

Geology of Rare Earth Deposits

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Rare Earth Elements are not rare....

- 200 x more abundant than Au
- LREE more abundant than HREE
- Occur in common minerals in low concentrations
- **Rarely** found in high concentrations in abundant minerals
- Due to coordination number, ionic radius, and charge

Rare Earth Elements

by Geology.com

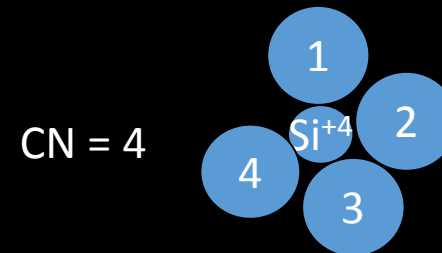
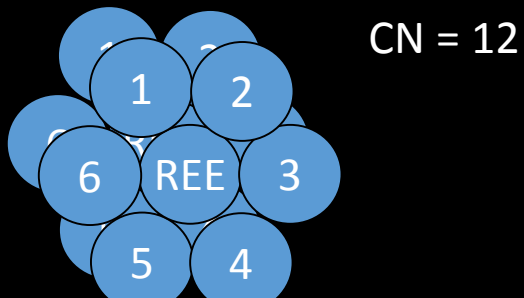
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| H | | | | | | | | | | | | | | | | He | |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La-Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac-Lr | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | |
| Lanthanides | | | | | | | | | | | | | | | | | |
| LREE | | | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| Actinides | | | | | | | | | | | | | | | | | |
| | | | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

The trouble with REE...

- REE have large radii, high charge, and just don't fit into the most common mineral structures (silicates)
- Coordination number (CN = # nearest neighbour anions around a cation in a mineral structure) is high for REE
- CN of some common minerals
 - Quartz (SiO_2) CN=4, Garnet ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) Ca CN = 8, Al CN = 6, Si CN = 4
- CN of REE between LREE and HREE
 - LREEs have high CN (>9)
 - HREEs have CN between 6-9

Bastnaesite CN = 11, Monazite CN = 9

Xenotime CN = 8



Major REE Minerals

- Bastnaesite $\text{REE}(\text{CO}_3)\text{F}$ is the most important REE ore or rare earth elements (60-70% rare earth oxides)
- Monazite $\text{REE}(\text{PO}_4)$ (50-78%)
- Xenotime YPO_4 (54-65%)
- Apatite $\text{Ca}_5(\text{PO}_4)_3$



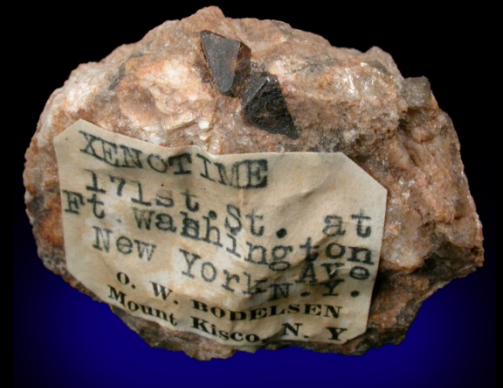
REE-enriched Apatite from
Kona Peninsula, Russia
Source credit John H Betts

Bastnaesite, Mountain Pass, CA
Photo credit Rob Lavinsky, Irocks.com



Xenotime crystals from a
pegmatite vein in granite, NY
Source credit John H Betts

Monazite, Madagascar
Photo source Mindat.org



Rare earth elements do not fit into most mineral structures and can only be found in a few geological environments

What are the most common geological environments that host rare earth elements?

