</sup>	1.02	Lu <sup>3+</sup>	0.861			No <sup>2+</sup>	1.05	Lr <sup>3+</sup>	0.89		

<sup>1</sup> Corrected to coordination number 6. Values for Fm-Lr ions are estimates (*CATE* chapter 13)

# Lanthanide contraction

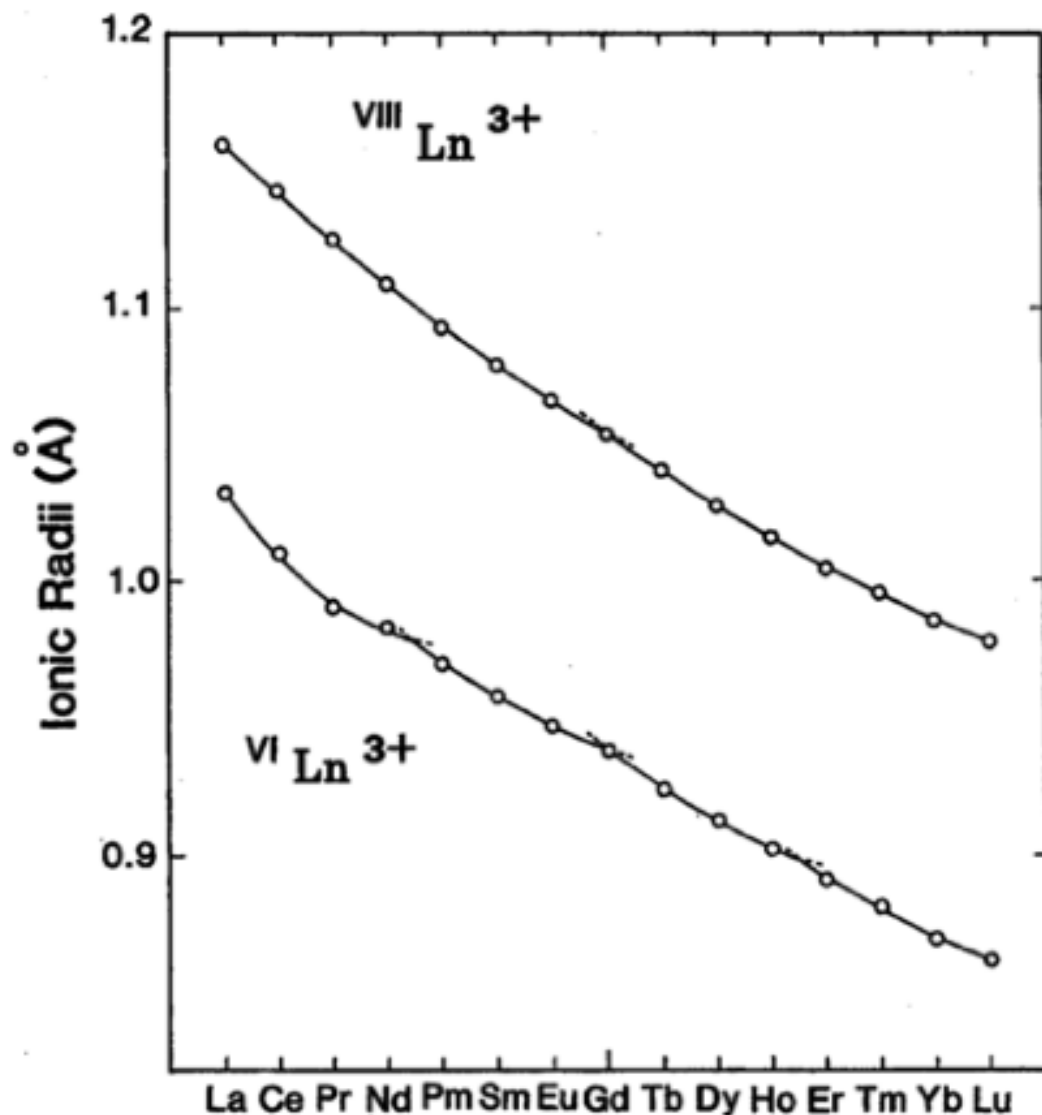
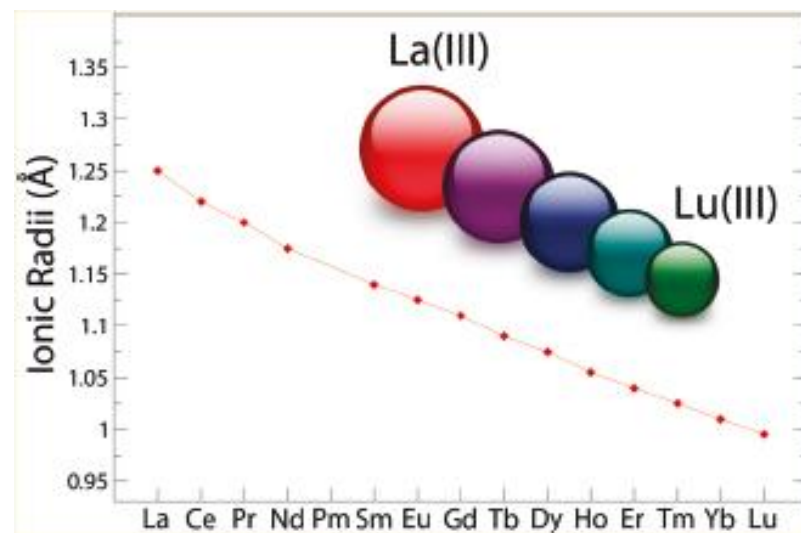


Fig. 1. The tetrad and octad effects seen in the ionic radii of  $^{VI}\text{Ln}^{3+}$  and  $^{VIII}\text{Ln}^{3+}$ , respectively. Ionic radii by Shannon (1976) are plotted against the atomic number.

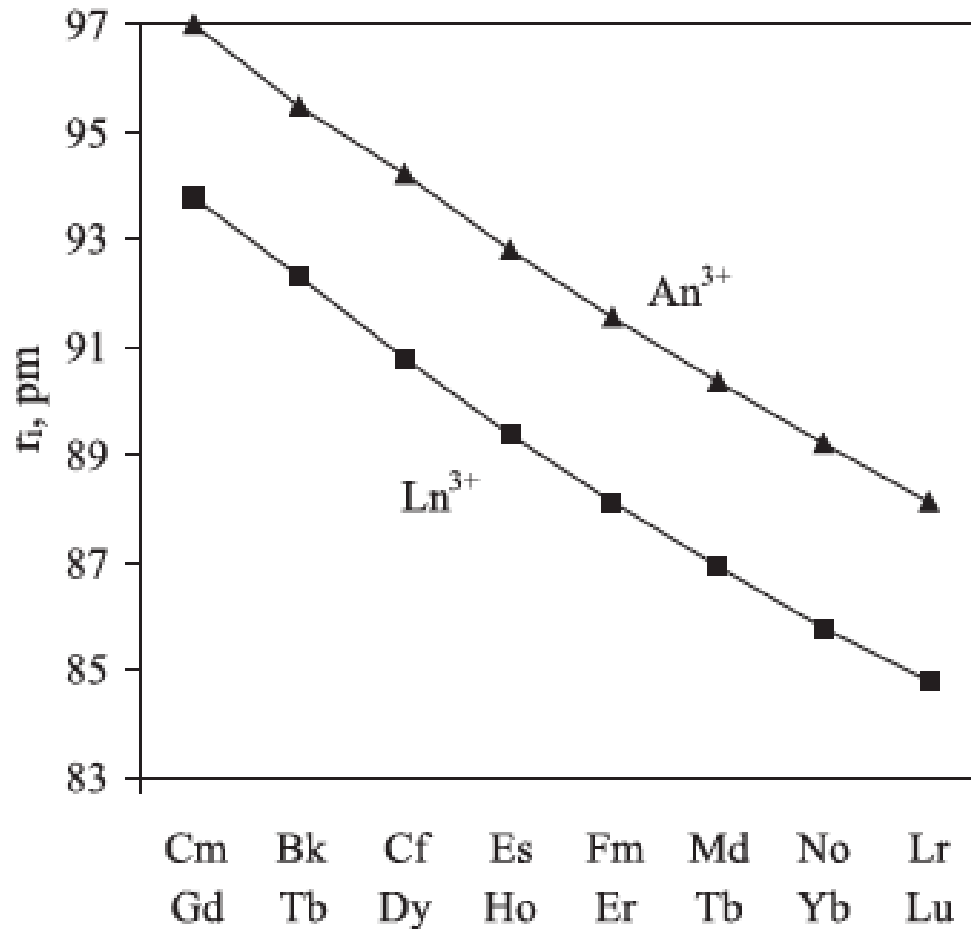
Kawabe, *Geochem. J.*, 26, 309 (1992) (fig 1 at left)

Most recent papers of many on this topic:

K. Raymond et al., *C. R. Chimie* 13 (2010) 849–852;  
D'Angelo et al., *Inorg Chem* 50, 4572 (2011) (EXAFS data, abstract graphic below)



