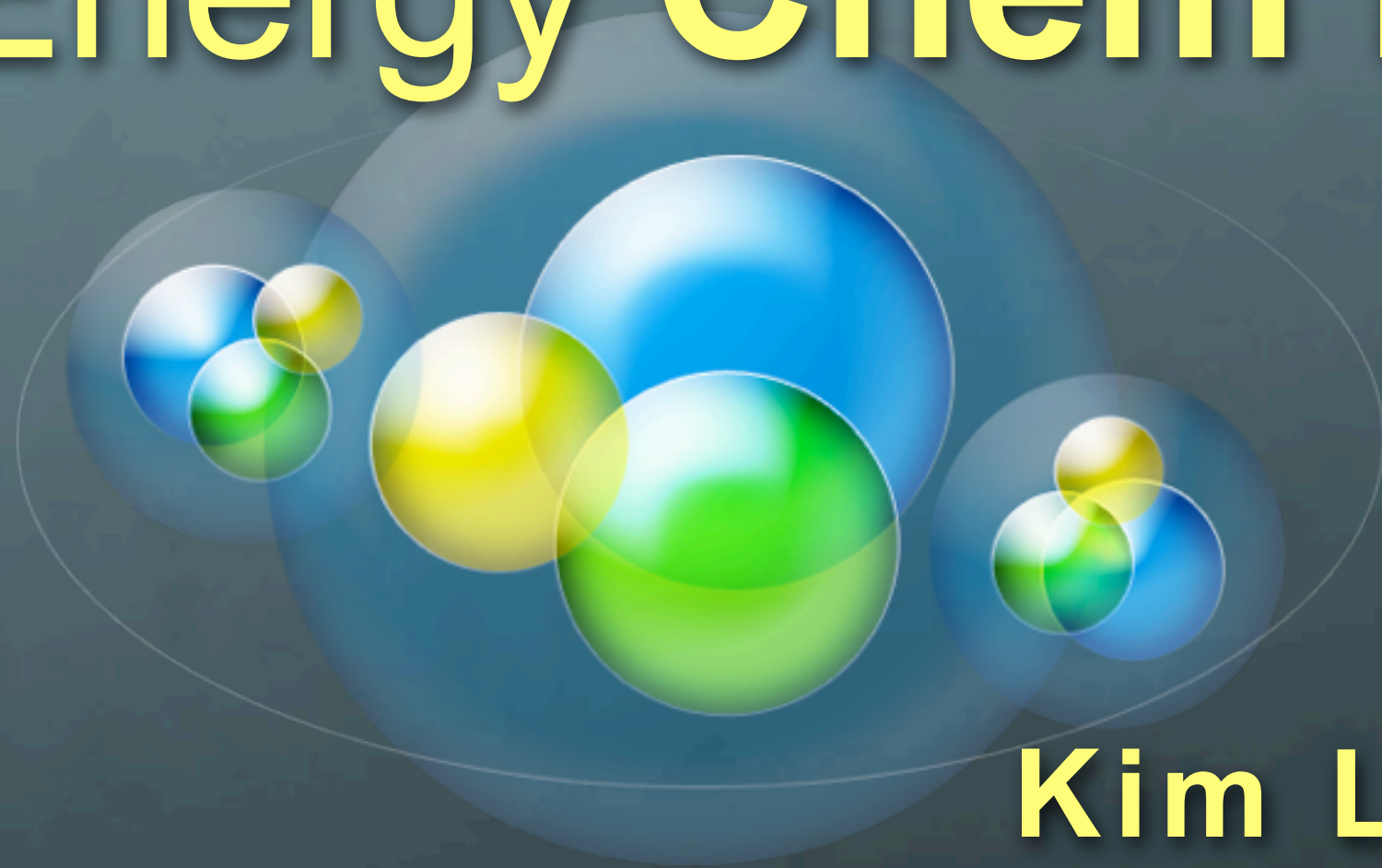


# Thorium and Fluorides:

## Energy Chem Engineered








*on the Fly*



**Kim L. Johnson**




**ChemInnovár 12 May 2011**

# Thorium & Fluoride Chem Overview

-  **Intro to Thorium Chemistry:**
  -  Chemical and Nuclear Differences with Uranium
  -  Geo-Chemical Kinship with the Rare Earths
-  **Intro to Fluoride Chemistry**
-  **Lftr** – the Alliance of Chemistry and Physics between all the following:
  -  • Thorium & Fissile Isotopes
  -  • Fission Products
  - Fluoride Salts



# Nuclear Differences of T with Uranium

	Thorium =	100% <u><math>^{232}\text{Th}</math></u>	Uranium =	99.3% <u><math>^{238}\text{U}</math></u>
	Half-Life (Billion Yr):	14.1		4.5
	Abundance (ppm in Crust):	~12		~3





 **Thorium** easily bred into Fuel fissioning more efficiently + forming far fewer long-lived **TrU**'s (Trans-Uranium metals) than  $^{238}\text{U}$ :

$^{232}\text{Th}$  + n  $\rightarrow$   $^{233}\text{U}$  + n  $\rightarrow$  ~91% fissions + ~9%  $^{234}\text{U}$  + n  $\rightarrow$   $^{235}\text{U}$  + n  $\rightarrow$  ~81% fissions + ~19%  $^{236}\text{U}$  + n  $\rightarrow$   $^{237}\text{U}$  (half-life: 7 da)  $\rightarrow$   $^{237}\text{Np}$  (2e6 yr, not very fissile) + n  $\rightarrow$   $^{238}\text{Pu}$  (88y, Best Battery isotope)

$^{238}\text{U}$  + n  $\rightarrow$   $^{239}\text{Pu}$  + n  $\rightarrow$  ~64% fissions + ~34%  $^{240}\text{Pu}$  + n  $\rightarrow$   $^{241}\text{Pu}$  (half-life: 14y)  $\rightarrow$   $^{241}\text{Am}$  (432 yr, not fissile)  
 $^{241}\text{Pu}$  + n  $\rightarrow$  ~73% fissions + ~27%  $^{242}\text{Pu}$  (373,000 yr, not fissile)



# Chemical Differences of T with Uranium

-  After Earth's atmosphere had built up free  $O_2$  thanks to **Photosynthesis**,  $O_2$ -bearing waters began oxidizing Uranium to its hexavalent state:
-   $U^{+6}$  compounds – in contrast to primordial  $U^{+4}$  – are all quite soluble in water
-  Leached by water, U compounds were widely dispersed
-  Having been scattered far and wide, U compounds today are found as complex, generally dilute deposits containing mixtures of  $U^{+4}$ ,  $U^{+5}$  and  $U^{+6}$ .



# T-Chem Differences with Uranium (con't)








- Unlike Uranium,  $\text{Th}^{+4}$  (constant) resists weathering. Nature's most common forms, **Thoria** ( $\text{ThO}_2$ ),  **$\text{Th}_3(\text{PO}_4)_4$**  and  **$\text{ThSiO}_4$**  are totally **water-insoluble** at all natural pH ranges: (pH >2)
- Even with boiling  $\text{H}_2\text{SO}_4$  /  $\text{HNO}_3$ , **Thoria** dissolves slowly and with great difficulty. So reprocessing  $\text{ThO}_2$  requires much more effort than for  $\text{UO}_2$ :
  - Hotter more concentrated  $\text{HNO}_3$  plus 5-15% **HF**/ **$\text{AlF}_3$**  to attack grain boundaries
  - Considerably more Corrosion of all Equipment due to **Aqueous HF** and Much Longer Time required for reprocessing
- $\text{ThO}_2$ -containing Solid Fuel is therefore considerably costlier to Fabricate and particularly Reprocess than  $\text{UO}_2$  Solids solo...

