Thorium and **Fluorides**:

Energy **Chem** Engineered

*on the **Fly***

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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**
  - **Fluoride Salts**
  - **Fission Products**

Nuclear Differences of T with Uranium

- Thorium = 100% ^{232}Th Uranium = 99.3% ^{238}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}U:

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

^{238}Uranium + n→→ ^{239}Pu + n → ~64% fissions + ~34% ^{240}Pu + n →

^{241}Pu (half-life: 14y)··→ ^{241}Am (432 yr, *not* fissile)

^{241}Pu + n → ~73% fissions + ~27% ^{242}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, **Th**$^{+4}$ (constant) **resists** weathering. Nature's most common forms, **Thoria** (ThO_2), **$Th_3(PO_4)_4$** and **$ThSiO_4$** are totally **water-insoluble** at all **natural pH ranges:** (pH >2)
  - Even with boiling H_2SO_4 / HNO_3, Thoria dissolves slowly and with great difficulty. So reprocessing ThO_2 requires much more effort than for UO_2:
    - Hotter more concentrated HNO_3 *plus* 5-15% HF/AlF_3 to attack grain boundaries
    - Considerably more Corrosion of all Equipment due to Aqueous HF and Much Longer Time required for reprocessing
  - **ThO_2-containing Solid Fuel is therefore considerably costlier to Fabricate and particularly Reprocess than 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

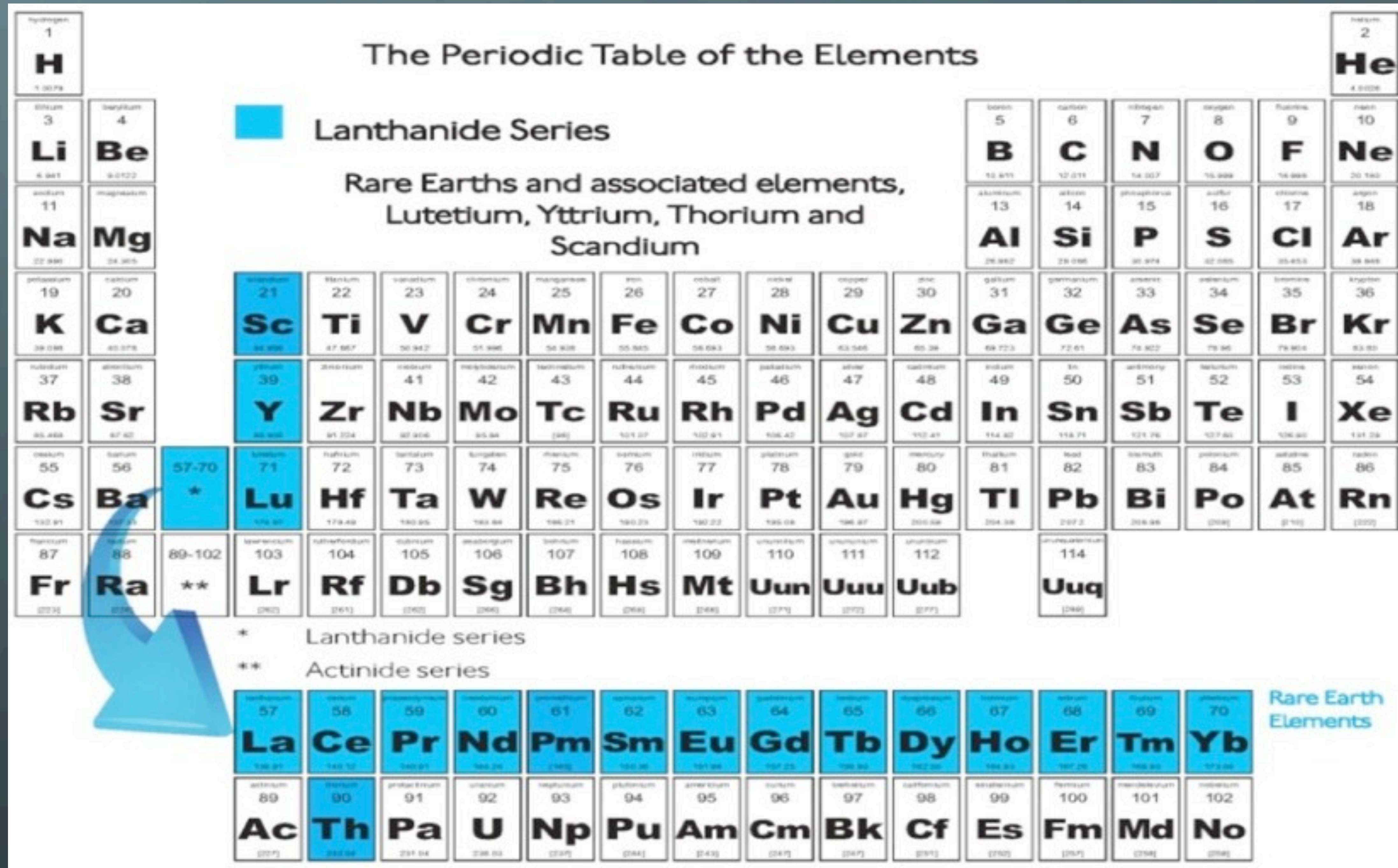
REEs – Ash from Ancient Stars

- ~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 (RadioIsotopes)
- 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)



REEs: "Chemical Magnets" for Thorium

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

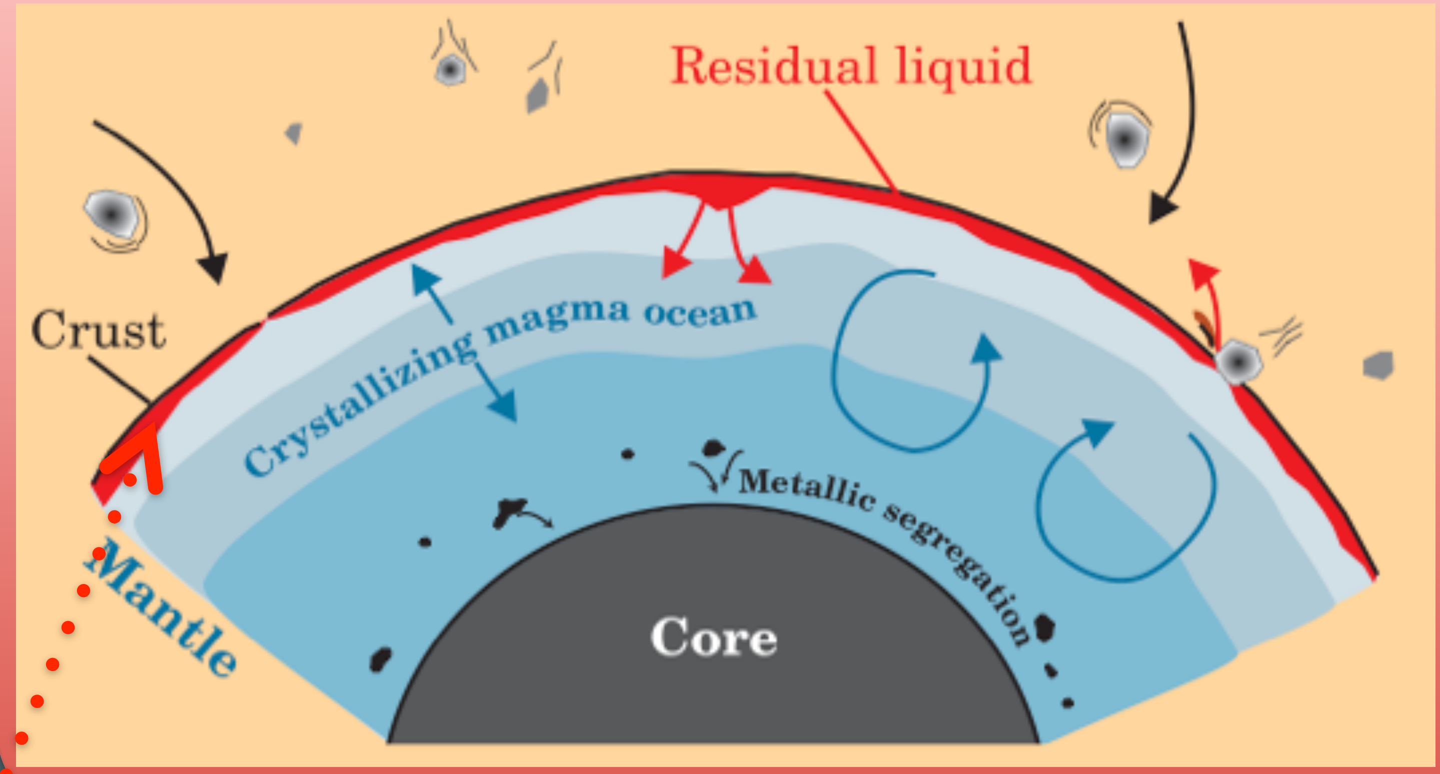
- Because **REEs** couldn't co-crystallize along with the common silicates of the Mantle (**Ca-Mg-Fe^{+2}** -SiO_3), Rare Earths were forced while yet **molten** closer and closer to the thin new Crust.