# Actinide contraction

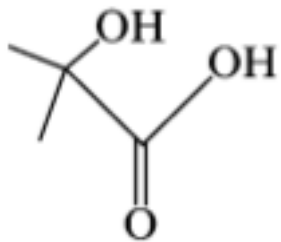


Bilewicz, "Ionic radii of heavy actinides,"  
*Radiochim Acta* 92, 69, 2004

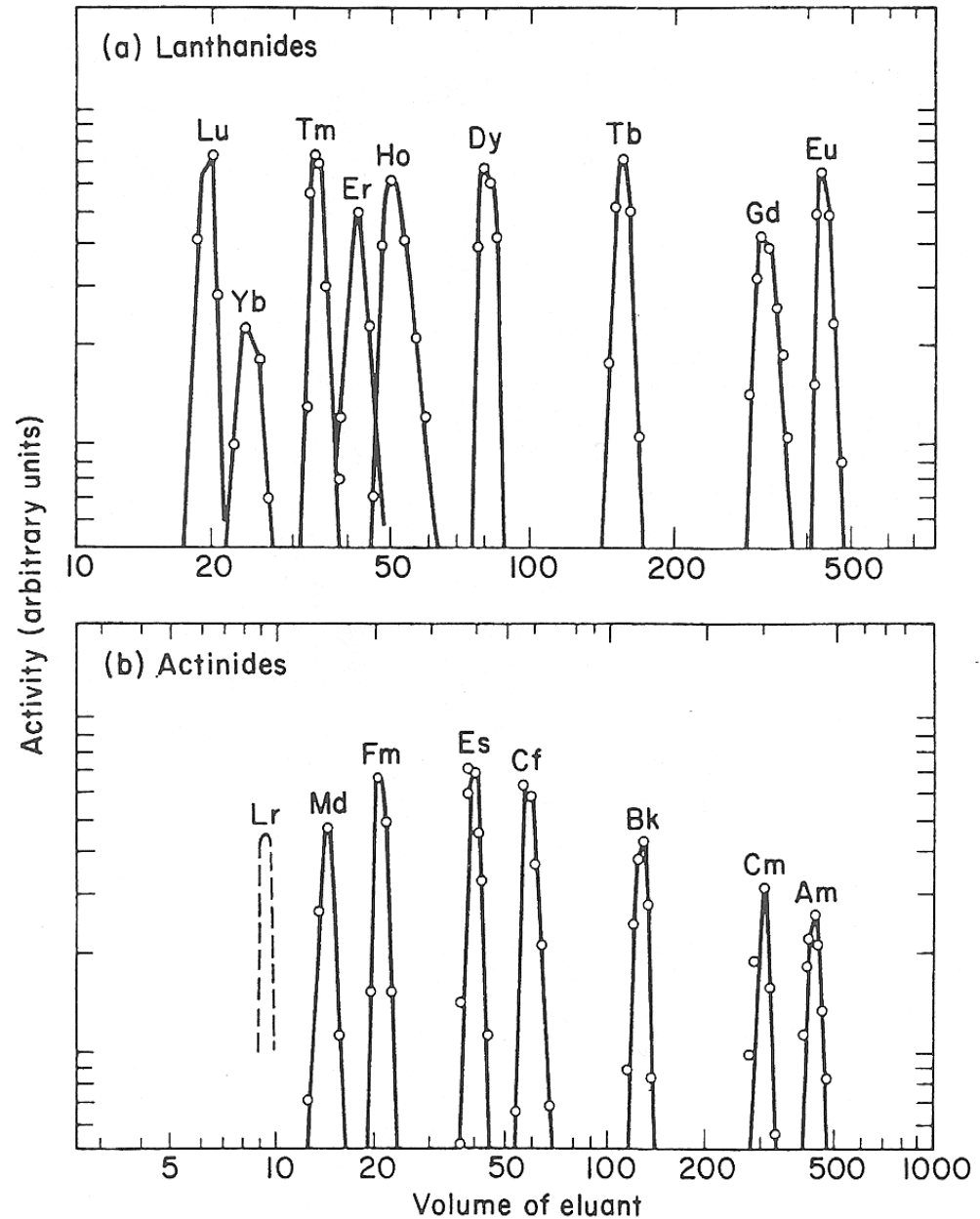
Fig. 4. Contraction of ionic radii of the heavy lanthanides(III) and actinides(III). The radii of  $Fm^{3+}$  and  $Md^{3+}$  are calculated from  $R_{max}$  by extrapolation procedure.

# Cation-exchange chromatographic separation

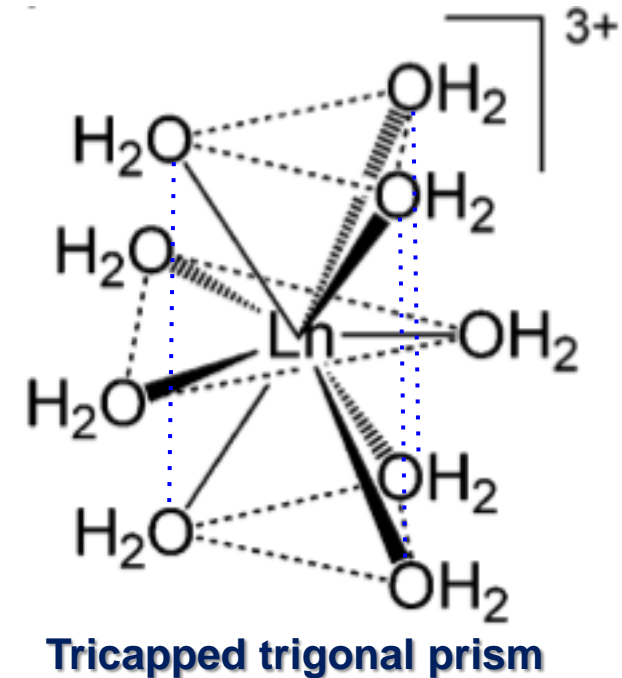
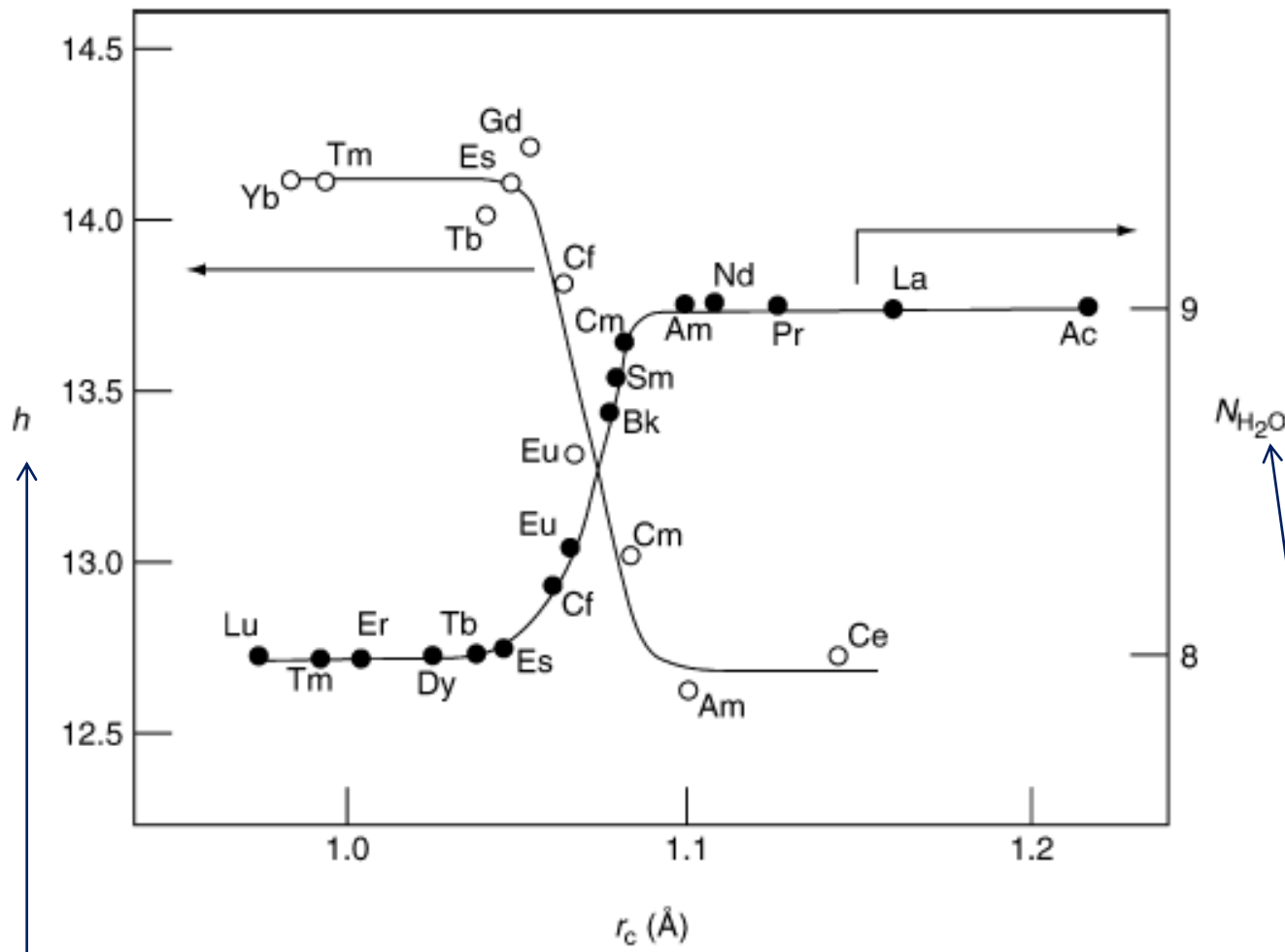
*Elution of tripositive lanthanide and actinide ions on Dowex 50 cation-exchange resin and AHIB (ammonium  $\alpha$ -hydroxyisobutyrate) eluant.  $Lr^{3+}$  band (dashed line) was predicted.*



**AHIB**



# Coordination of $\text{Ln}^{3+}$ and $\text{An}^{3+}$ aquo ions



$\text{Ln}^{3+}$ : Furet *et al.* *J. Am. Chem. Soc.* 130, 2181 (2008)

$\text{Cm}^{3+}$ : Skanthakumar, Antonio, Soderholm, *Inorg. Chem.* 46, 3485

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 $\text{Ln}^{3+}$ and $\text{An}^{3+}$ aquo ions