**Thorium thus remained concentrated where it first wound up –  
– within easy reach in Earth's primordial deposits of Rare Earths**



# Geo-Chemical Kinship with the **Rare Earths**

**Rare Earth Elements or REEs are:**

-  **Large Part of the Ash of Ancient Stars**
-  **Trivalent Metals with Practically Identical Chem**
-  **Chemical Magnets within the Earth for Thorium**
  -  **Form with Thorium a Dynamic Duo for a Living Planet**
-  **Real **REE-Minders** that the US must:**
  -  **Rebuild the **Industrial + Intellectual Prop.** Base we once had**
  -  **Develop the **Best Use for Thorium****



# REEs – Ash from Ancient Stars

- ~Half of the Elements heavier than Iron (including REEs) form gradually in Big Stars in the course of large-stellar lives:
  - Slow rate of adding neutrons to nuclei, building elements up to **Bismuth**
- However a Supernova's huge neutron bursts synthesize during the first ~15 minutes of Supernova Detonation:
  - ~Half of All Elements Heavier than Iron that exist
  - All elements past Bismuth and most **R.I.s** (Radiolotopes)
- Once blasted deep into Space, some R.I.s experience *Spontaneous Fission*:
  - Enriches planet-forming Stardust with additional **Rare Earth Elements**
  - REEs** comprise ~40% of all *Primordial* Fission Products.



# REEs: Practically Identical Chemistry



REEs include: Lanthanum thru Lutetium, plus *Yttrium* (always included), Scandium (sometimes) and Thorium (historically ignored – considered a Liability)



Exclusively  $M^{+3}$  (Metals that are Tri-Valent), **except for Cerium** (REE deposits' most plentiful metal) and **Thorium** (typically the third most abundant metal after Ce / La in most REE deposits):



$Ce^{+3} / Ce^{+4}$



$Th^{+4}$  (exclusively Tetra-Valent)

The Periodic Table of the Elements

**Lanthanide Series**

Rare Earths and associated elements, Lutetium, Yttrium, Thorium and Scandium

Hydrogen 1 H 1.0079	Helium 2 He 4.0026	Boron 5 B 10.811	Carbon 6 C 12.011	Nitrogen 7 N 14.007	Oxygen 8 O 15.999	Fluorine 9 F 18.998	Neon 10 Ne 20.180	Sodium 11 Na 22.990	Magnesium 12 Mg 24.305	Aluminum 13 Al 26.982	Silicon 14 Si 28.086	Phosphorus 15 P 30.974	Sulfur 16 S 32.065	Chlorine 17 Cl 35.453	Argon 18 Ar 39.948	Potassium 19 K 39.098	Calcium 20 Ca 40.078	Scandium 21 Sc 44.956	Titanium 22 Ti 47.867	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.938	Iron 26 Fe 55.845	Cobalt 27 Co 58.933	Nickel 28 Ni 58.693	Copper 29 Cu 63.546	Zinc 30 Zn 65.38	Gallium 31 Ga 69.723	Germanium 32 Ge 72.61	Arsenic 33 As 74.922	Selenium 34 Se 78.96	Bromine 35 Br 79.904	Krypton 36 Kr 83.80	Rubidium 37 Rb 85.468	Sr 87.62	Yttrium 39 Y 88.906	Zirconium 40 Zr 91.224	Niobium 41 Nb 92.906	Molybdenum 42 Mo 95.94	Technetium 43 Tc [98]	Ruthenium 44 Ru 101.07	Rhodium 45 Rh 102.91	Palladium 46 Pd 106.42	Silver 47 Ag 107.87	Cadmium 48 Cd 112.41	Indium 49 In 114.82	Sn 118.71	Antimony 51 Sb 121.76	Te 127.60	Iodine 53 I 126.90	Xenon 54 Xe 131.29	Cesium 55 Cs 132.91	Ba 137.33	Lanthanum 57 La 138.91	Hafnium 72 Hf 178.49	Tantalum 73 Ta 180.95	Tungsten 74 W 183.84	Rhenium 75 Re 186.21	Osmium 76 Os 190.23	Iridium 77 Ir 192.23	Pt 195.08	Au 196.97	Hg 200.59	Thallium 81 Tl 204.38	Pb 207.2	Bi 208.98	Po [209]	At [210]	Rn [222]	Francium 87 Fr [223]	Ra [226]	Actinium 89 Ac [227]	Rutherfordium 104 Rf [261]	Dubnium 105 Db [262]	Seaborgium 106 Sg [266]	Berkelium 107 Bk [267]	Californium 108 Cf [271]	Einsteinium 109 Es [272]	Fermium 110 Fm [277]	Mendelevium 111 Md [273]	Nobelium 112 No [274]	Lutetium 71 Lu 174.967	Hf 178.49	Ta 180.948	W 183.84	Re 186.207	Os 190.234	Ir 192.222	Pt 195.084	Au 196.967	Hg 200.59	Tl 204.38	Pb 207.2	Bi 208.98	Po [209]	At [210]	Rn [222]
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\* Lanthanide series