- 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)**.

(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**.

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

REE "Magnets" for Thorium

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

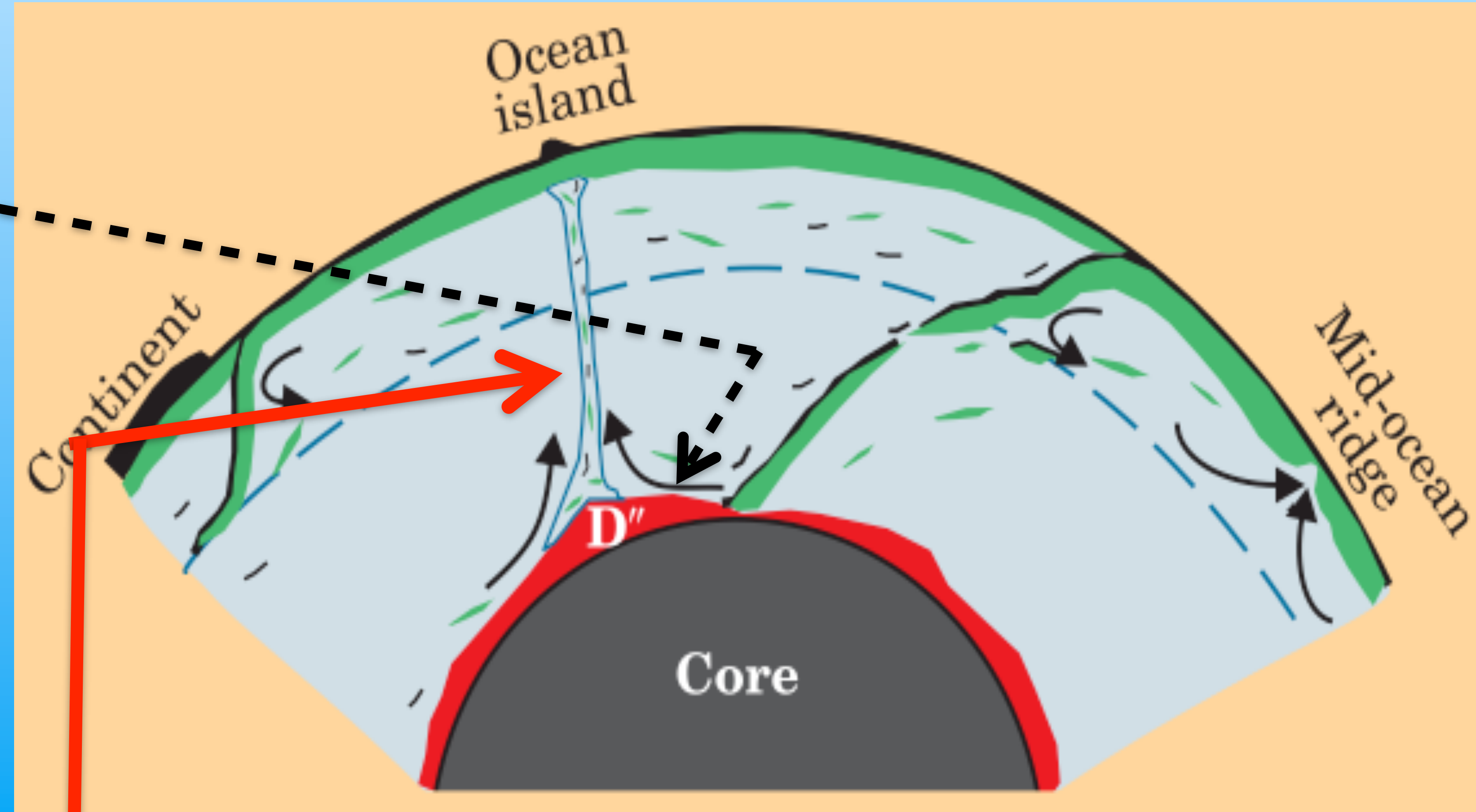
Labeled by geologists **D"** (**double-prime**), **REE-Rich D"** reportedly:

- Lies **~2700 km** under the Crust, resting atop the **Iron Core.**
- Contains **~40%** of Earth's Inventory of **REEs** and **R.I.s** (RadioIsotopes).
- 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