General Geological Classification scheme of REE deposits

1) Magmatic rare earth deposits

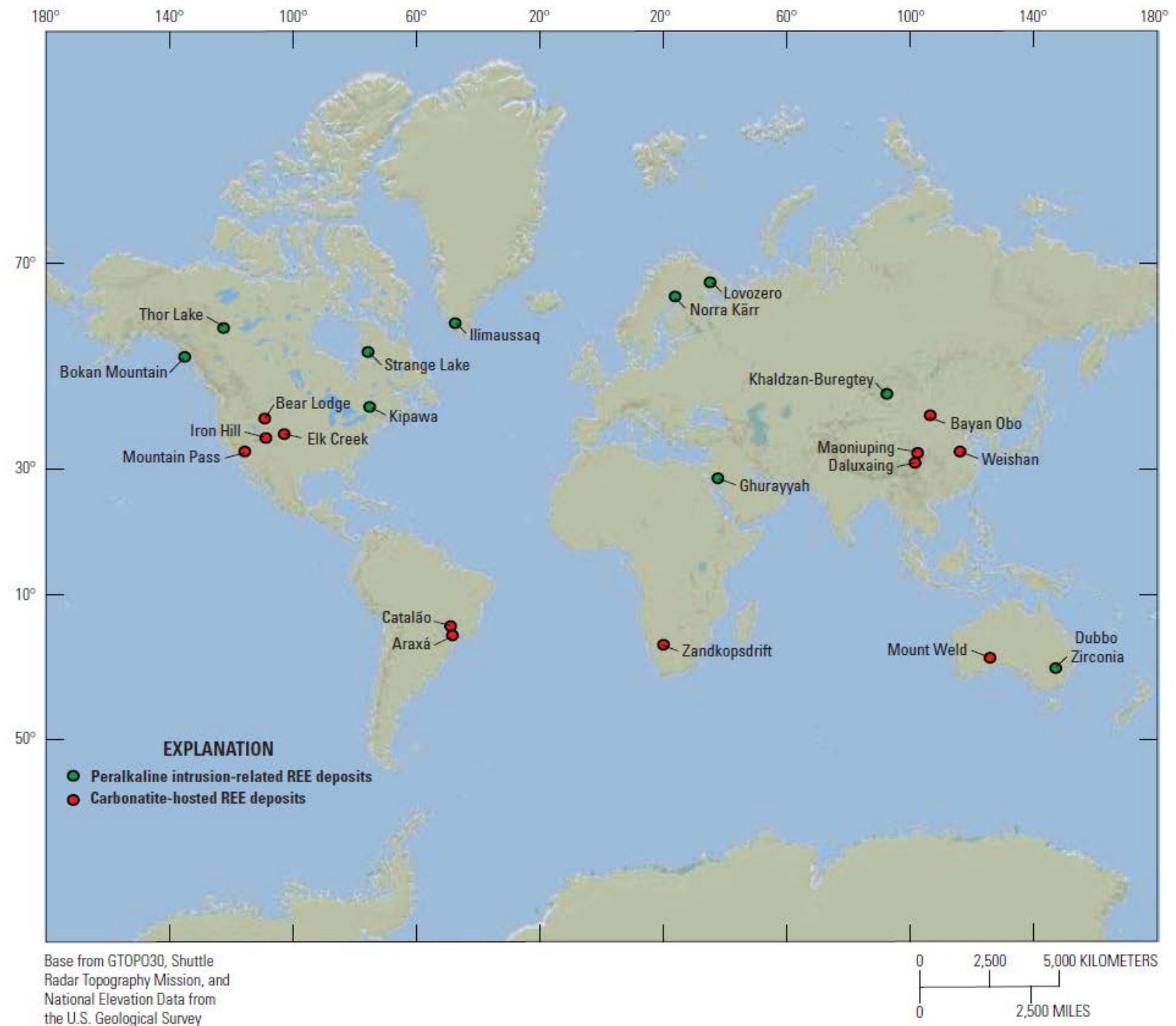
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| a) Carbonatite Deposits | Mountain Pass, CA; Bear Lodge WY |
| b) Peralkaline deposits | Thor Lake, NWT; Bokan Mountain, AK |
| c) Pegmatitic Apatite | Fe-district, Mineville NY |

2) Sedimentary rare earth deposits

- | | |
|---------------------------------------|-----------------------------|
| a) Residual / placer deposits | Elliot Lake Mining District |
| b) Phosphorite Deposits phosphates | Florida/Idaho/midwest |
| c) Ion adsorption clays | Chinese Clay Deposits |
| d) REE-bearing coals | Pennsylvania??? |

Carbonatite (red)
and Peralkaline
(green) REE
deposits,

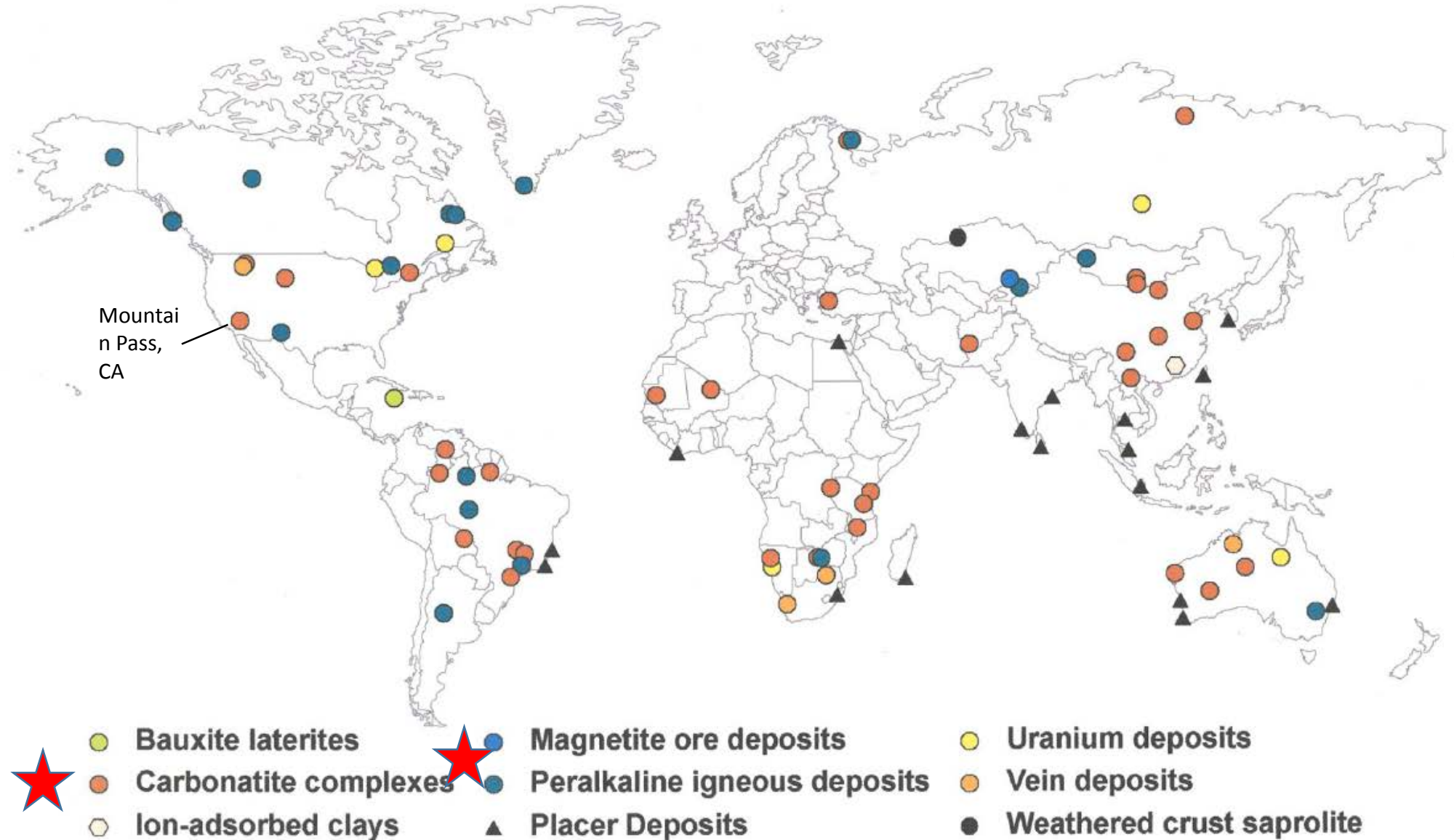
Figure from USGS
Scientific
Investigations
Report 2010-
5070-J