\*\* Actinide series

Rare Earth Elements

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb

Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No



# REEs: "Chemical Magnets" for Thorium

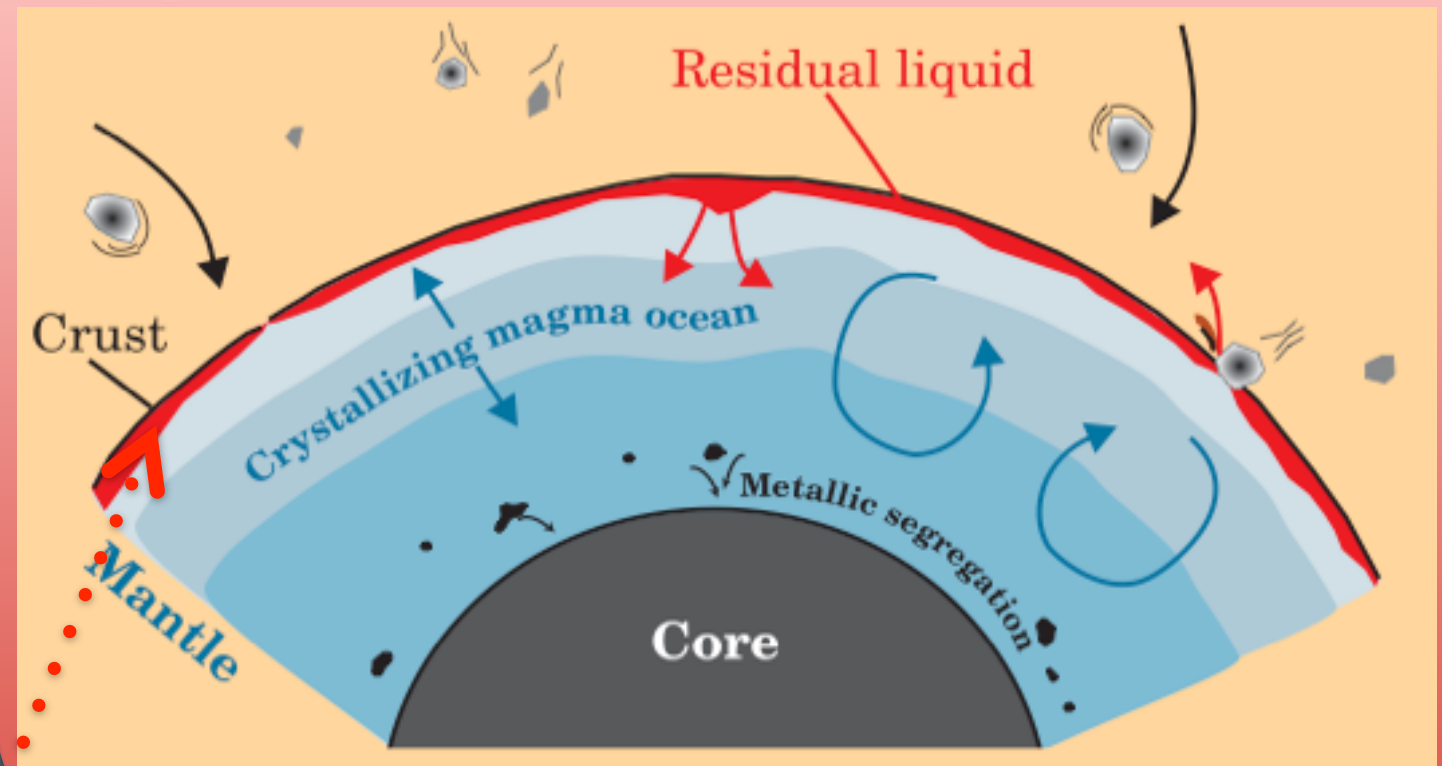
**Early Molten Earth** \* crystallized from the Base of its primordial Mantle upward.

- ▶ Because **REEs** couldn't co-crystallize along with the common silicates of the Mantle (**Ca-Mg-Fe<sup>+2</sup>-SiO<sub>3</sub>**), Rare Earths were forced while yet **molten** closer and closer to the thin new Crust.
- ▶ During the journey upward, the migrating REEs gathered (via similar physical chemistry) and pulled along practically all of the mantle's **Thorium** and much of its **Uranium**, **heavy** Alkali Metals (**K/Rb/Cs**) and other metals that couldn't crystallize easily with the Mantle.
- ▶ Before ~30 Ma old, the Mantle began crystallizing into different phases (various **blue** shades). Also forming just beneath the thickening new Crust was a separate, **still-molten phase**, highly enriched in REEs.

This **REE-Rich Region** is shown in **Red** in Figure (A).

\* See **Notes** below for **reference** on figures and concepts of this slide and the next.

**(A)\* Earth <30 Millions Yrs Old**



- ▶ Some time after ~30 Ma however, Earth's primordial crust cooled, lost buoyancy and began to subduct into the now-solid Mantle (nevertheless still plastic and able to flow)
- ▶ The subducting Crust dragged Earth's early **REE-Rich Region**, now solidified and strongly adhering, deep into the Mantle.



# REE “Magnets” for Thorium

Most likely location **today** for the Earth’s early **REE-Rich Region** is the **Core-Mantle Boundary**.

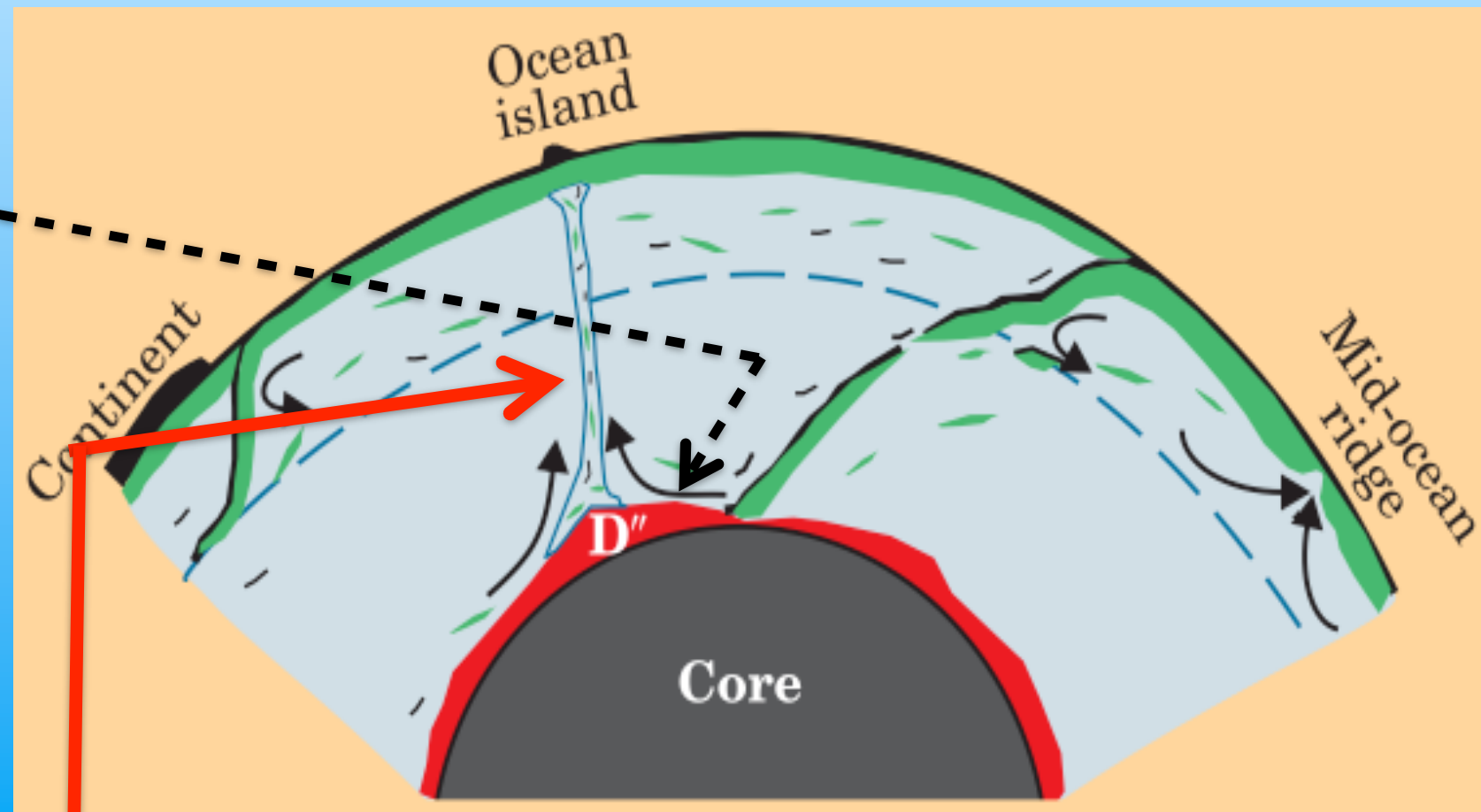
Labeled by geologists **D''** (double-prime), **REE-Rich D''** reportedly:

- ▶ Lies ~**2700 km** under the Crust, resting atop the **Iron Core**.
- ▶ Contains ~**40%** of Earth’s Inventory of **REEs** and **R.I.s** (Radiolotopes).
- ▶ Generates ~**9 TW** of **Heat** (~¼ of what leaves Earth’s interior). This makes **D''** the *most Thermogenic Structure within the Earth*.