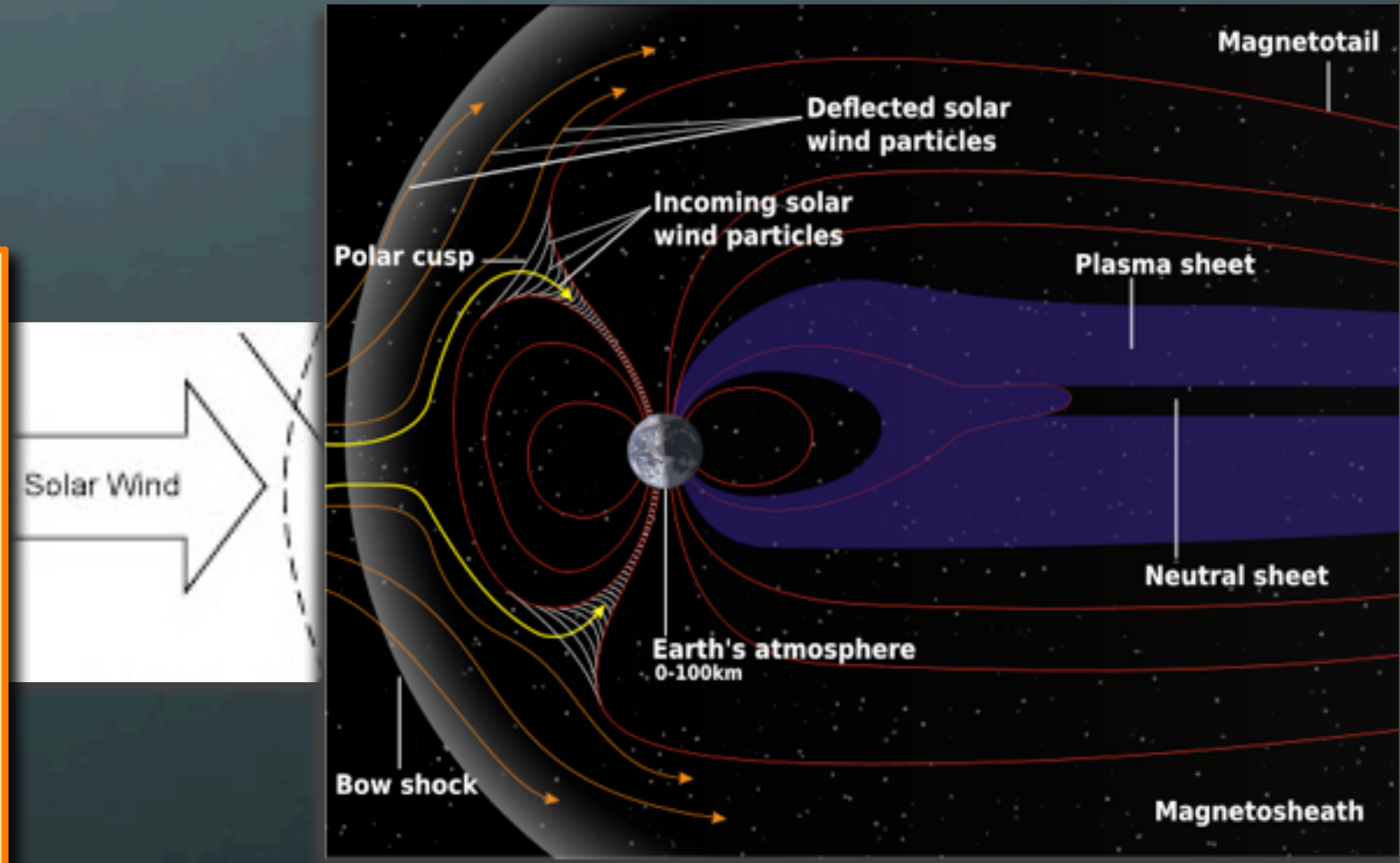
Dynamic Core: Molten metallic Iron moving in complex convection currents is the mechanism for **Geomagnetism**.

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

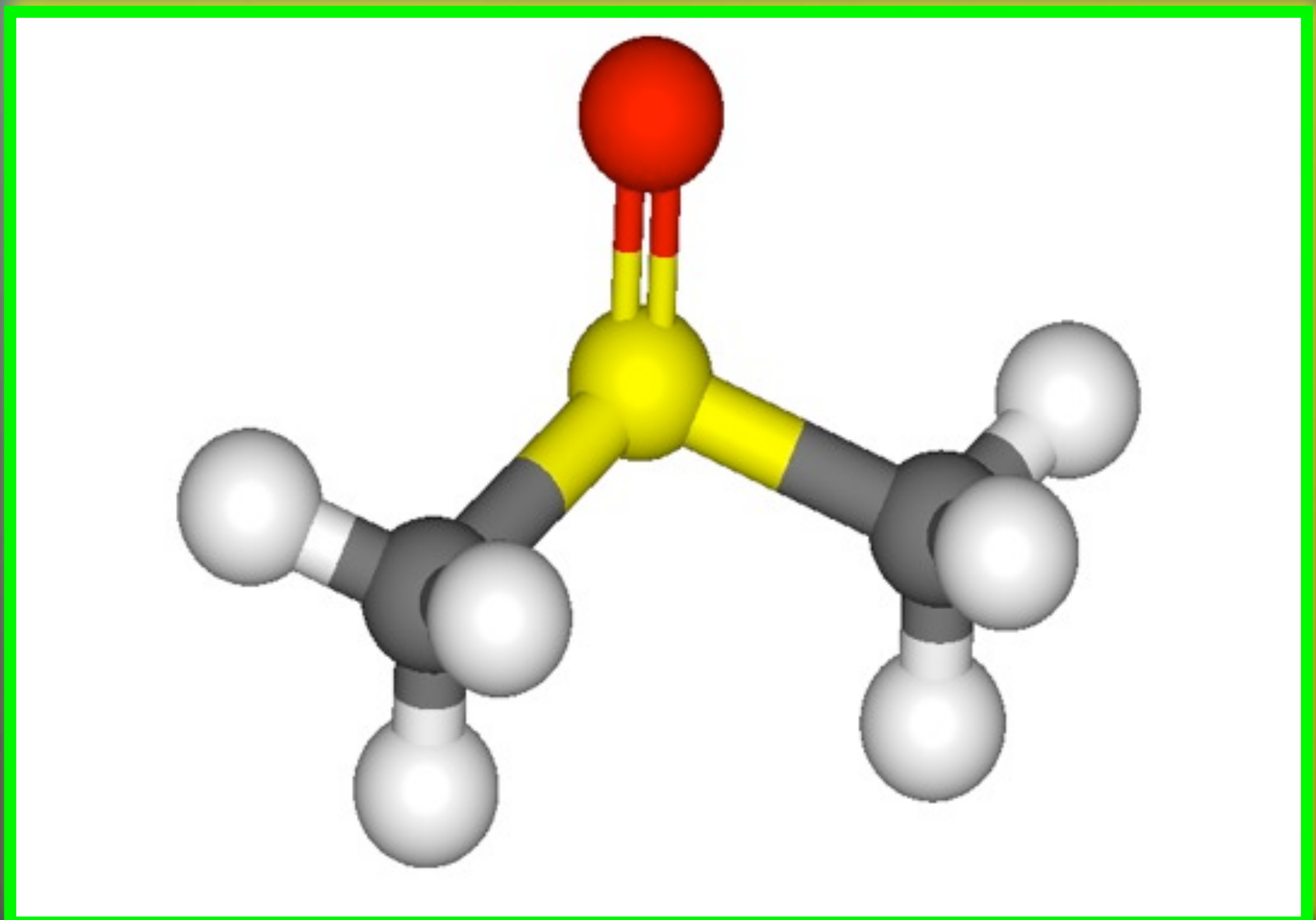
Liquid Fluoride Thorium Reactor

Alliance of Chemistry & Physics:

- **'T' & 'Fl'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"

$\{^{235}UF_6 + 4\ ^{238}UF_6\} + \{UF_3$ ~500 ppm in FS$\} \rightarrow \{5\ UF_4 + UF_3$ ~250 ppm$\}$