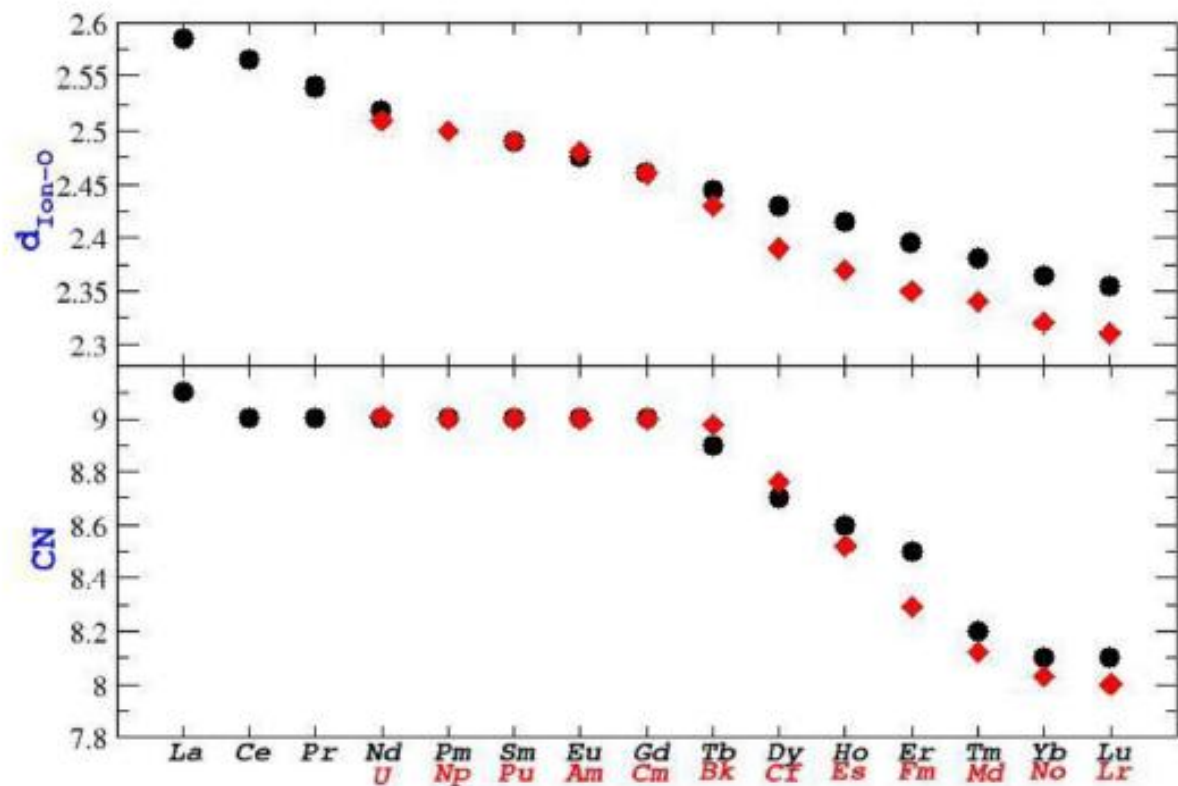
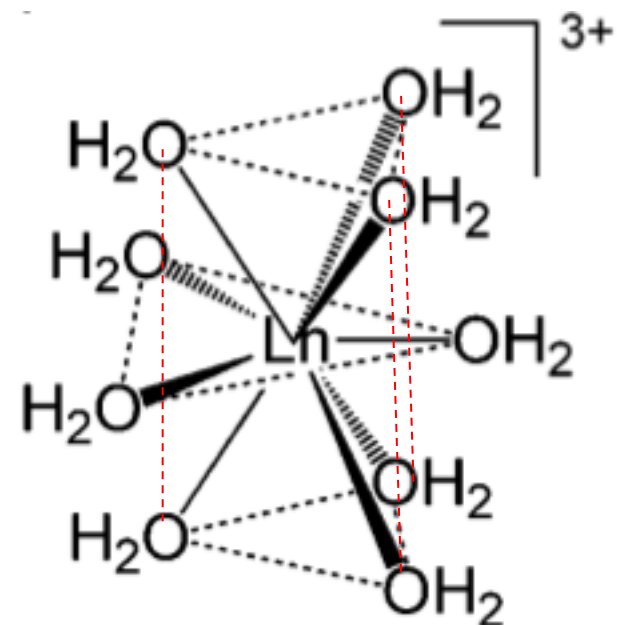


Fig. 1 First hydration shell CN in the Ln(III), circles, and An(III), diamonds, series as obtained from refs. [17,25], respectively.



tricapped trigonal prism:  
 Furet *et al.* *J. Am. Chem. Soc.* **130**, 2008, 2181;  
 Skanthakumar, Antonio, Soderholm, *Inorg. Chem.*, **46** 3485

Martelli *et al.* *Pure Appl. Chem.*, **85**, 237–246, 2013  
 Ref 17 D'Angelo, Spezia, *et al.* *Inorg. Chem.* **50**, 4572 (2011).  
 Ref 25 Duvail *et al.* *J. Chem. Phys.* **135**, 044503 (2011).

# Hydrolysis: acid-base reaction

- $M^+(aq) + H_2O(l) = MOH(aq) + H^+(aq)$ 
  - no reaction, *e.g.*  $K^+$
- $M^{2+}(aq) + H_2O(l) = M(OH)^+(aq) + H^+(aq)$ 
  - slight reaction, *e.g.*  $Ca^{2+}$

acid                      base                      conjugate base                      conjugate acid
- $M^{3+}(aq) + H_2O(l) = M(OH)^{2+}(aq) + H^+(aq)$ 
  - significant hydrolysis; can proceed to additional steps
  - For  $Bk^{3+}$ ,  $\log^* \beta_{11} = \log \beta_{11} - 14 = -5.66$
- $M^{4+}(aq) + H_2O(l) = M(OH)^{3+}(aq) + H^+(aq)$ 
  - predominant hydrolysis
  - For  $Bk^{4+}$ ,  $\log^* \beta_{11}$  unknown but for  $Pu^{4+}$ ,  $\log^* \beta_{11} = 0.6$
  - will proceed to additional steps, for example
  - $MOH^{3+}(aq) + H_2O(l) = M(OH)_2^{2+} + H^+(aq)$

# 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:  $Bk^{3+} + Cl^- = BkCl^{2+} \quad \beta_{11} = K_{11} = [BkCl^{2+}]/\{[Bk^{3+}][Cl^-]\}$

## – Complexation reactions with ligand deprotonation: $*K_q$ and $*\beta_q$

- Example:  $Pu^{4+} + OH^- = Pu(OH)^{3+} \quad \beta_{11} = [Pu(OH)^{3+}]/\{[Pu^{4+}][OH^-]\}$   
 $Pu^{4+} + H_2O = Pu(OH)^{3+} + H^+ \quad *\beta_{11} = [Pu(OH)^{3+}][H^+]/[Pu^{4+}] = \beta_{11} \cdot K_w$

	$Cm^{3+}$	$Bk^{3+}$	$Cf^{3+}$	$Es^{3+}$	$Fm^{3+}$
$OH^-$	8.08	8.34	8.38	8.86	10.2
$F^-$		2.89	3.03		
$Cl^-$		-0.18		-0.18	
glycolate $HOCH_2CO_2^-$	2.85	2.65			
acetate		2.05	2.11		



# Lanthanide and Actinide Oxides

	CeO <sub>2</sub>	Pr <sub>6</sub> O <sub>11</sub>						Tb <sub>4</sub> O <sub>7</sub>						
La <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	Pr <sub>2</sub> O <sub>3</sub>	Nd <sub>2</sub> O <sub>3</sub>	Pm <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Tb <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>	Ho <sub>2</sub> O <sub>3</sub>	Er <sub>2</sub> O <sub>3</sub>	Tm <sub>2</sub> O <sub>3</sub>	Yb <sub>2</sub> O <sub>3</sub>	Lu <sub>2</sub> O <sub>3</sub>
			NdO metallic		SmO	EuO							YbO	

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



5

	ThO <sub>2</sub>	PaO <sub>2</sub>	UO <sub>2</sub>	NpO <sub>2</sub>	PuO <sub>2</sub>	AmO <sub>2</sub>	CmO <sub>2</sub>	BkO <sub>2</sub>	CfO <sub>2</sub>					
Ac <sub>2</sub> O <sub>3</sub>					Pu <sub>2</sub> O <sub>3</sub>	Am <sub>2</sub> O <sub>3</sub>	Cm <sub>2</sub> O <sub>3</sub>	Bk <sub>2</sub> O <sub>3</sub>	Cf <sub>2</sub> O <sub>3</sub>	Es <sub>2</sub> O <sub>3</sub>				

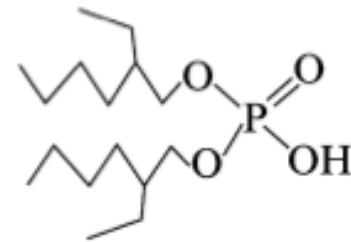
# Stoichiometric Chlorides of f Elements

<u>La</u>	<u>Ce</u>	<u>Pr</u>	<u>Nd</u>	<u>Pm</u>	<u>Sm</u>	<u>Eu</u>	<u>Gd</u>	<u>Tb</u>	<u>Dy</u>
LaCl <sub>3</sub>	CeCl <sub>3</sub>	PrCl <sub>3</sub>	NdCl <sub>3</sub>	PmCl <sub>3</sub>	SmCl <sub>3</sub>	EuCl <sub>3</sub>	GdCl <sub>3</sub>	TbCl <sub>3</sub>	DyCl <sub>3</sub>
			NdCl <sub>2</sub>		SmCl <sub>2</sub>	EuCl <sub>2</sub>			
							Gd <sub>2</sub> Cl <sub>3</sub>	Tb <sub>2</sub> Cl <sub>3</sub>	
<u>Ac</u>	<u>Th</u>	<u>Pa</u>	<u>U</u>	<u>Np</u>	<u>Pu</u>	<u>Am</u>	<u>Cm</u>	<u>Bk</u>	<u>Cf</u>
			UCl <sub>6</sub>						
		PaCl <sub>5</sub>	UCl <sub>5</sub>						
	ThCl <sub>4</sub>	PaCl <sub>4</sub>	UCl <sub>4</sub>	NpCl <sub>4</sub>					
AcCl <sub>3</sub>			UCl <sub>3</sub>	NpCl <sub>3</sub>	PuCl <sub>3</sub>	AmCl <sub>3</sub>	CmCl <sub>3</sub>	BkCl <sub>3</sub>	CfCl <sub>3</sub>
						AmCl <sub>2</sub>			CfCl <sub>2</sub>