Averaging ~**200-km** thick, each area of **D''** deforms in response to what the Mantle above is doing:

- ▶ Subducting Tectonic-Plate Mantle (cooler, sinking **Green** material of Fig. B) make regions of **D''** lying below the slabs thinner and thus cooler.

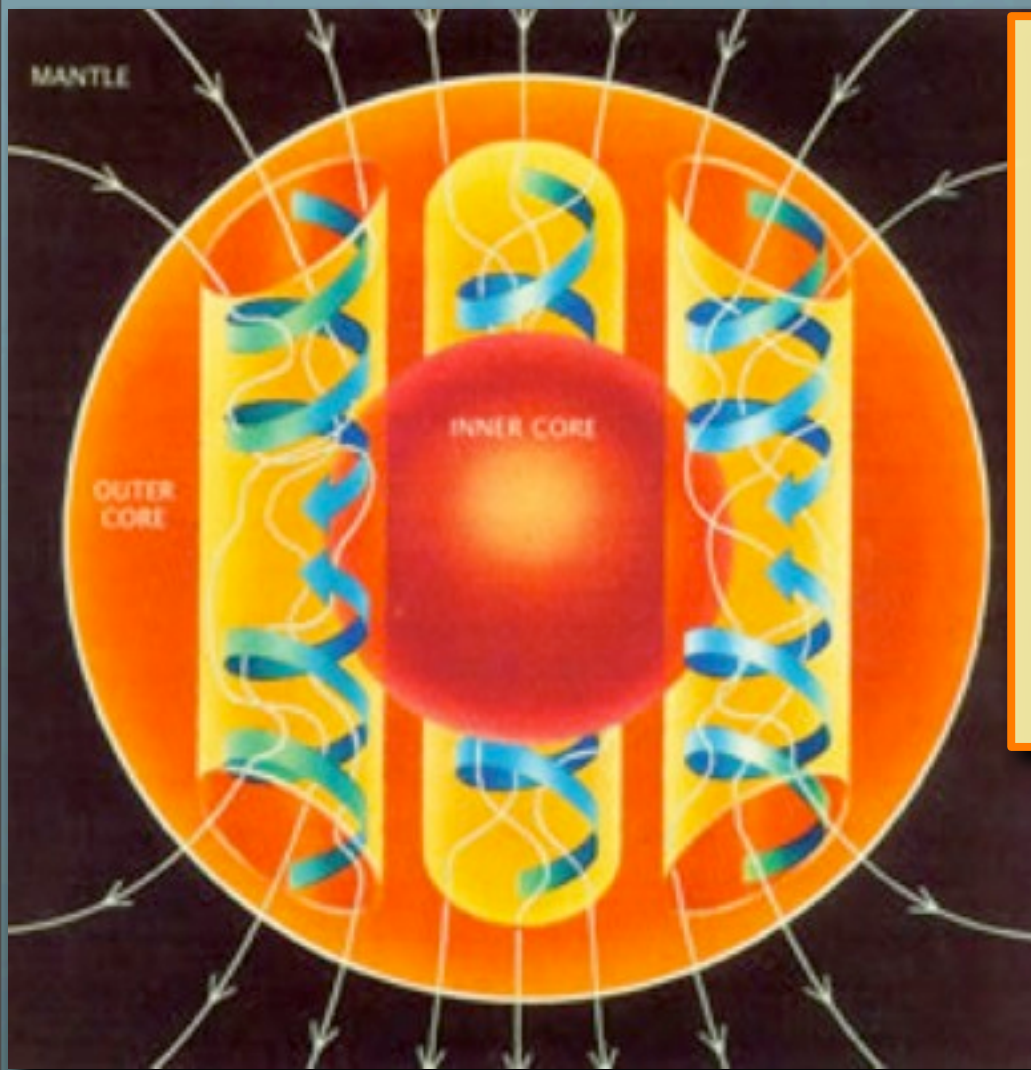
## (B) *Earth Today*



- ▶ **Mantle Plumes** (hot, rising zones under Hawaii, etc) **stretch** the height of **D''** beneath. This makes **D''** under mantle plumes generate even *more heat* and **sustains** our planet’s many hot spots with strong convection.



# REEs and Thorium: Dynamic Duo for a Living Planet



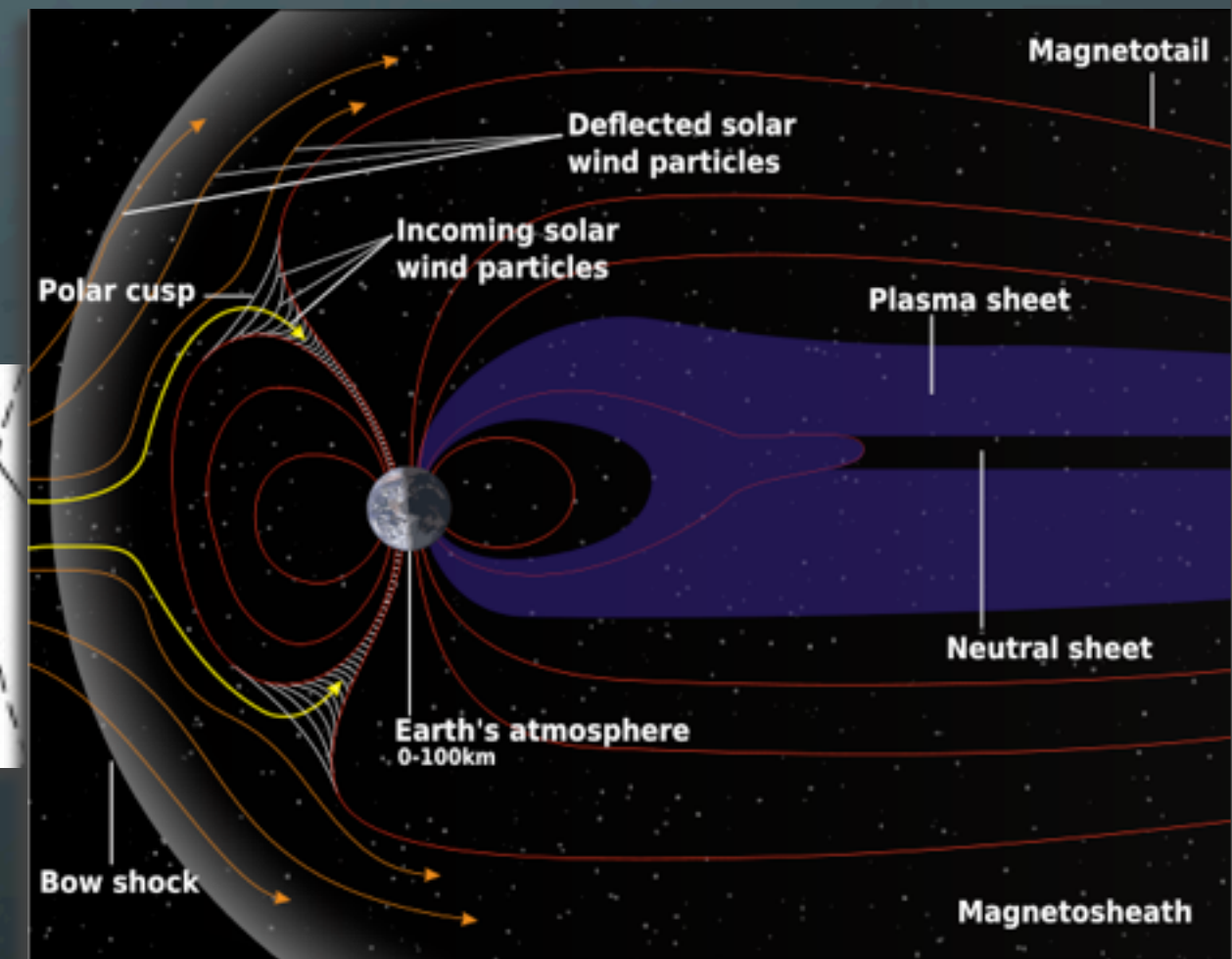
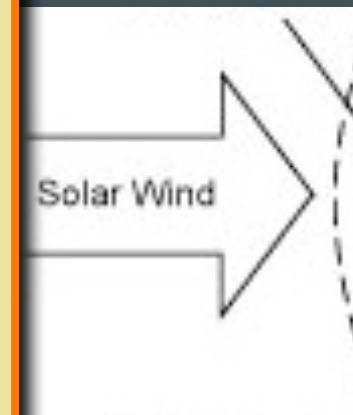
**Dynamic Core:** Molten metallic Iron moving in complex convection currents is the mechanism for **Geomagnetism**.