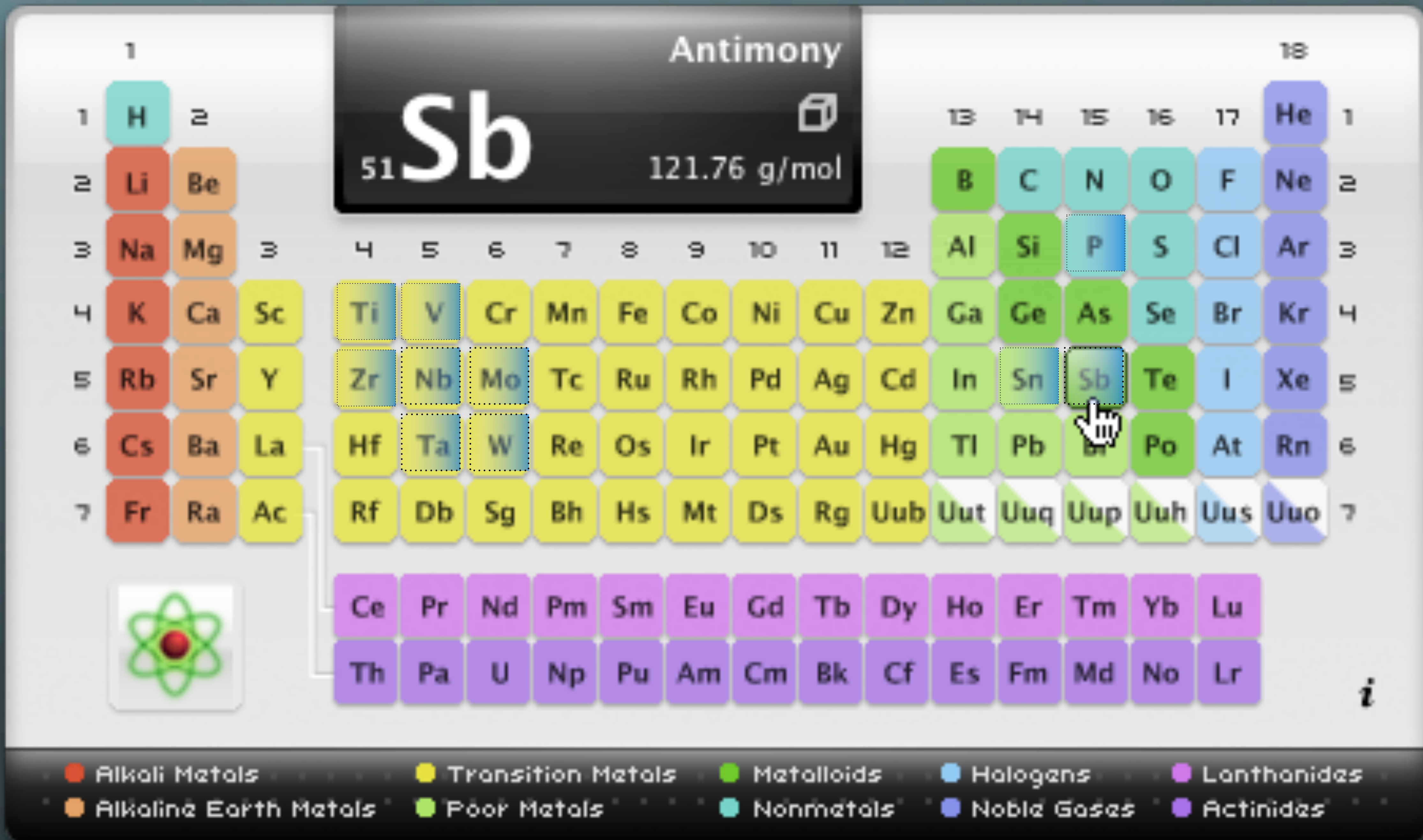
Lftr (2-fluid classic)

$\{^{233}UF_{\sim 5} + \sim 6\ \text{'M'}F_x\} + \{MF_{(x-1)}$ ~1000ppm in FS$\}$

$\rightarrow \{^{233}UF_4 + \sim 7\ MF_x + MF_{(x-1)}$ ~900ppm in FS$\}$

MF_x: Multivalent Fluorides for Azeotropes and Corrosion Control

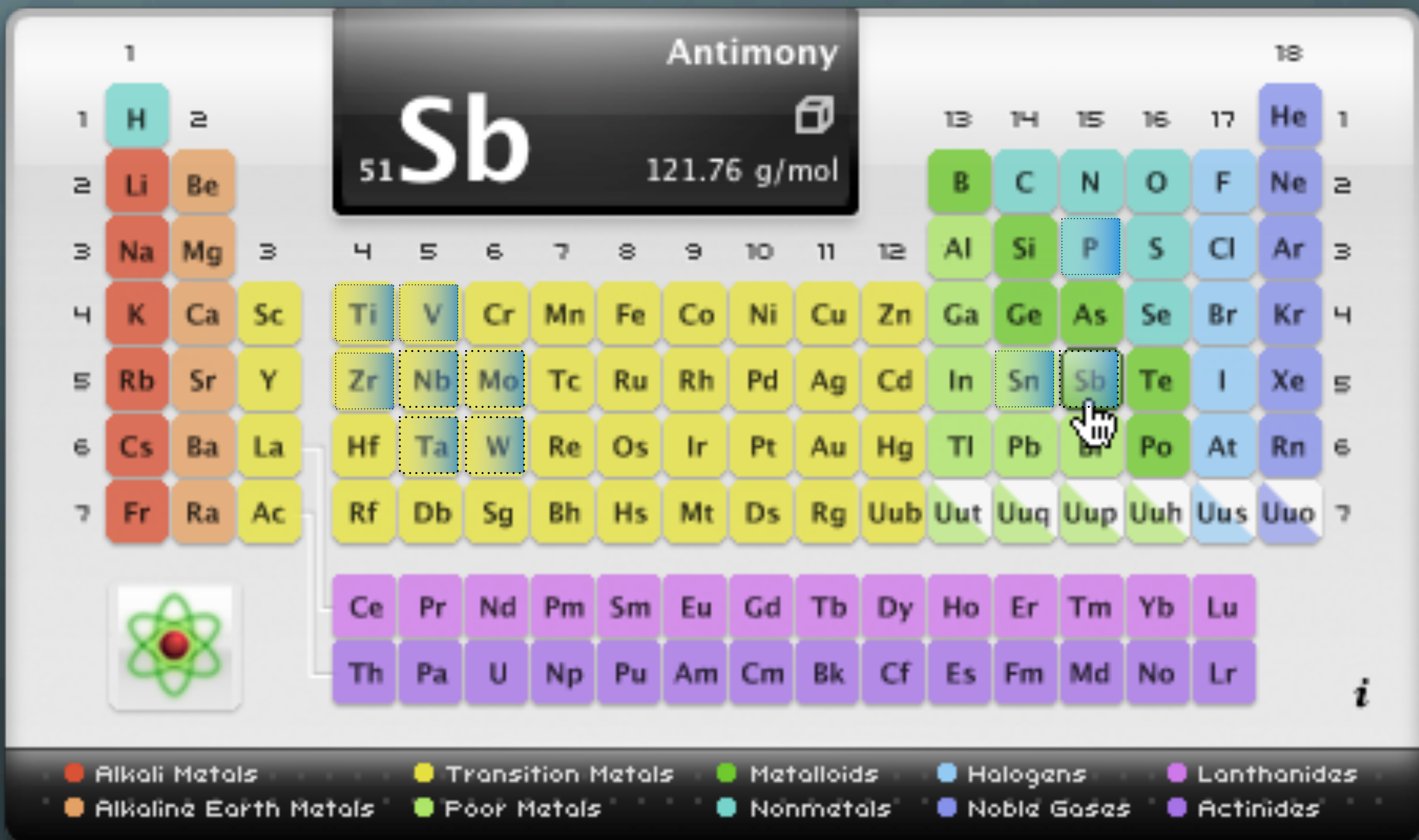
M(s) chosen from the *shaded* elements **fill the bill** (chemically or physically)