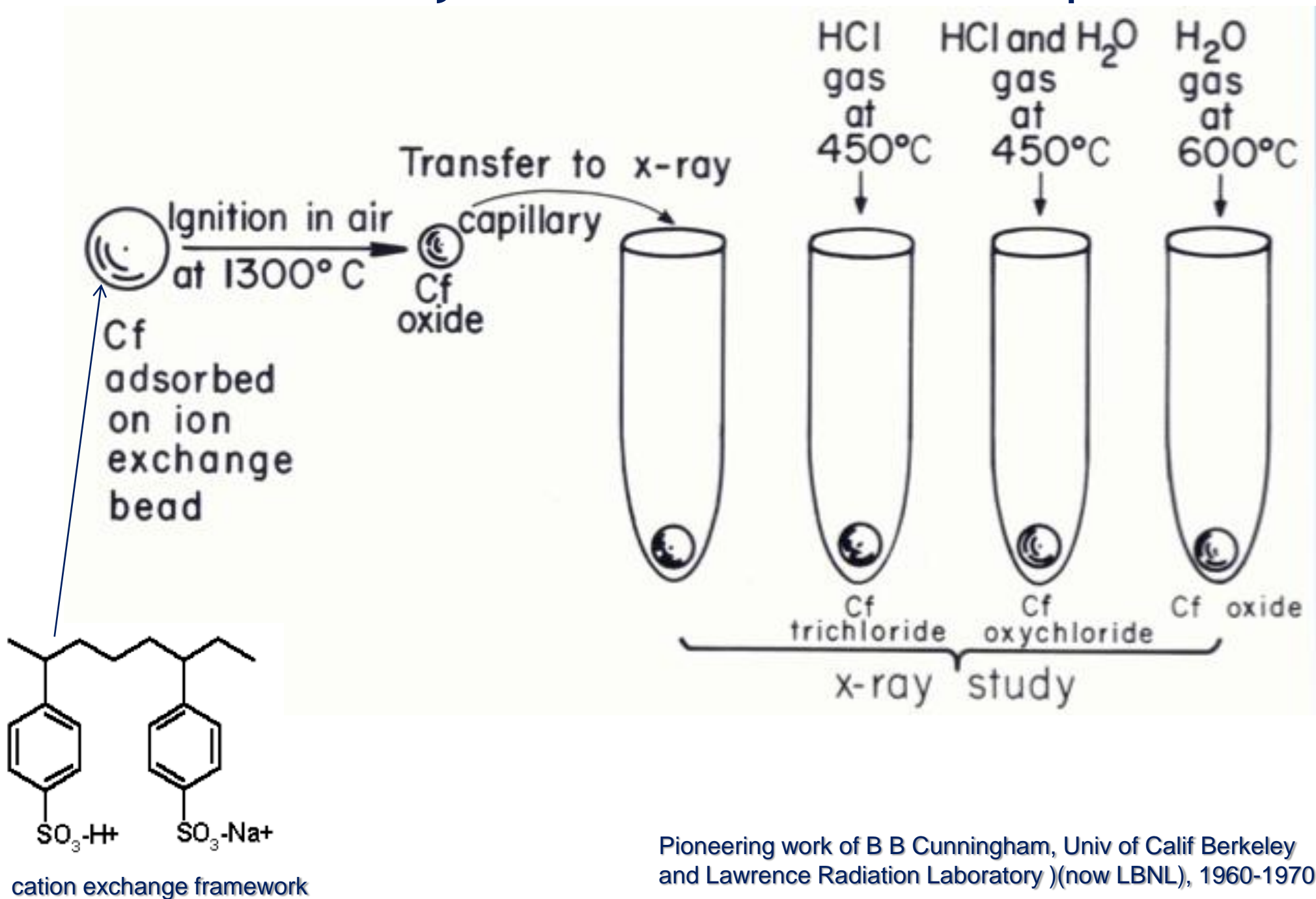
Note: Solid reduced Es halides (samples believed to be EsCl<sub>2</sub> and EsBr<sub>2</sub>) were made at ORNL in the 1970s and their spectra were reported: Fellows *et al.*, *Inorg. Nucl. Chem. Lett.* 11, 737 (1975); *Symposium Commemorating the 25<sup>th</sup> Anniversary of Elements 99 and 100*, 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<sup>7</sup>)
  - 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  $\Delta_f H^\circ(\text{Bk}^{3+}, \text{aq})$



# Ultramicroscale synthesis of trans-Cm compounds

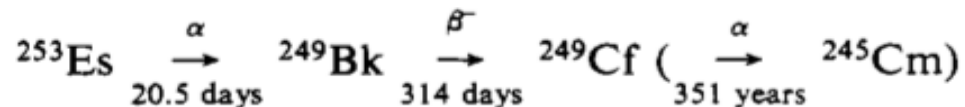


# Californium

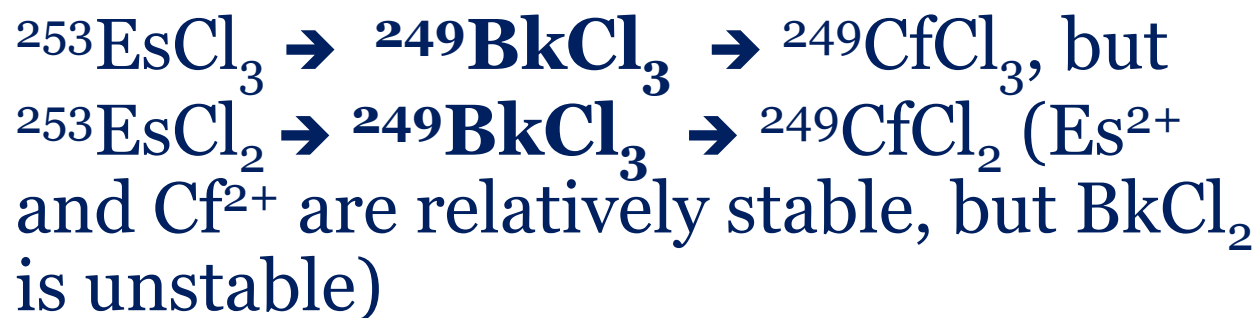
- Discovered by Thompson, Street, Ghiorso, Seaborg, 1950 by cyclotron bombardment
- Lowest-Z actinide with accessible +2 state
  - Even accessible by polarography in aqueous solution
  - $\text{Am}^{2+}$  has been claimed in nonaqueous solution and halides
- $^{252}\text{Cf}$  has fission branch that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