Enabling this strong and long-lasting convection are:

- ▶ Thorium, Uranium and Potassium-40 in REE-Rich D" resting on the Core. 2-4 G.a., Uranium and Potassium generated up to 80% of this Decay Heat.
- ▶ Today however, it is **Thorium** that provides the bulk of R.I. Heating that sustains geomagnetism.

The resulting **Magnetic Field** even sustains **Life** by:

- ▶ Rerouting harmlessly around our Planet the **Solar Wind**:
  - Constant stream of charged particles (electrons/protons/etc) ejected from the Sun at high velocities (up to **900 km/sec**)
- ▶ Preventing the **Solar Wind** from stripping away Earth's Atmosphere and Water.





# Lack of **Thorium** = **Death** to Formerly-Dynamic Planet

**Early Mars** had a strong magnetic field, a much denser atmosphere and significant quantities of water.

Unfortunately not endowed with enough Thorium & other RIs to adequately slow its internal cooling, Mars suffered:

- ▶ **Solidification of its iron core.**  
Complete some 3.5 Billion years ago, this event effectively shut down Mars' Magnetic Field.
- ▶ **Loss to the Solar Wind** of the bulk of its Atmosphere and practically all Water on the surface of Red Planet.








# Thorium plus Fluorides Keep Earth Economies Alive



Thorium + Fluoride Salts  
come together in Lftr, the  
**Liquid Fluoride  
Thorium Reactor**

**Alliance of Chemistry & Physics:**

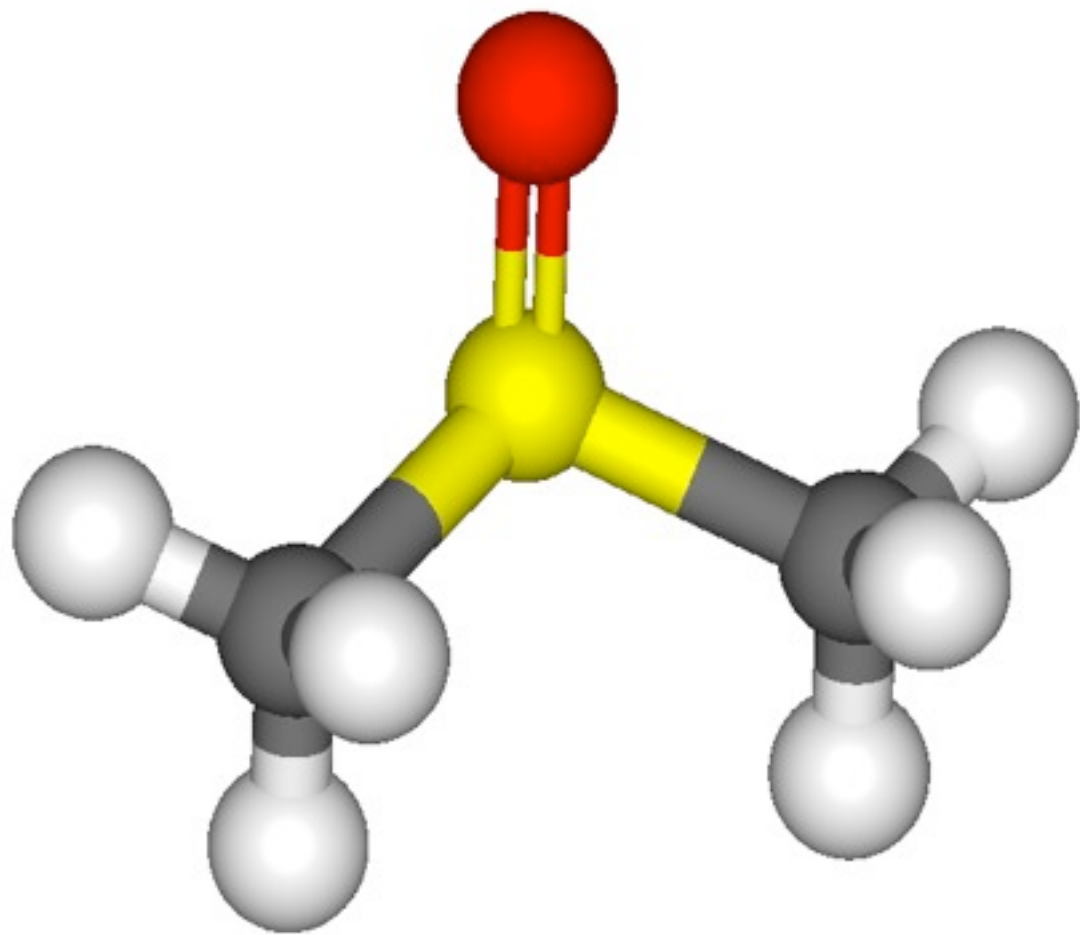
-  **'T' & 'FI's** (Thorium, Fissile Isotopes)
-  **'F' Salts** (Fluoride Salts)
-  **'FP's** (Fission Products)



# Fluoride Chemistry: Key to Affordable Nuclear Energy



**Fluoride Chemistry** facilitates **Lftr** efficiency by permitting it easily and *economically* to:



1. **Refuel** "on the fly" and at full power
2. **Remove** various *volatile* FP Fluorides at full-power operation
3. **Control** fuel-salt buildup of **Rare Earths** & other *involatile* FPs that would otherwise waste valuable neutrons.