REE-Y deposits types

Different types of REE deposits located globally
Majority are carbonatite and peralkaline in origin

Map courtesy of David Lentz, University of New Brunswick



Carbonatites

- Carbonatites are igneous rocks that contain >50 wt % carbonate (CO_3^{2-}) minerals
- Only 330 known locations on Earth
- Usually (almost exclusively) form in continental rift zones
- Geochemically enriched in incompatible elements (Cs, Rb, Ba, REE)
 - Can host several wt % REE oxides
- Possibly form by partial melting of crustal rocks or mantle degassing
- Known carbonatites in NA include Mountain Pass, CA; Oka and Saint-Honoré, QC; Gem Park and Iron Hill, CO; Magnet Cove, Arkansas

Ol Doinyo Lengai carbonatite volcano

Photo by Celia Nyamweru, USGS



Peralkaline REE Deposits

- Peralkaline rocks are igneous rocks that are oversaturated with Na_2O and K_2O with respect to Al_2O_3
 - $\text{Al}_2\text{O}_3 < (\text{Na}_2\text{O} + \text{K}_2\text{O})$
- Magma may form from partial melting of metasomatized (hydrothermally altered) mantle
- Peralkaline granites form in island arc and mountain building regions (including Appalachia)
- REE-bearing minerals include apatite, xenotime, monazite and lesser bastnaesite
- Sinha et al (1989) identified peralkaline granites in Concord and Salisbury plutonic suites of Appalachia
- Mildly peralkaline rocks associated with Robertson River batholith in Virginia

REE associated with Pegmatites and/or Magnetite – Apatite Deposits

- Pegmatites are course-grained felsic igneous intrusive rocks that are rich in incompatible elements (including REE)
- Commonly enriched in apatite $\text{Ca}_5(\text{PO}_4)_3$
- A closed Fe mine near Mineville, NY has apatite in waste tailings that are enriched in REE
- Measured 5.8-20.6 wt % REE oxides (Staatz et al., 1980)
- Estimated 11 wt % REE oxides (McKeown and Klemic, 1956)
- With an estimated 10 million tons of waste
- Potentially 88 000 tons of REE oxides remaining