MF_x: 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_x is SbF_5.**
- ***Liquid phase*: $SbF_4^+ SbF_6^-$**

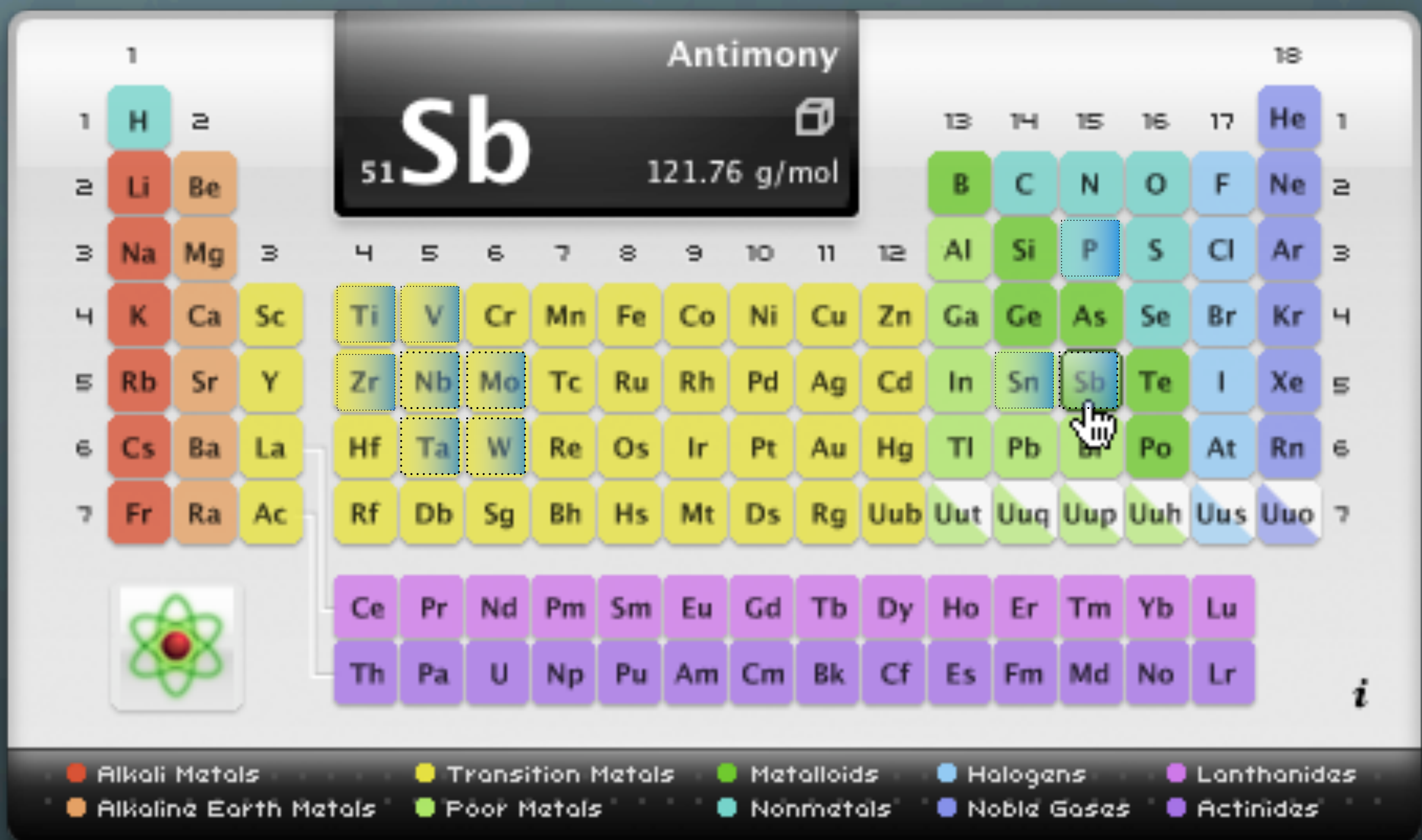


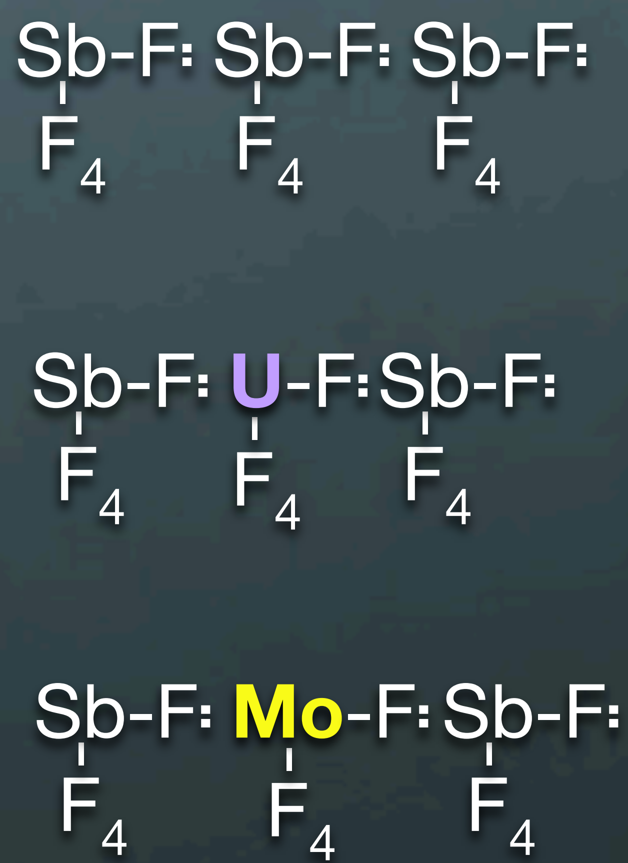
MF_x: Multivalent Fluorides
for Azeotropes and Corrosion Control

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

- Typical example of a versatile MF_x is SbF_5
- Liquid phase: $SbF_4^+ \, SbF_6^-$