# Einsteinium

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



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

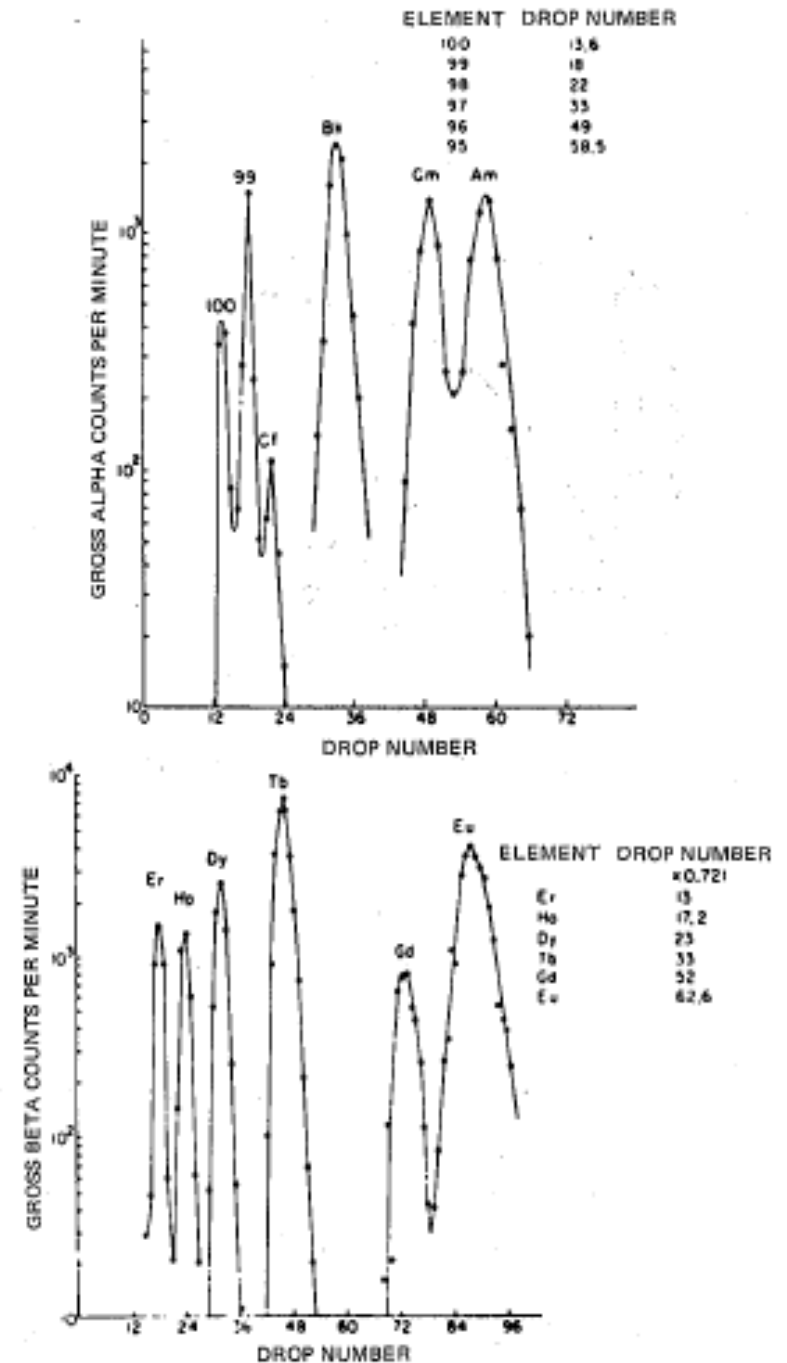


Metal prepared 1971, 1979



# Chemical identification of Es

S. G. Thompson, B. G. Harvey, G. R. Choppin,  
and G. T. Seaborg, *J. Amer. Chem. Soc.* 76,  
6229 (1954).



# Es<sup>3+</sup> absorption spectra

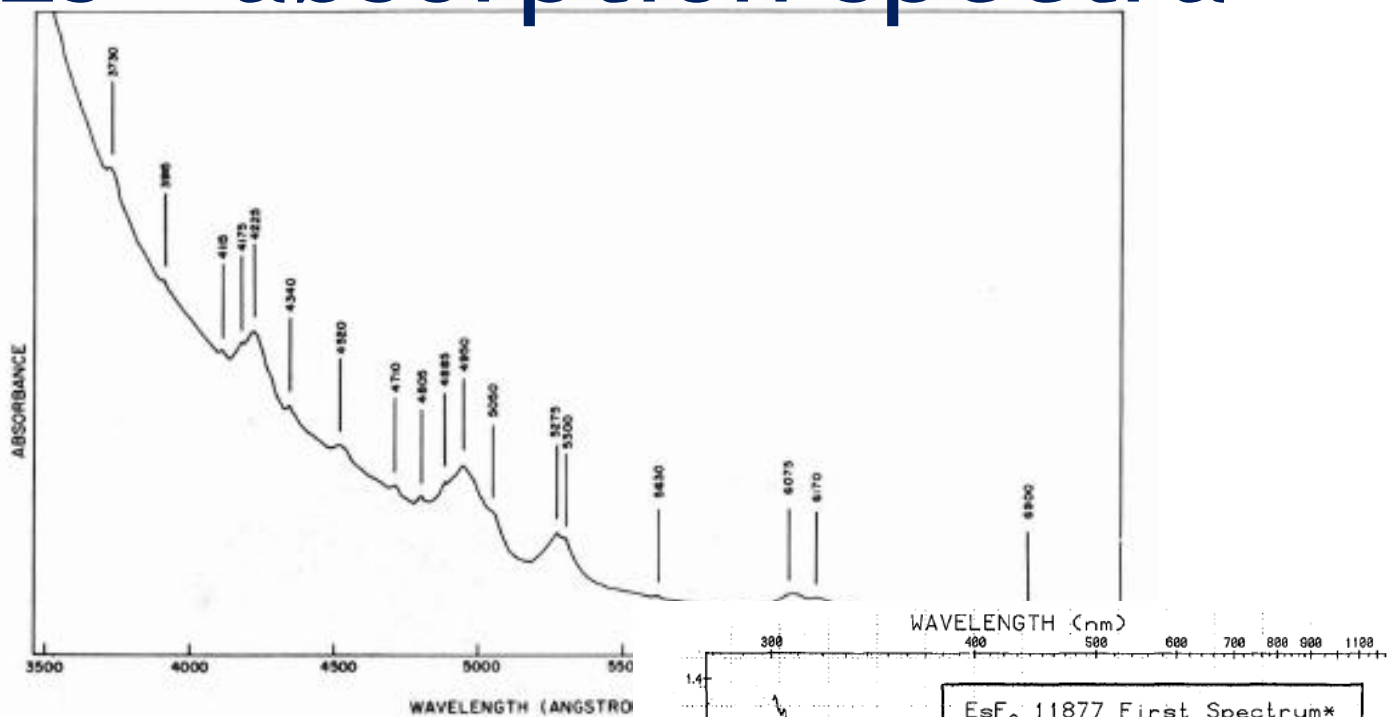


Fig. 7. Solution absorptior

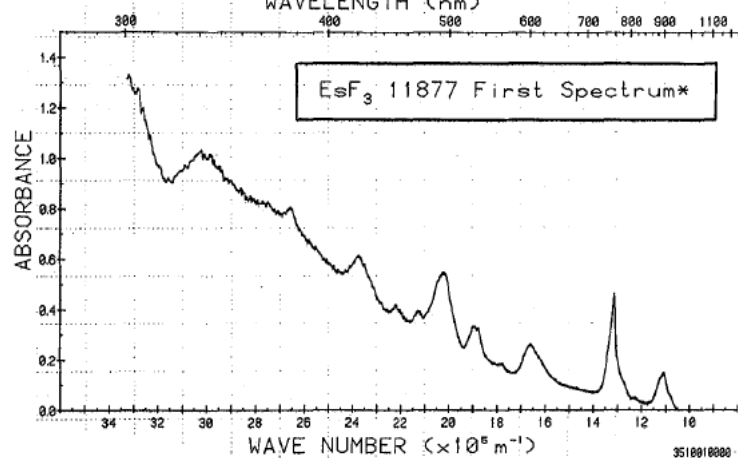


Fig. 16. First absorption spectrum of EsF<sub>3</sub>.

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



# Es<sup>3+</sup>(aq) absorption spectrum

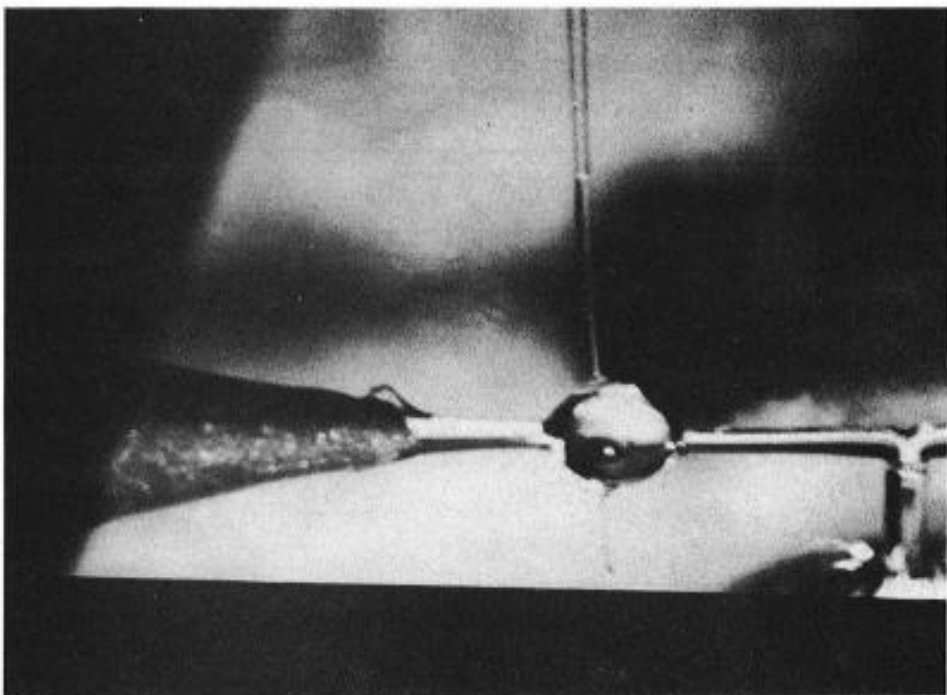


Fig. 5. Photomicrograph of light-pipe gap loaded with  $\approx 60 \mu\text{l}$  of solution.

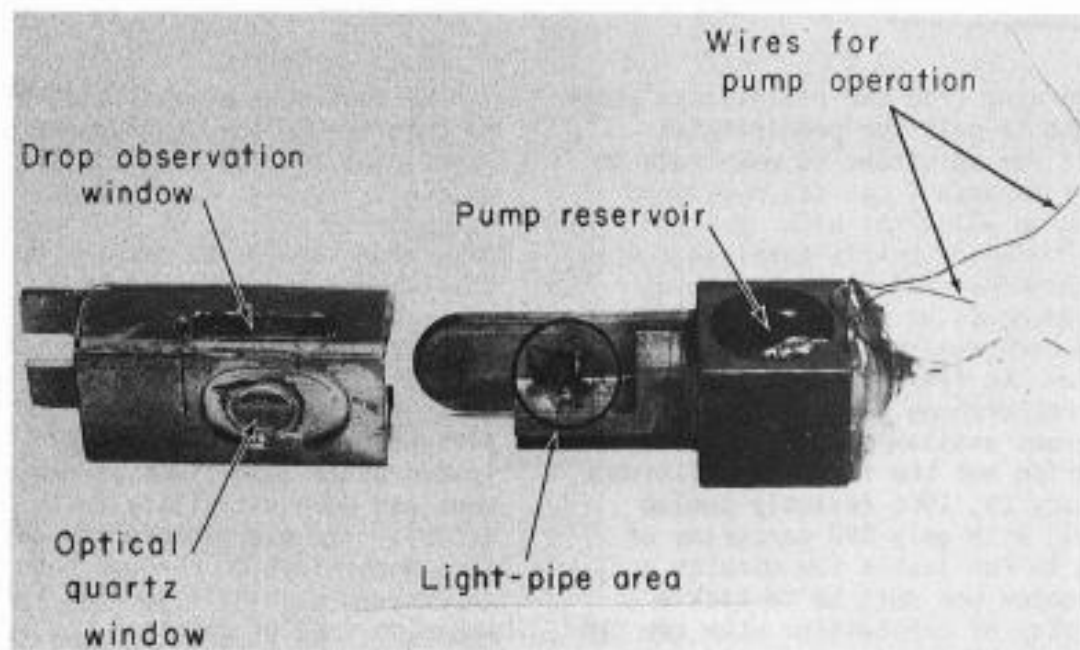


Fig. 2. Photograph of a light-pipe, microabsorption cell.