Photo credit Fred Haynes



General Geological Classification scheme of REE deposits

1) Magmatic rare earth deposits

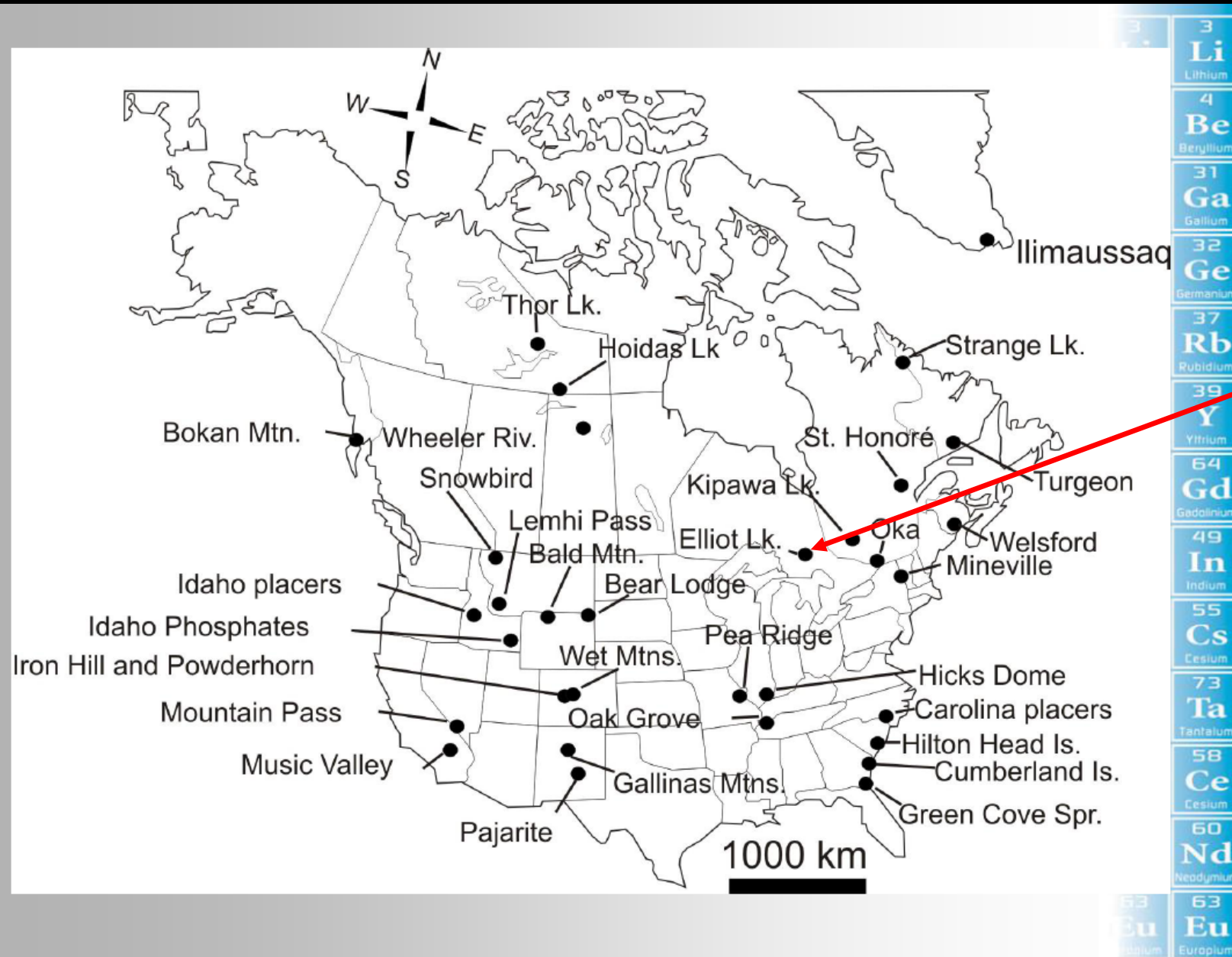
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2) Sedimentary rare earth deposits

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| a) Residual / placer deposits | Elliot Lake Mining District |
| b) Phosphorite Deposits | Florida/Idaho/midwest phosphates |
| c) Ion adsorption clays | Chinese Clay Deposits |
| d) REE-bearing coals | Pennsylvania??? |

Paleoplacer (Uranium) Deposits of REE

- Placer Uranium/Au deposits at Elliot Lake, Ontario have commercially produced REE
- Ore is hosted by pyritic quartz-pebble conglomerates formed from intense weathering of an Archean granite source rock ~1.4 Ga
- Source rock is Canadian Shield – some of Earth's oldest rock
- Small placer deposits occur in Oak Grove TN, Idaho, Carolinas, Florida
 - Most REE occurs in monazite in these small deposits



Elliot Lake Uranium Mining District

Locations of North
American rare earth
concentrations from Castor
(2008)

Paleoplacer (Uranium) Deposits of REE

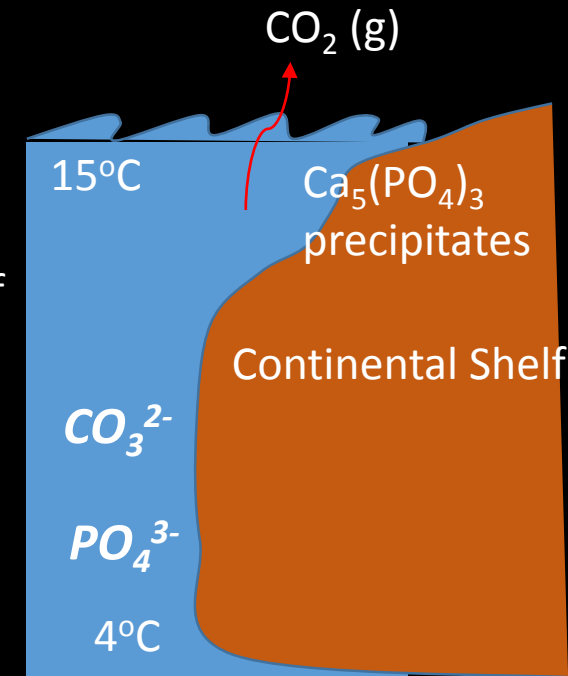
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- REE are associated with uranium minerals including: uraninite, brannerite, and uranothorite, monazite and zircon is also present
- HREE are more concentrated than LREE
- Average grade ~1600 ppm REE