Vapor phase: Forms dimers & trimers that tend to entrain other higher fluorides





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**

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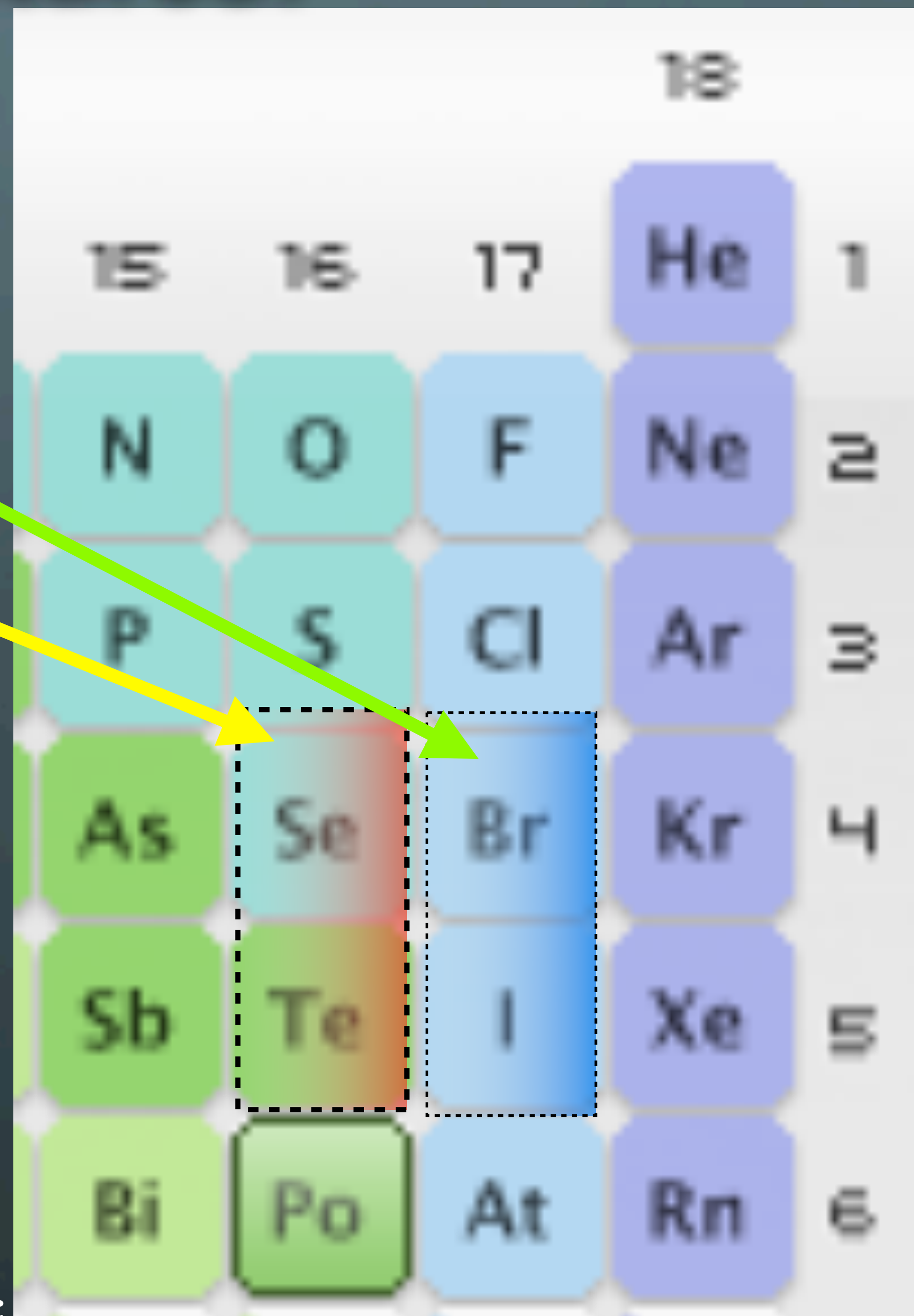
- With FS kept "slightly reducing," Hastelloy is protected from grain-boundary corrosion:

$$F_4M\text{-}MF_4 \longleftrightarrow F_3M\text{-}{:}MF_5$$

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**
  - **Chalogen FPs**



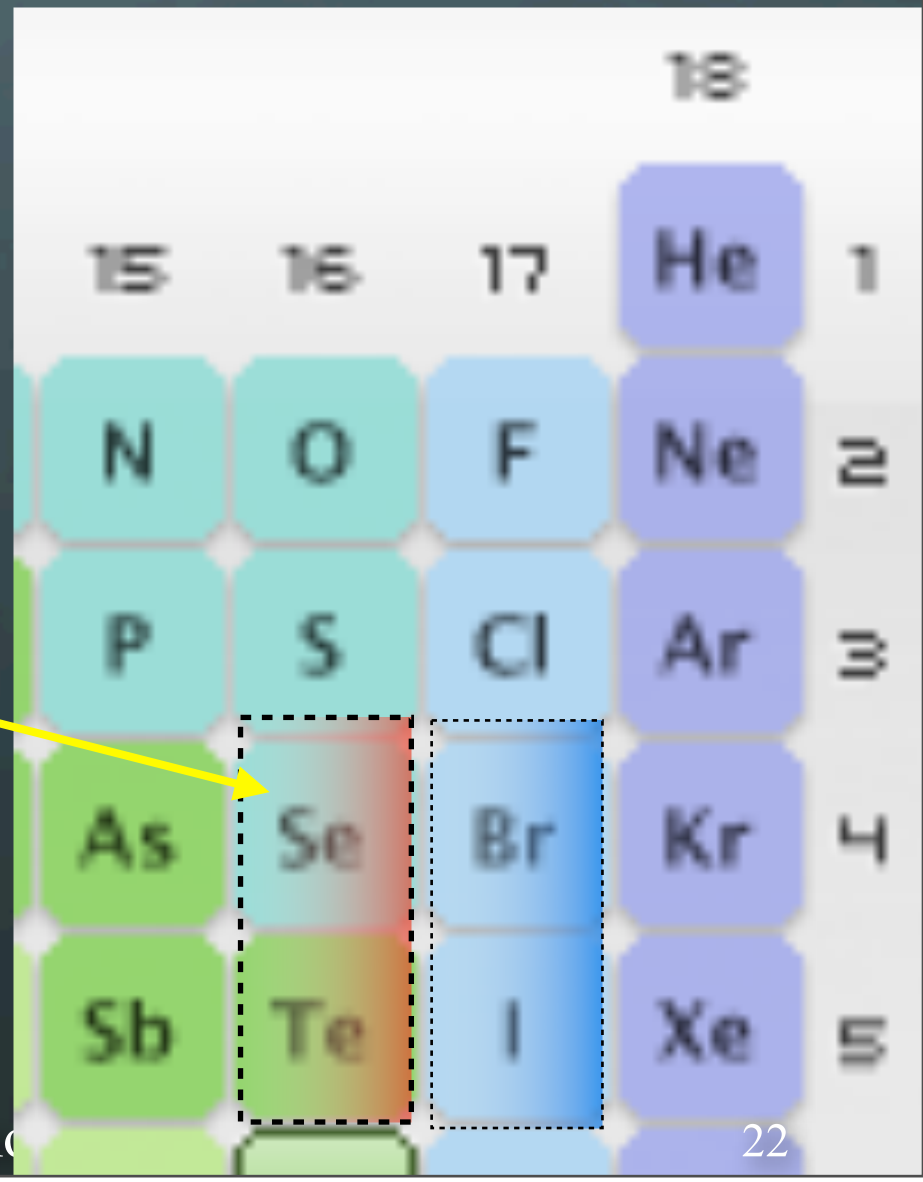
MF_x: Multivalent Fluorides for
Controlling Corrosion in the Fuel Salt