B. B. Cunningham, J. R. Peterson, R. D. Baybarz, and T. C. Parsons, *Inorg. Nucl. Chern. Lett.* 1, 519 (1967);  
 J. R. Peterson, Symposium Commemorating the 25th Anniversary of Elements 99 and 100, LBL-7701, pp 55-60

# Crystallography of Es compounds

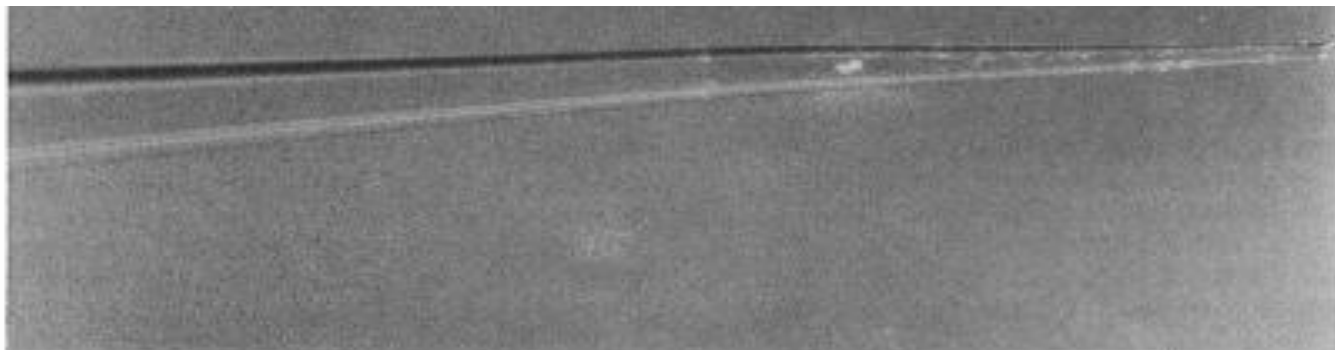
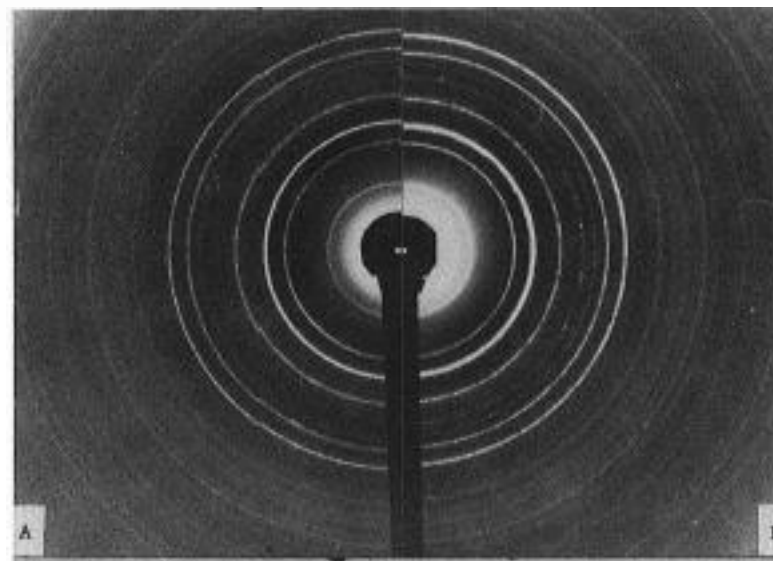


Fig. 8. Photomicrograph of a sample of einsteinium oxide on the wall of a quartz tube.



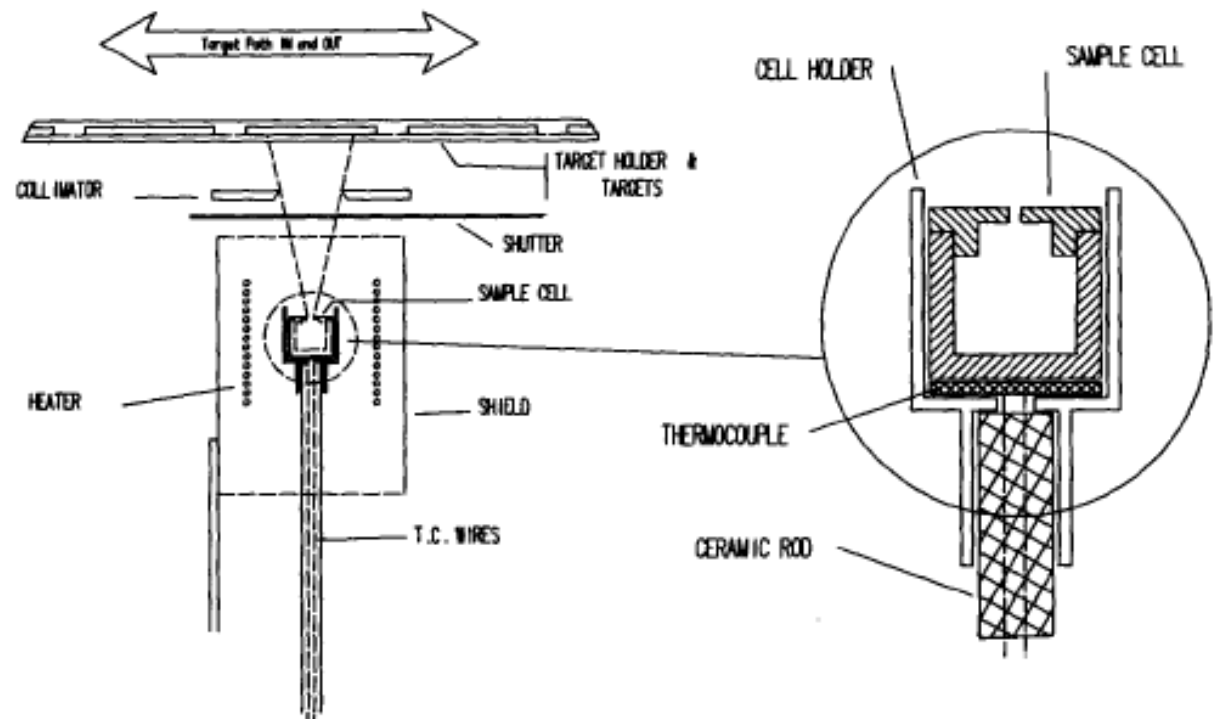
Electron diffraction patterns:



R. G. Haire and R. D. Baybarz, *J. Inorg. Nucl. Chem.* 35, 489 (1973).

# 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

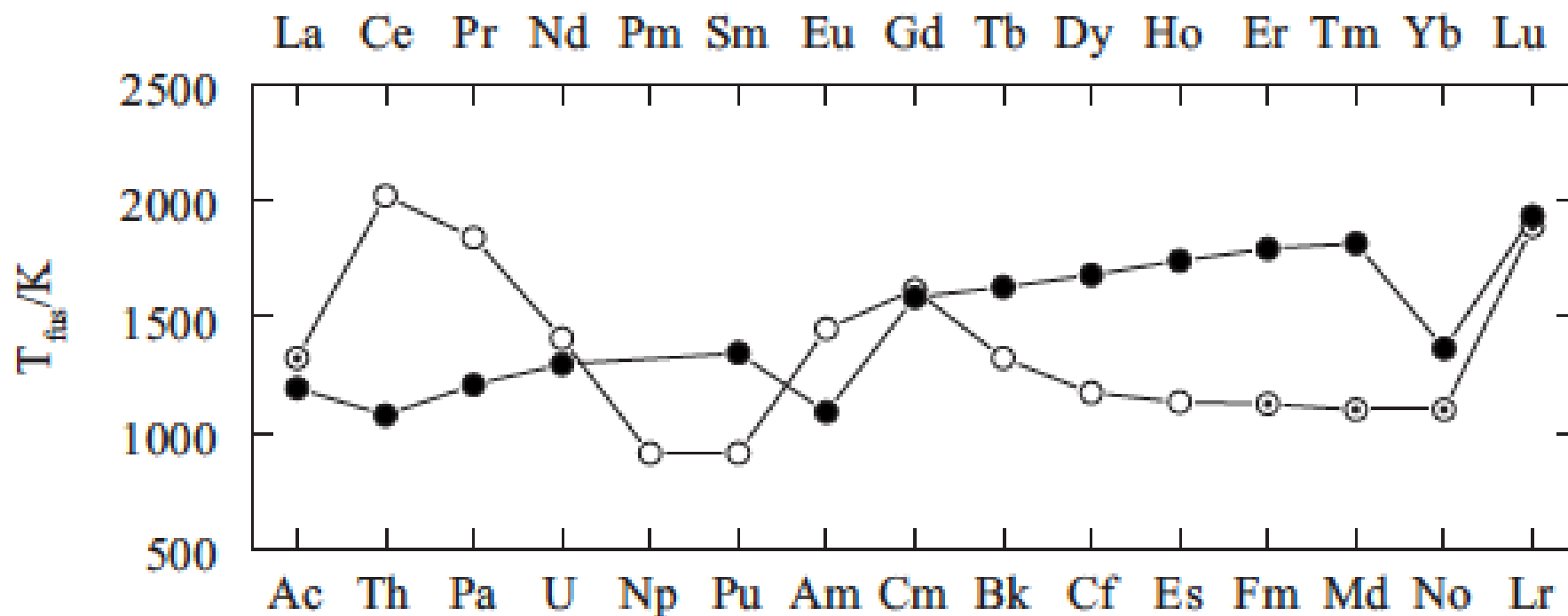


FIG. 11. The melting point of the lanthanide (●) and actinide (○) metals. The estimated values are indicated by ⊙.

# Stability of f element metals

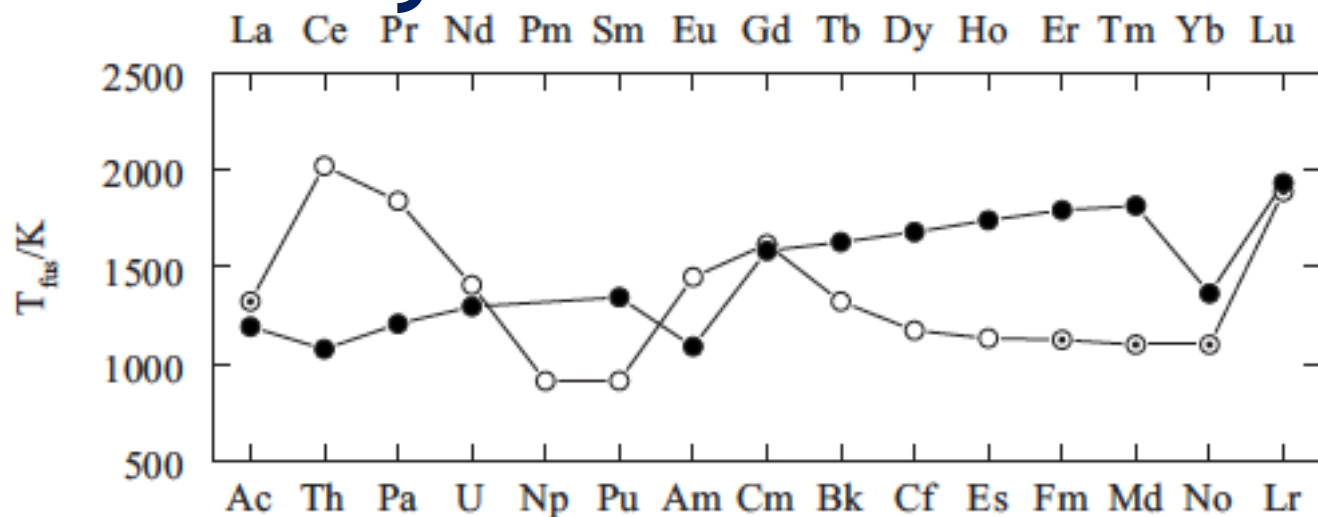


FIG. 11. The melting point of the lanthanide ( $\bullet$ ) and actinide ( $\circ$ ) metals. The estimated values are indicated by  $\odot$ .