REE in phosphorite deposits

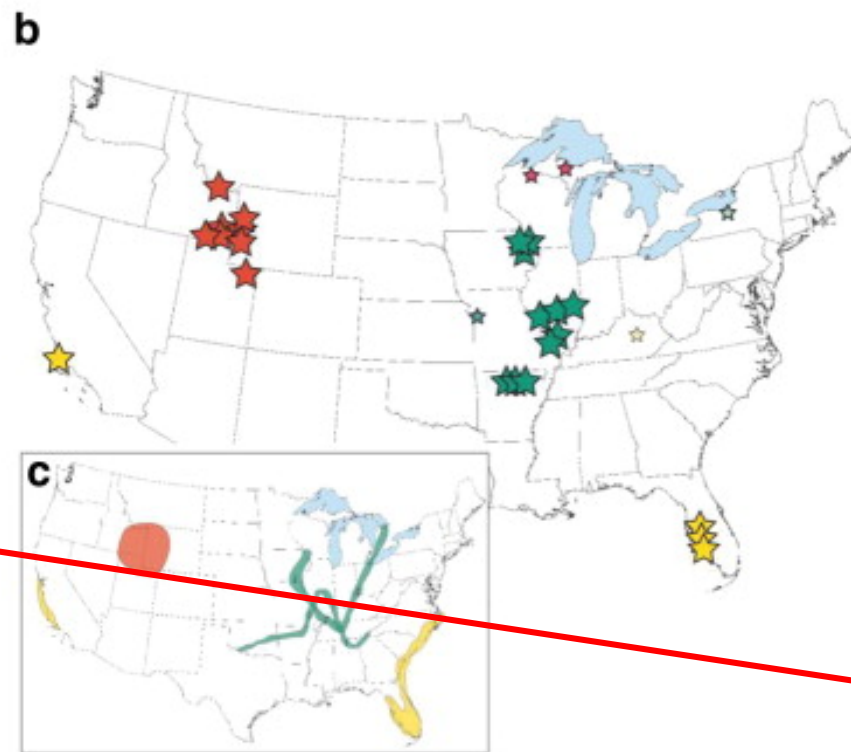
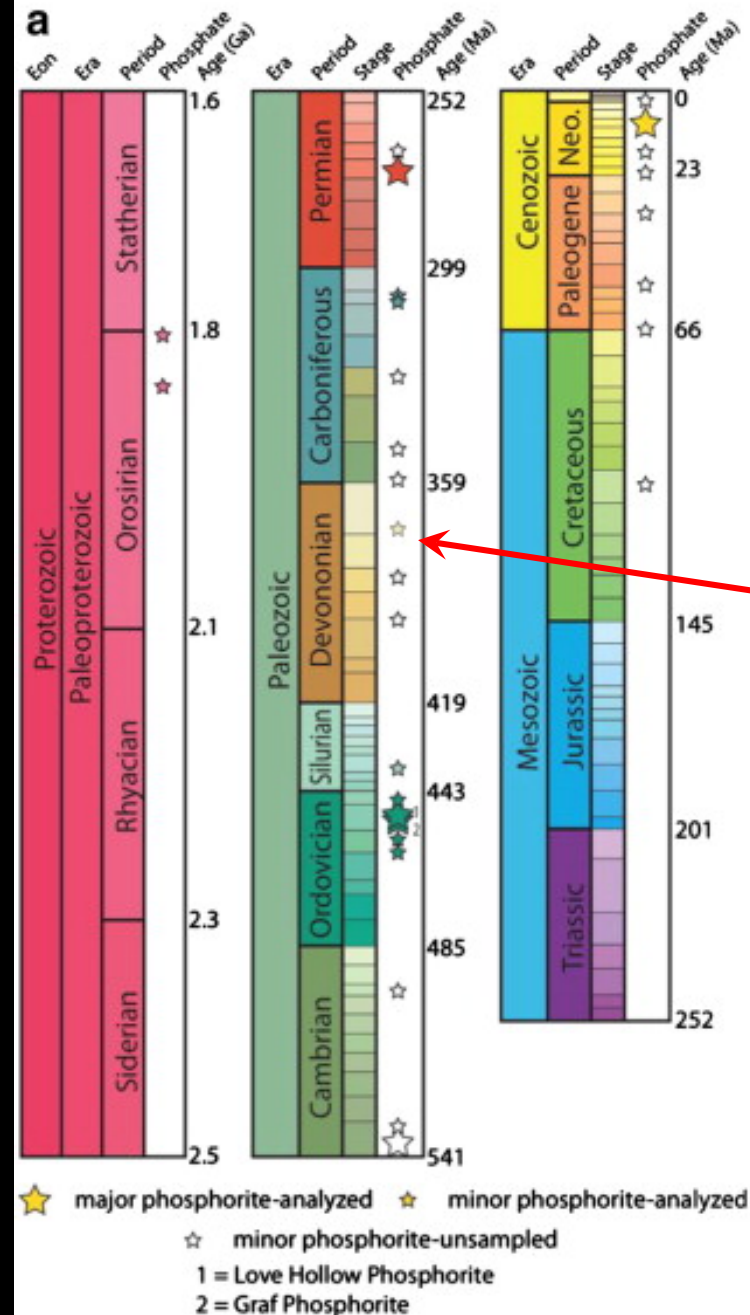
- Phosphorite deposits form as chemical precipitates on continental shelves,
- Upwelling of cold, phosphate rich waters causes warming and decreases in solubility
- REE substitutes for Ca in the mineral francolite $(\text{Ca}, \text{Mg}, \text{Sr}, \text{Na})_{10}(\text{PO}_4, \text{SO}_4, \text{CO}_3)_6\text{F}_{2-3}$

Low solubility of carbonate and phosphate (.003 ppm) at higher T, continental shelf