# Refueling on the Fly

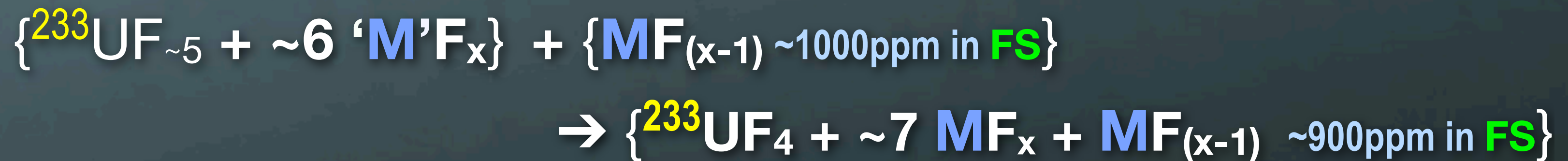


**Fuel Salt running low on nuclear fuel** (any of the 3 possible FIs) **readily receives more in *Fluid* form:**

## Denatured or “D-Lftr”



## Lftr (2-fluid classic)









# MF<sub>x</sub>: Multivalent Fluorides

## for Azeotropes and Corrosion Control

**M**'s – chosen from elements shaded below – fill the bill (chemically or physically)

Typical example of a versatile MF<sub>x</sub> is SbF<sub>5</sub>.

*Liquid phase:* SbF<sub>4</sub><sup>+</sup> SbF<sub>6</sub><sup>-</sup>

1

1 H 2

2 Li Be

3 Na Mg 3

4 K Ca Sc

5 Rb Sr Y

6 Cs Ba La

7 Fr Ra Ac

4 Ti 5 V 6 Cr 7 Mn 8 Fe 9 Co 10 Ni 11 Cu 12 Zn

23 Zr 24 Nb 25 Mo 26 Tc 27 Ru 28 Rh 29 Pd 30 Ag 31 Cd 32 In 33 Sn 34 Sb 35 Te 36 I 37 Xe

58 Hf 59 Ta 60 W 61 Re 62 Os 63 Ir 64 Pt 65 Au 66 Hg 67 Tl 68 Pb 69 Bi 70 Po 71 At 72 Rn

82 Rf 83 Db 84 Sg 85 Bh 86 Hs 87 Mt 88 Ds 89 Rg 90 Uub 91 Uut 92 Uuq 93 Uup 94 Uuh 95 Uus 96 Uuo

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Antimony

51 Sb 121.76 g/mol

13 B 14 C 15 N 16 O 17 F 18 He

19 Ne 20 Ar 21 Kr 22 Xe 23 Rn

Alkali Metals

Alkaline Earth Metals

Transition Metals

Poor Metals

Metalloids

Nonmetals

Halogens

Noble Gases

Lanthanides

Actinides



# MF<sub>x</sub>: Multivalent Fluorides

## for Azeotropes and Corrosion Control

**M**'s – chosen from elements shaded below – fill the bill (chemically or physically)

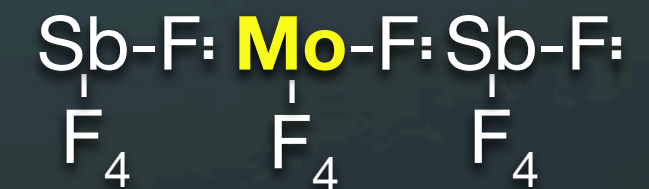
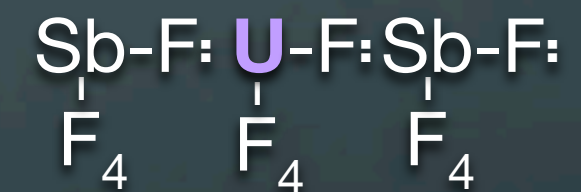
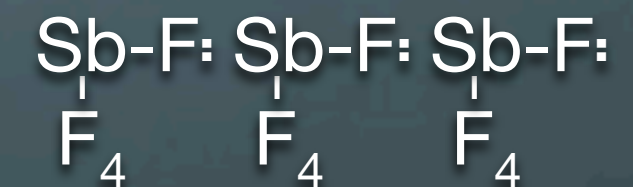
Typical example of a versatile MF<sub>x</sub> is SbF<sub>5</sub>

Liquid phase: SbF<sub>4</sub><sup>+</sup> SbF<sub>6</sub><sup>-</sup>      *Vapor phase*: Forms dimers & trimers that tend to entrain other higher fluorides

Antimony  
51 Sb 121.76 g/mol

Legend:

- Alkali Metals
- Alkaline Earth Metals
- Transition Metals
- Poor Metals
- Metalloids
- Nonmetals
- Halogens
- Noble Gases
- Lanthanides
- Actinides





# $MF_x$ : Multivalent Fluorides for Controlling Corrosion in the Fuel Salt

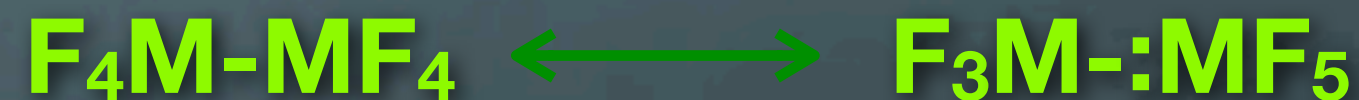


Reducing the oxidation state of  $MF_x$  to  $MF_{(x-1)}$   
greatly reduces corrosion from FPs in the Fuel Salt



# $\text{MF}_x$ : Multivalent Fluorides for Controlling Corrosion in the Fuel Salt

- Reducing the oxidation state of  $\text{MF}_x$  to  $\text{MF}_{(x-1)}$  greatly reduces corrosion from FPs in the Fuel Salt
- With FS kept “slightly reducing,” **Hastelloy** is protected from grain-boundary corrosion:





# $MF_x$ : Multivalent Fluorides for Controlling Corrosion in the Fuel Salt

- Slightly-reducing Fuel Salt protects structures by tying up as complex anions elemental FPs that would otherwise compromise structures:

- Halogen FPs

- Chalcogen FPs

			18	
15	16	17	He	1
N	O	F	Ne	2
P	S	Cl	Ar	3
As	Se	Br	Kr	4
Sb	Te	I	Xe	5
Bi	Po	At	Rn	6



# MF<sub>x</sub>: Multivalent Fluorides for Controlling Corrosion in the Fuel Salt



Slightly-reducing Fuel Salt protects structures by tying up as complex anions elemental FPs that would otherwise compromise structures:

**F<sub>3</sub>M-:** + **Te<sub>x</sub>Se<sub>y</sub>** (polymers, plate out onto and attack Nickel grain boundaries)



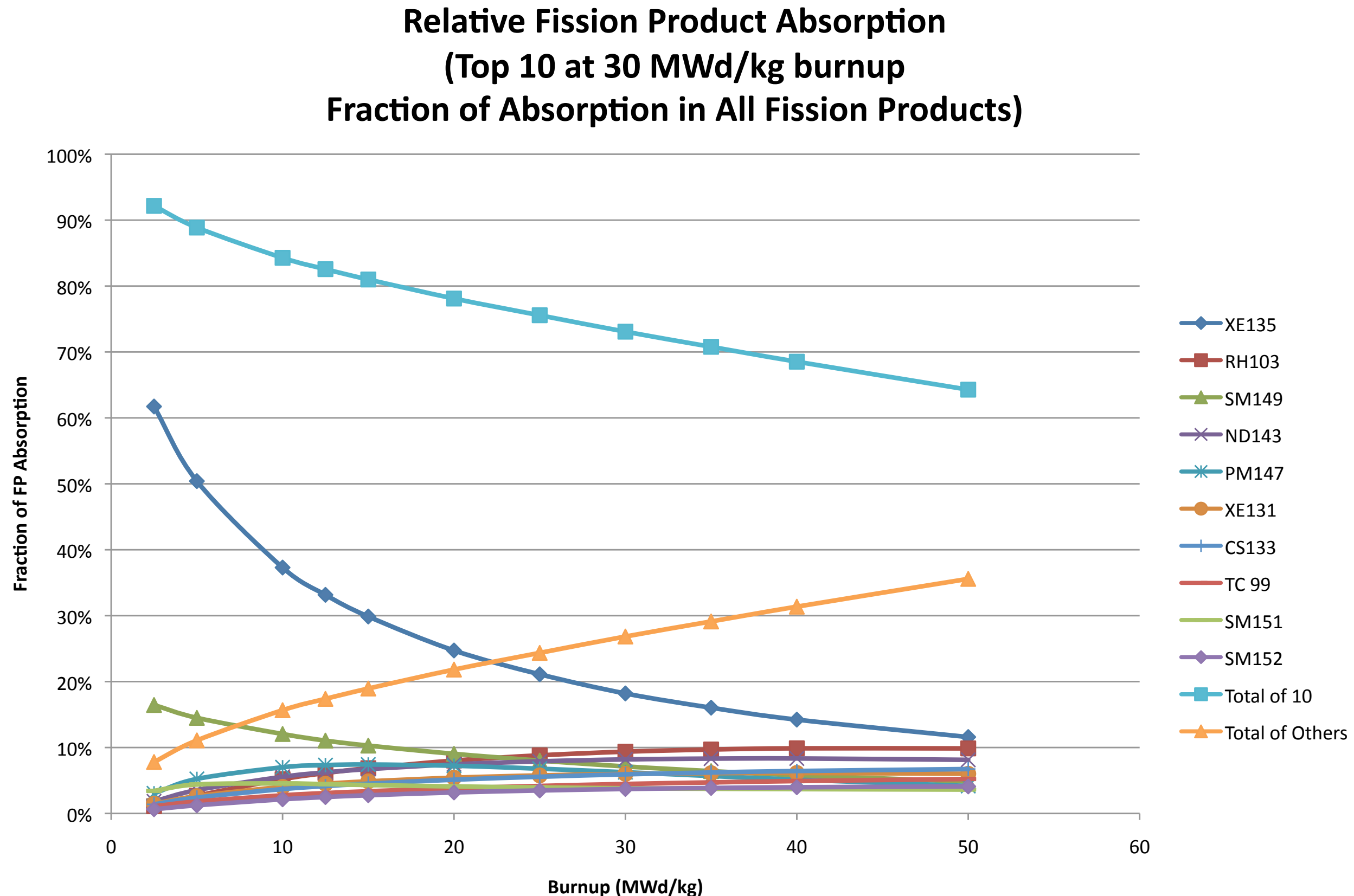
Chalogens made ionic

			18	
15	16	17	He	1
N	O	F	Ne	2
P	S	Cl	Ar	3
As	Se	Br	Kr	4
Sb	Te	I	Xe	5



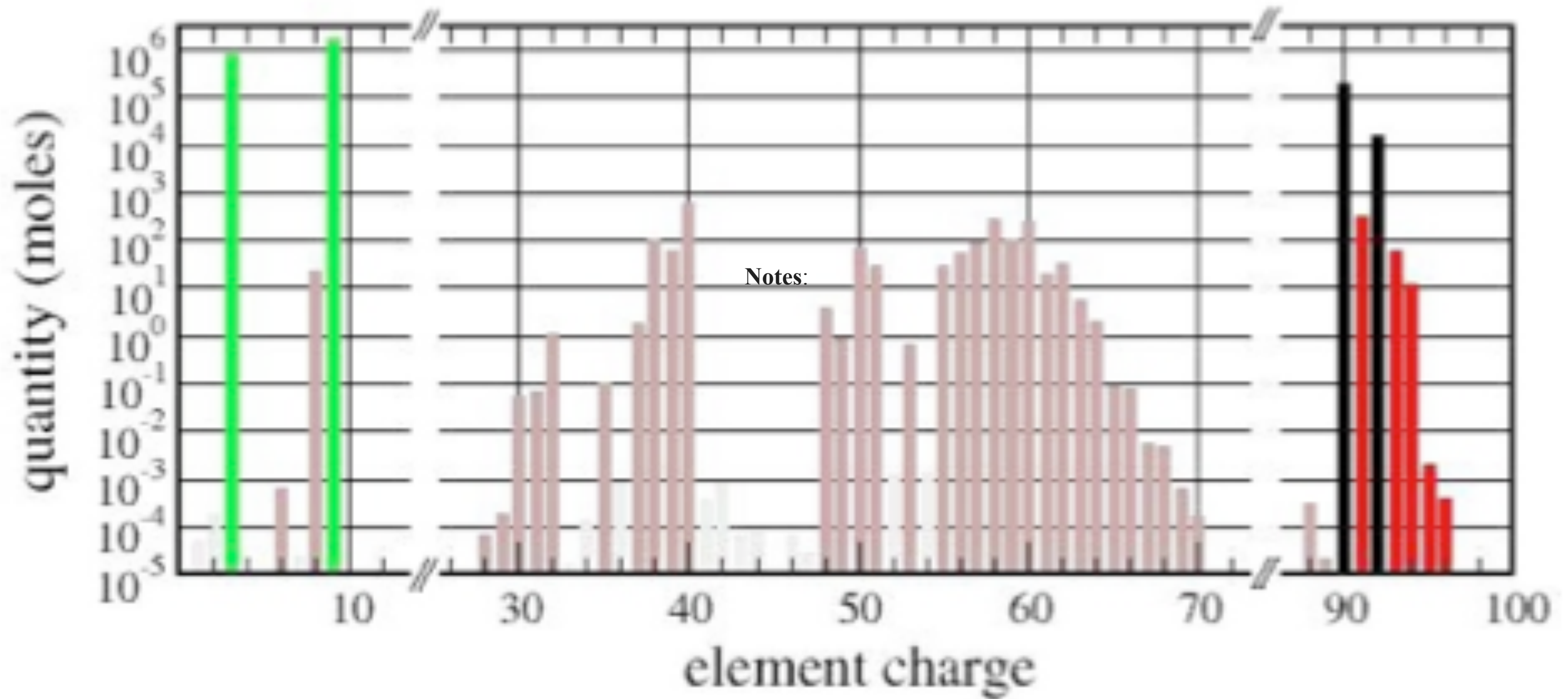
# Top 10 Neutron-Absorbing FPs versus All Others