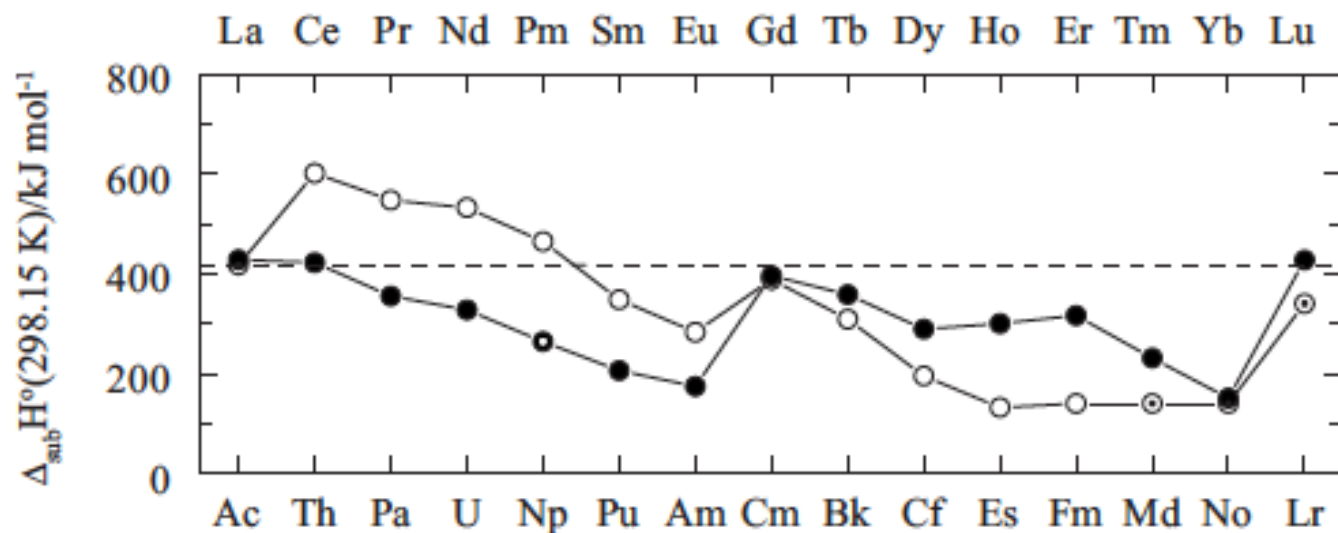
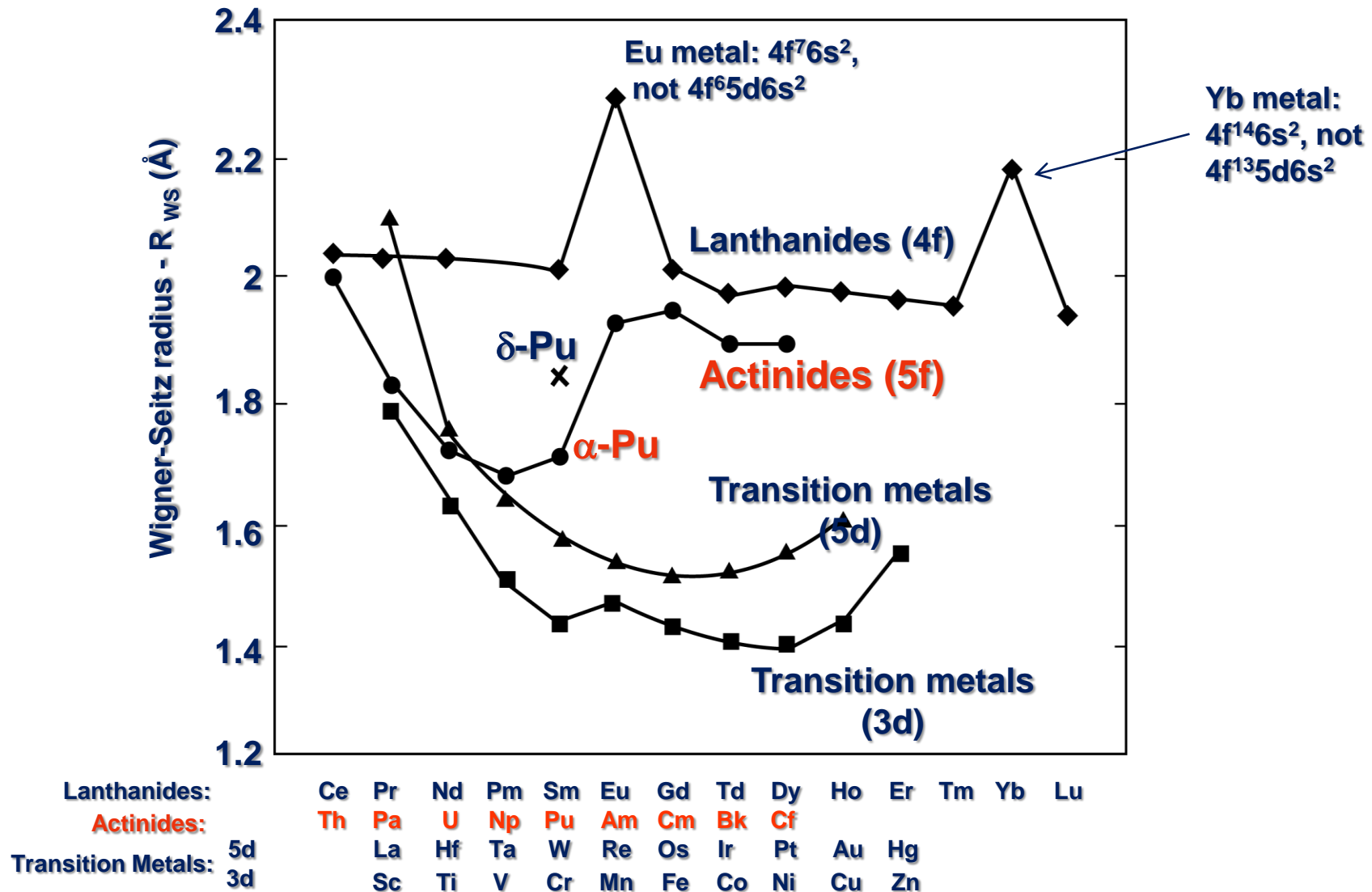


FIG. 14. The sublimation enthalpy at  $T=298.15 \text{ K}$  of the lanthanide ( $\bullet$ ) and actinide ( $\circ$ ) metals. The estimated values are indicated by  $\odot$ .

# 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  $\text{Md}^{3+}(\text{aq})$  to  $\text{Md}^{2+}(\text{aq})$  with Zn dust to show that  $\text{Md}^{2+}(\text{aq})$  exists
  - First evidence of an  $\text{An}^{2+}(\text{aq})$  ion
- David *et al.* (1981) used radiopolarography to establish electrochemical properties of the redox process
 
$$\text{Md}^{3+}(\text{aq}) + e^- = \text{Md}^{2+}(\text{aq})$$
- Mikheev (1972 and later) claimed  $\text{Md}^+(\text{aq})$  repeatedly but Hulet *et al.* (1979) refuted this claim

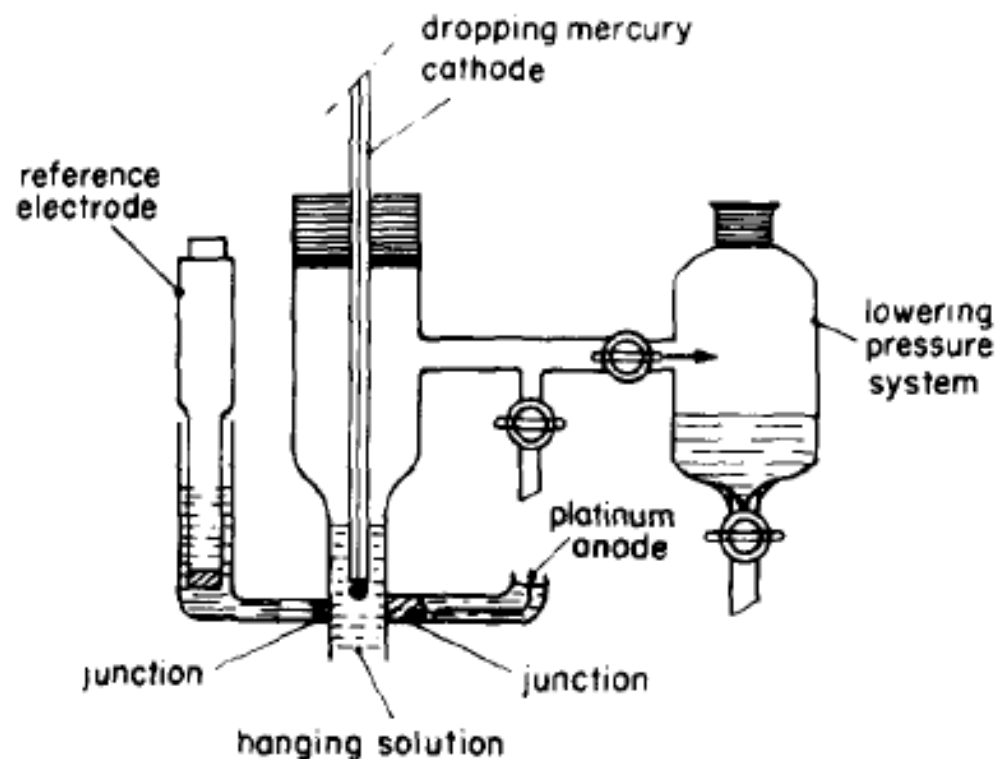
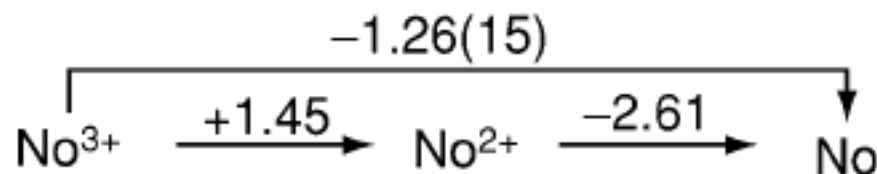


Fig. 2. Radiopolarographic device.