High solubility of carbonate and phosphate (0.3 ppm) at low T, deep ocean



Continental US Phosphorites



Emsbo et al 2015 Gondwana Research

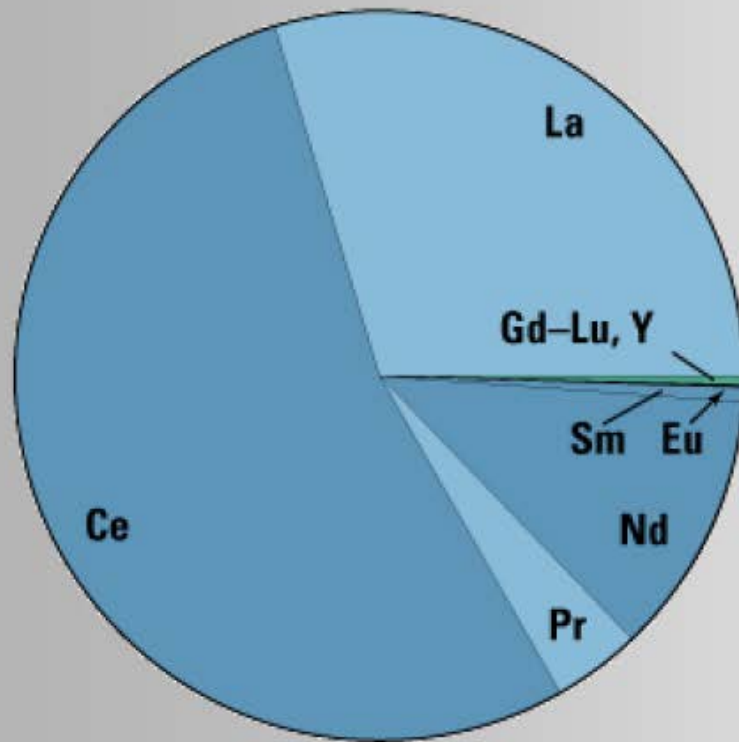
- Up to 5000 ppm REE, mean value of ~1000 ppm
- Enriched in HREE, mean ~500 ppm
- Upper Devonian and Mississippian Phosphorites (>380 Ma) up to 18000 ppm REE
- Nearly 100% extractable with dilute acid

Ion Exchangeable REE in Clay Deposits

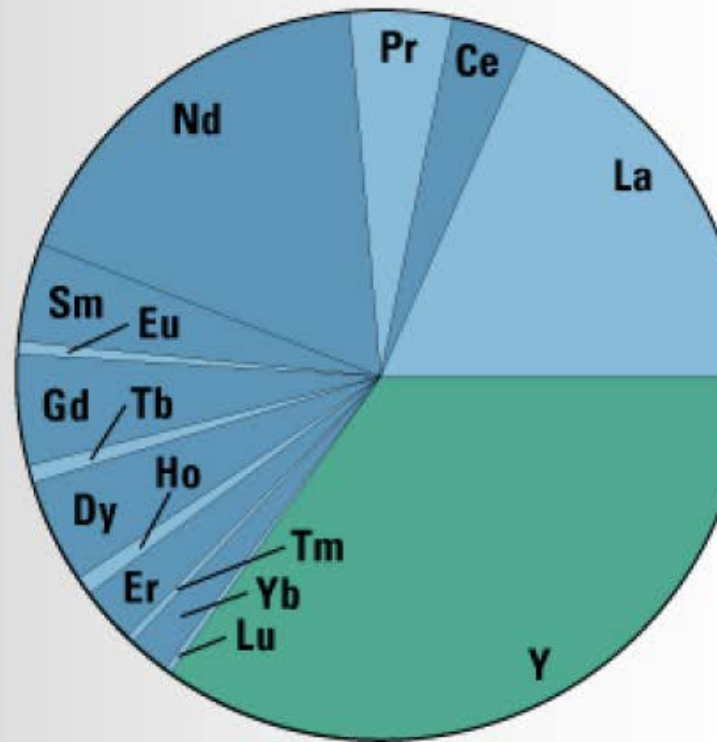
- REE found in soils deposited after weathering of granitic source rocks
- Occur primarily in China, sometimes called laterite deposits
- REE adsorbed to kaolinite, halloysite and illite clay minerals
- Ore is relatively low-grade, generally only 0.05% to 0.5% REO, with high heavy REE
- Easily extractable REE are highly profitable due to low extraction costs