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

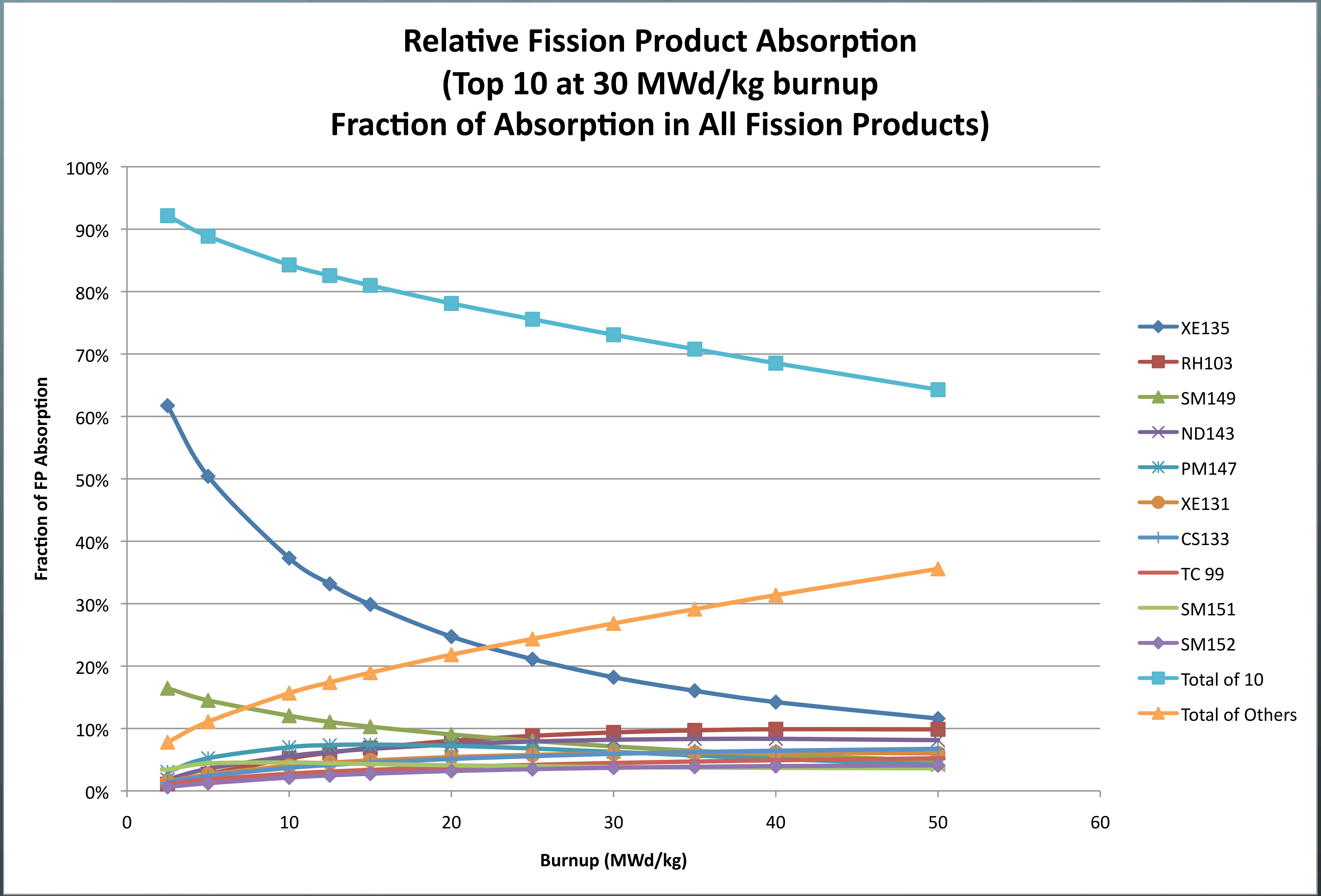
F_3M-: + Te_xSe_y **(polymers,** plate out onto and attack **Nickel** grain boundaries)