## No FP Removal





# Elemental MSR Inventory — Periodically Sparged and Fluorinated (epithermal, France)

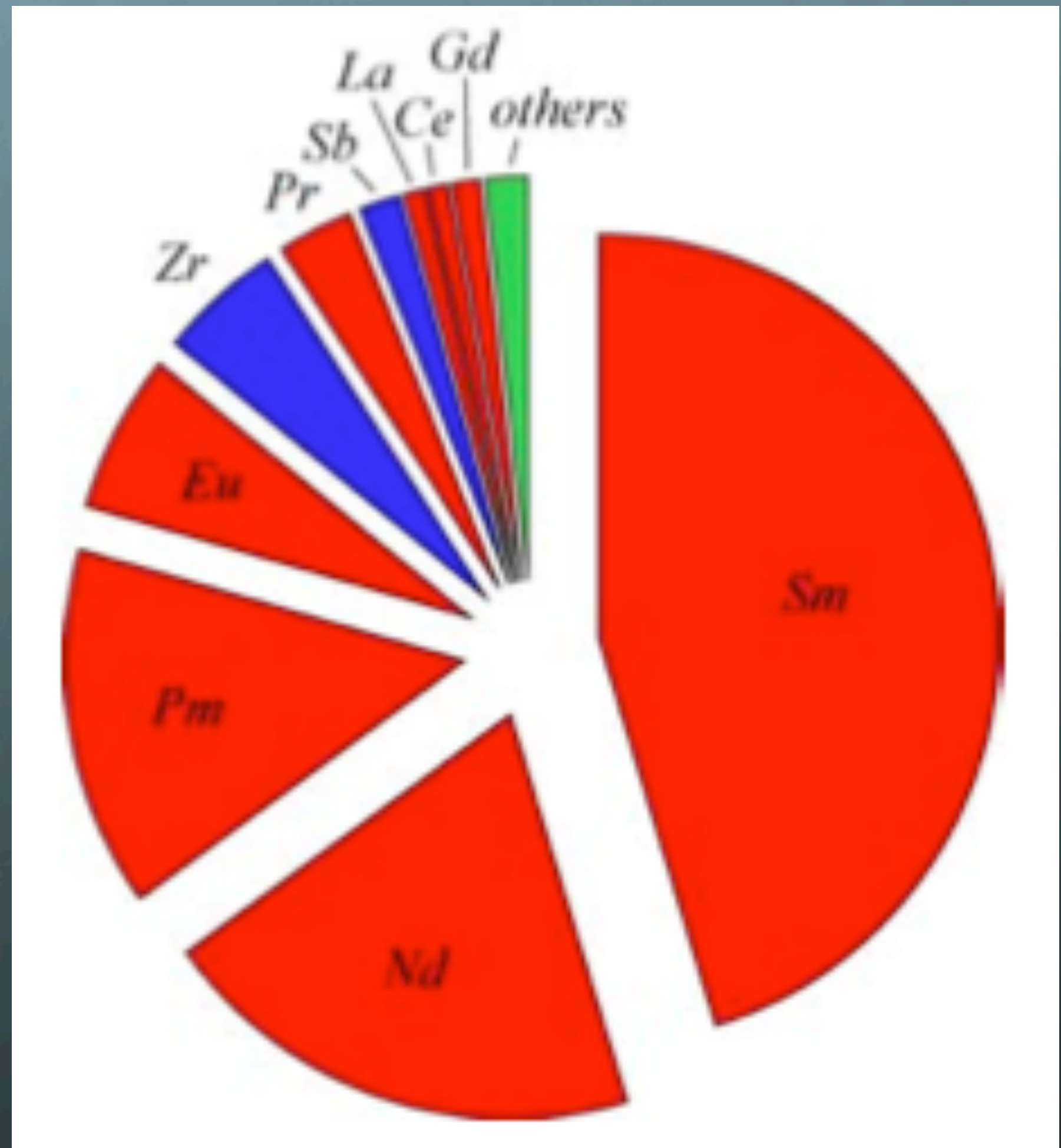




# Top Ten Neutron-Absorbing FPs in the French Fuel Salt



Noble and “F-able”  
Fission Products  
only *periodically*  
removed

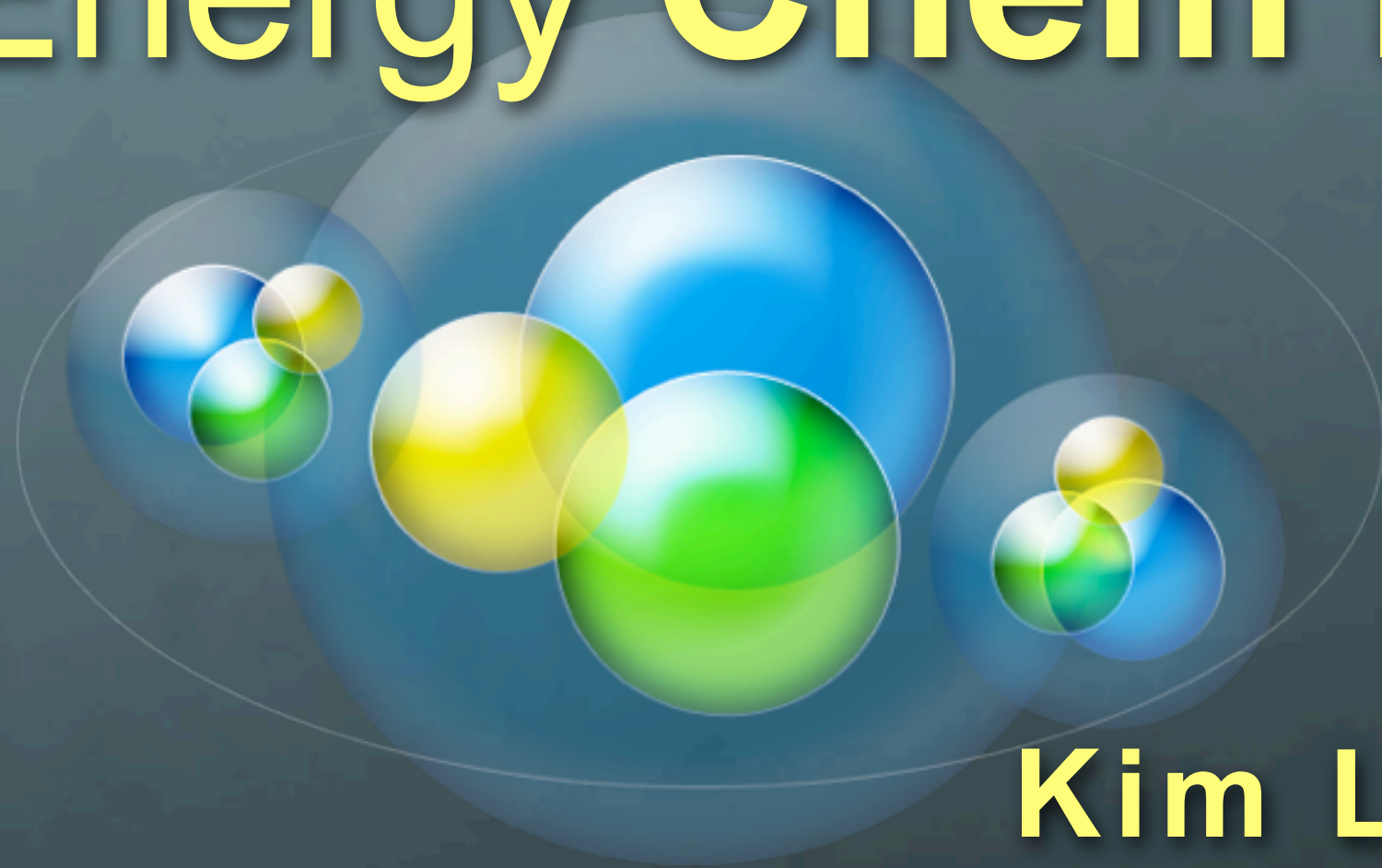




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**Kim L. Johnson**

**ChemInnovár 12 May 2011**