Relative proportions of REE in carbonatites vs laterites

Bastnäsite ore, Mountain Pass, California



Lateritic ore, southern China



USGS facts sheets

- Laterite deposits contain higher concentrations of HREE

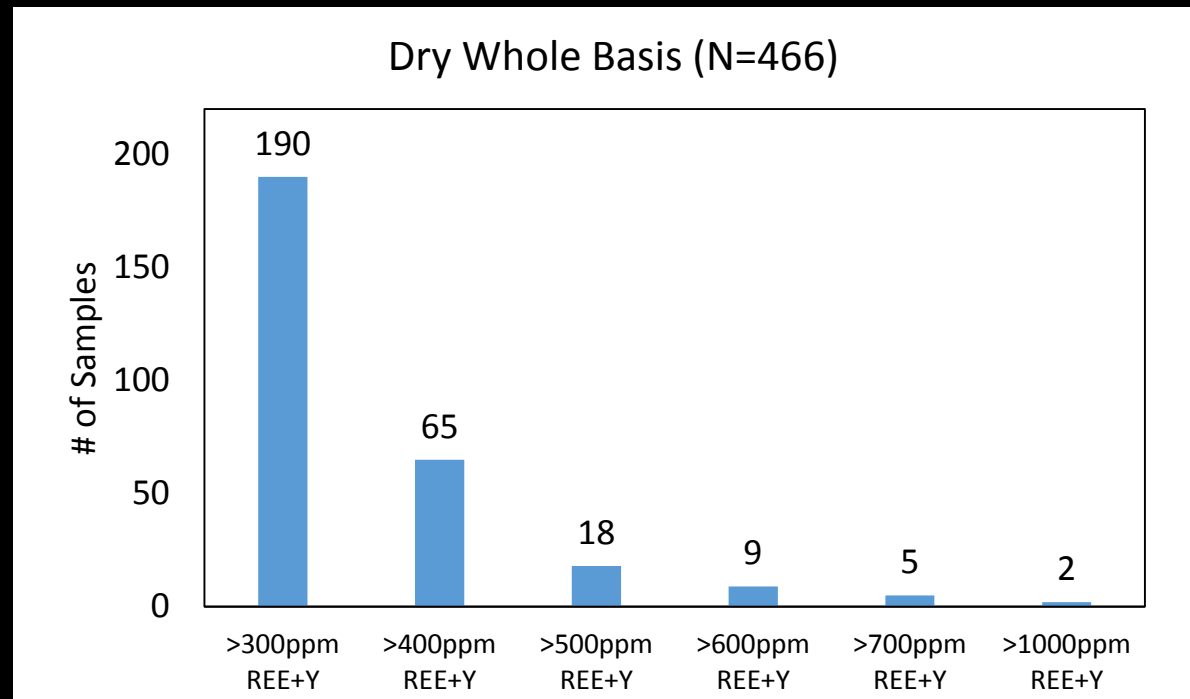
| | |
|------------------------|------------------------|
| 3 Li Lithium | 3 Li Lithium |
| 4 Be Beryllium | 4 Be Beryllium |
| 31 Ga Gallium | 31 Ga Gallium |
| 32 Ge Germanium | 32 Ge Germanium |
| 37 Rb Rubidium | 37 Rb Rubidium |
| 39 Y Yttrium | 39 Y Yttrium |
| 64 Gd Gadolinium | 64 Gd Gadolinium |
| 49 In Indium | 49 In Indium |
| 55 Cs Cesium | 55 Cs Cesium |
| 73 Ta Tantalum | 73 Ta Tantalum |
| 58 Ce Cesium | 58 Ce Cesium |
| 60 Nd Neodymium | 60 Nd Neodymium |
| 63 Eu Europium | 63 Eu Europium |

Are REE Laterite deposits in the US?

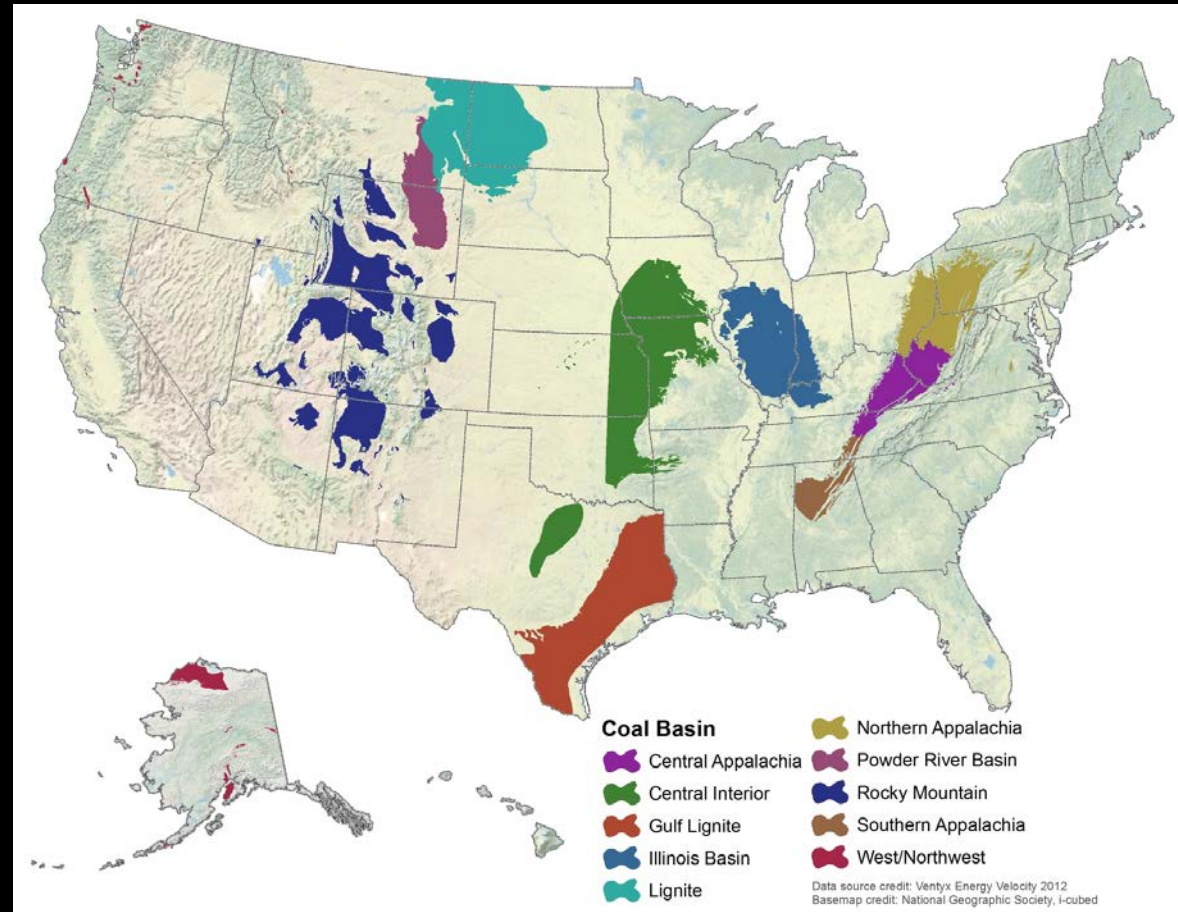
- Similar granitic source rocks in Eastern US (Appalachia) may have weathered to form REE-enriched laterite deposits
- Rozelle et al., 2016 reported highly exchangeable sources of REE from PA clay samples
- Foley and Ayuso (2015) found REE-enriched regolith (2900 ppm) weathered from the mildly peralkaline Robertson River batholith
- Formation of REE laterites dependent on both enriched source material AND chemical weathering conditions
- A detailed study of Th/K may indicate formation of laterite deposits
 - $\text{Th/K} > 17$ possibly indicative of leaching and K depletion
 - High Th/K field samples have been collected