$$\longrightarrow F_3\overset{+}{M}\text{-Te-(Se-Te-Te-Se-)}_n\text{Te}^-$$

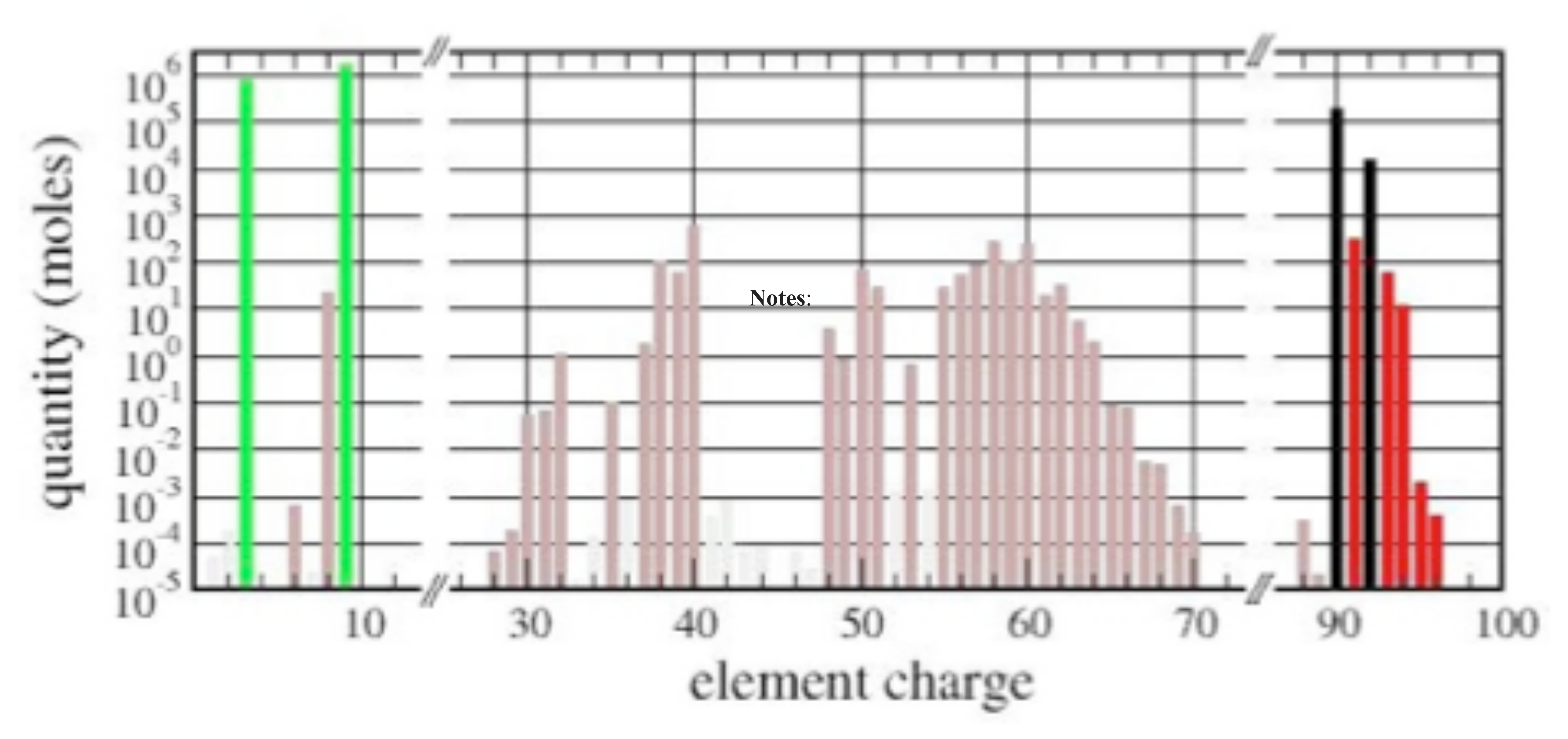
Chalogens made <u>ionic</u>



Top 10 Neutron-Absorbing FPs versus All Others
No FP Removal

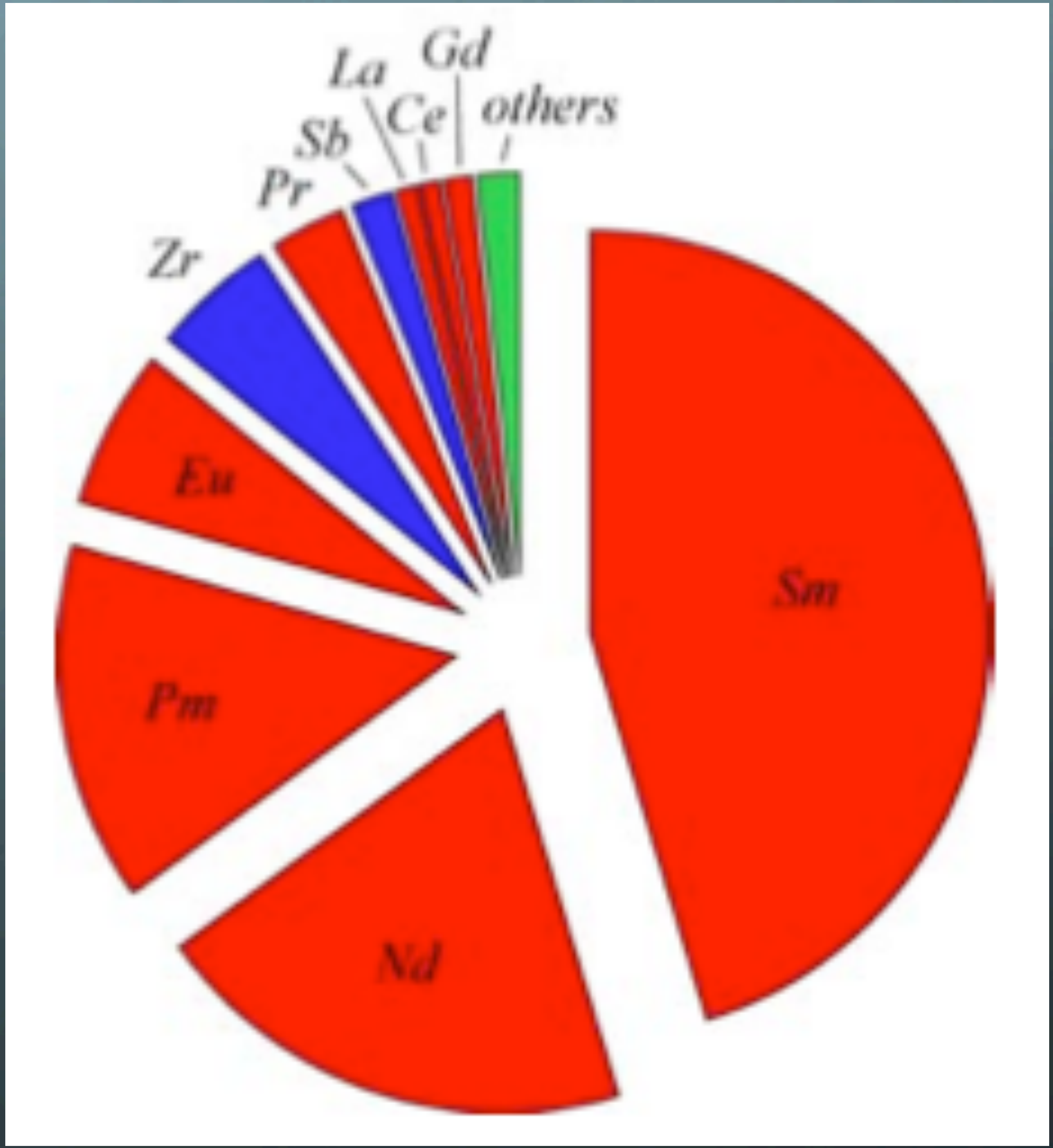


Elemental MSR Inventory — Periodically Sparged and Fluorinated (epithermal, France)



Top Ten Neutron-Absorbing FPs in the French Fuel Salt

- Noble and "F-able" Fission Products only *periodically* removed



Thorium and **Fluorides**:

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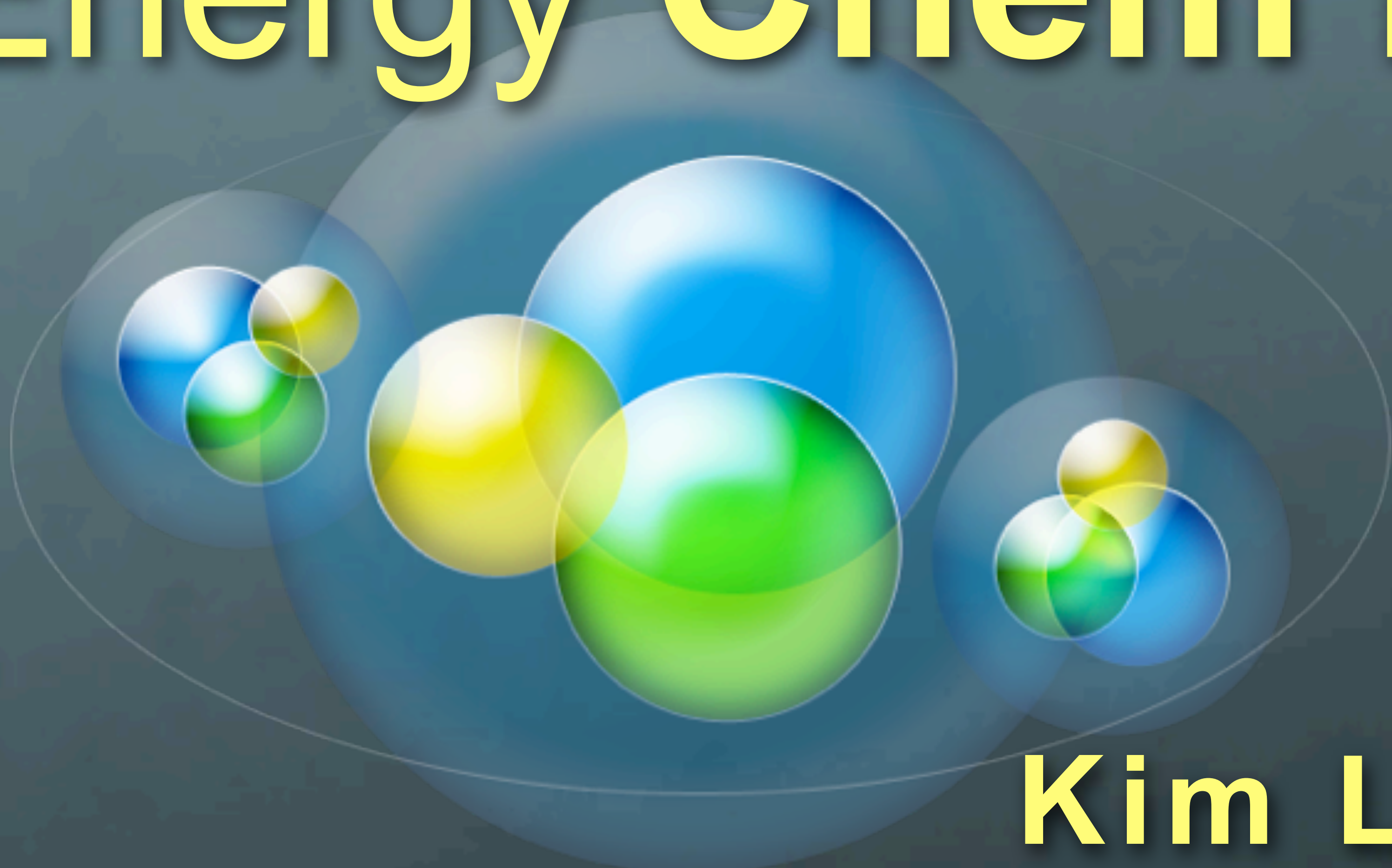

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