# Nobelium

- First reported by international team at Nobel Institute in Stockholm, 1957
  - $^{244}\text{Cm} + ^{13}\text{C} \rightarrow ^{253 \text{ or } 255}\text{No}$  (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  $\text{No}^{3+}$



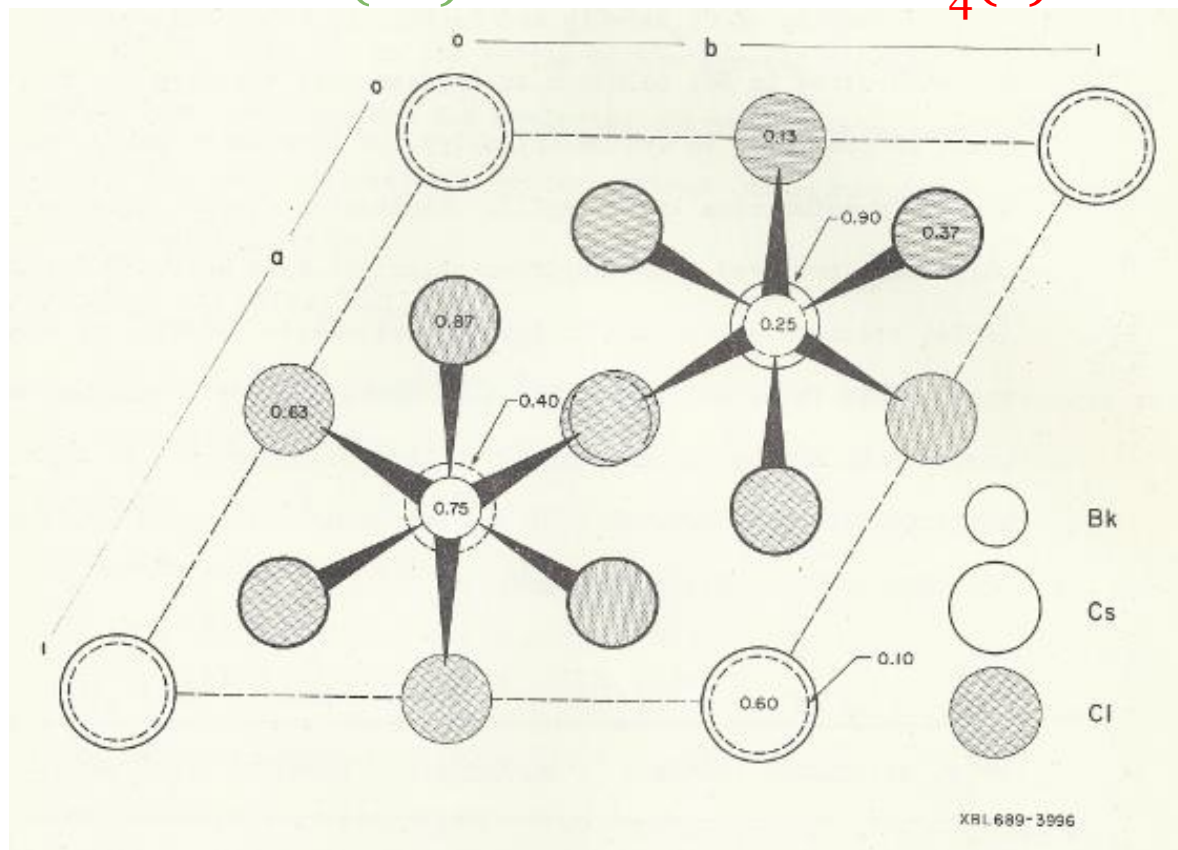


# Lawrencium

- 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

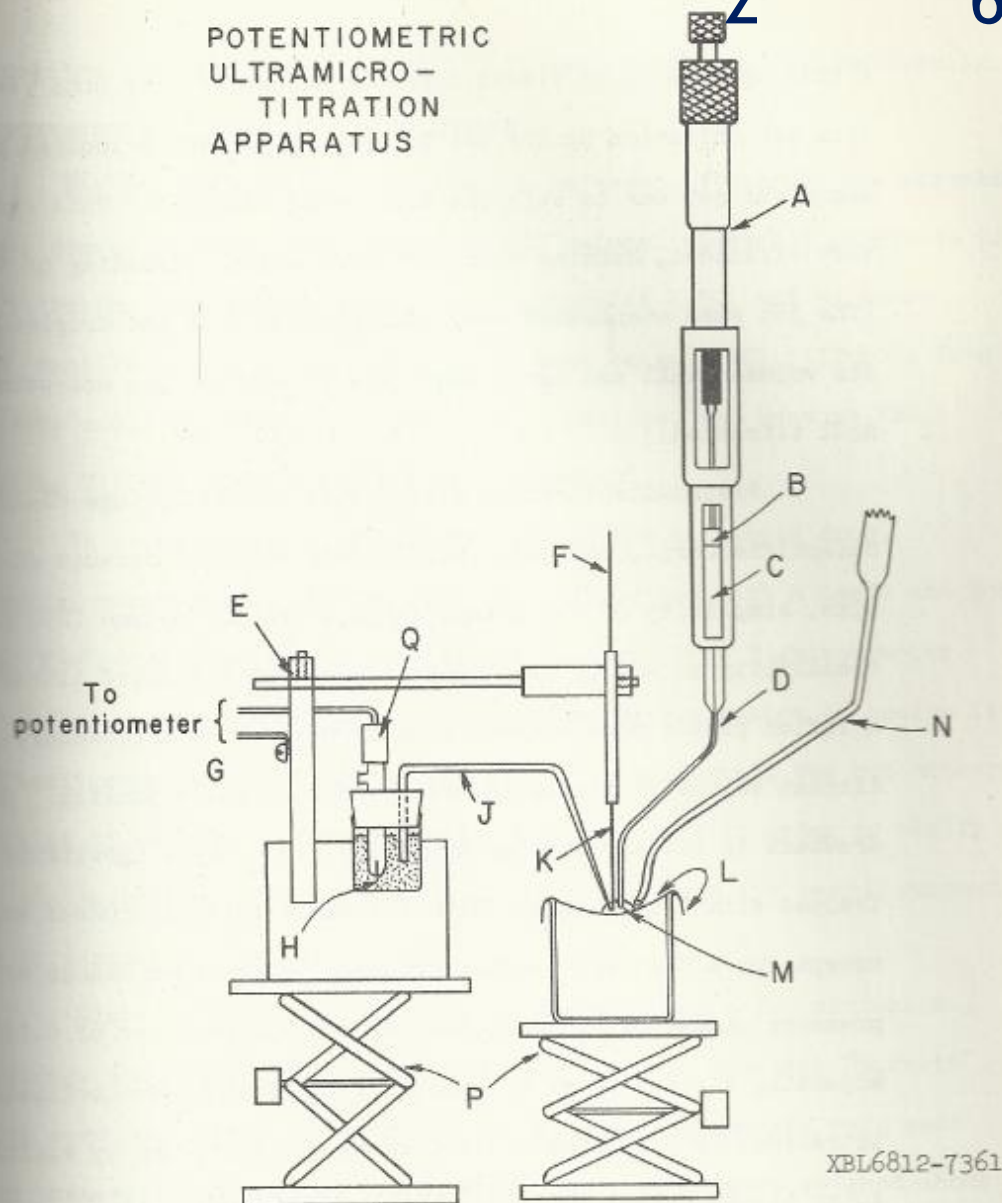
- $\text{Cs}_2\text{CeCl}_6$ ,  $\text{Cs}_2\text{PuCl}_6$ , and  $\text{Cs}_2\text{BkCl}_6$ 
  - Stable M(IV) salts where  $\text{MCl}_4(\text{s})$  is unknown



Sources: L R Morss, PhD thesis, UCRL-18951 and L. R. Morss and J. Fuger, "Preparation and Crystal Structures of Dicesium Berkelium Hexachloride and Dicesium Sodium Berkelium Hexachloride", *Inorg. Chem.* **8**, 1433

- 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 $\text{Cs}_2\text{BkCl}_6$



- |   |  |
|---|--|
| A. Micrometer, readable to $\pm 0.01 \mu\text{l}$ | J. Agar- $\text{K}_2\text{SO}_4$ salt bridge |
| B. Teflon piston                                  | K. Platinum wire                             |
| C. Pyrex titrant cylinder                         | L. Parafilm                                  |
| D. Capillary buret tip                            | M. Titration drop                            |
| E. Electrode support                              | N. Argon jet                                 |
| F. Silver wire                                    | P. Variable-height platforms                 |
| G. Potentiometer leads                            | Q. Reference electrode                       |
| H. $\text{K}_2\text{SO}_4$ solution               |  |

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  $\text{AnO}^+$  [*i.e.*,  $\text{An}^+\text{O}(\text{g})$ ],  $\text{AnO}_2^+$ , and  $\text{AnO}_2^{2+}$
  - Ionization energies of  $\text{AnO}$ ,  $\text{AnO}^+$ ,  $\text{AnO}_2$ , and  $\text{AnO}_2^+$
- Order of reactivities in gas phase
  - $\text{Th}^+ \geq \text{Pa}^+ \geq \text{U}^+ \approx \text{Np}^+ > \text{Cm}^+ \geq \text{Pu}^+ > \text{Bk}^+ > \text{Am}^+ \approx \text{Cf}^+ \geq \text{Es}^+$

# Transplutonium Actinides -- References

- Morss *et al.*, *The Chemistry of the Actinide and Transactinide Elements*, 3rd or 4<sup>th</sup> ed., chapters 8-15
- J K Gibson and J Marçalo, *Coord. Chem. Reviews*, 250, 776 (2006)
- <http://www.pbs.org/wgbh/nova/physics/stability-elements.html>
- David Pogue PBS “Hunting the Elements”, 2012
- PBS 2013: The Mystery of Matter: Search for the Elements

# Upcoming NAMP Radiochemistry Webinars

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- Environmental/Bioassay Radiochemistry Series

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