REE in Coal-related Sedimentary Rocks

- Overburden and underburden related to coal seams may be resources of REE
- Sedimentary rocks accumulate REE from physical and/or chemical erosion of source material
- 466 field samples collected, few with >600 ppm REE have been collected

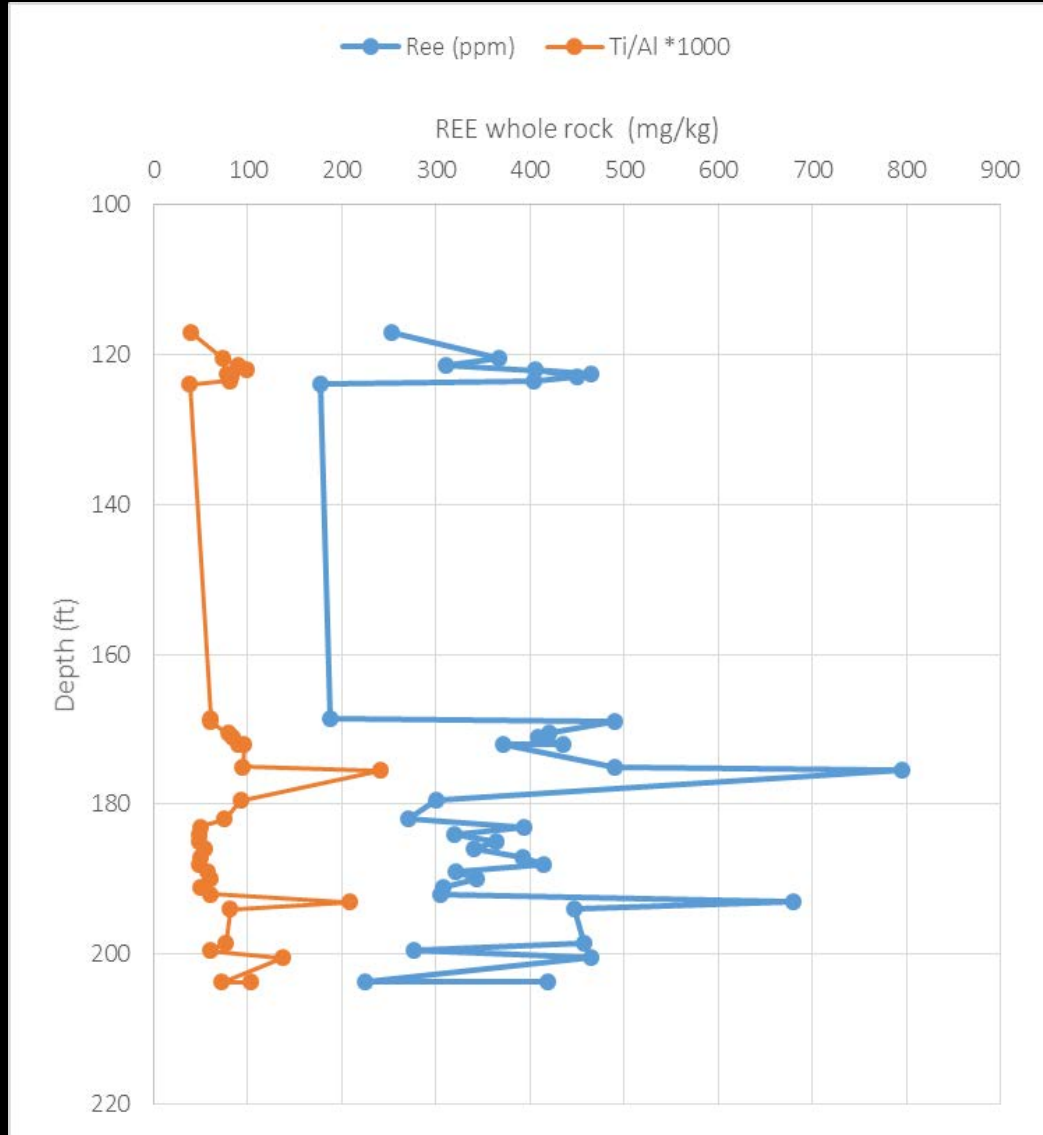


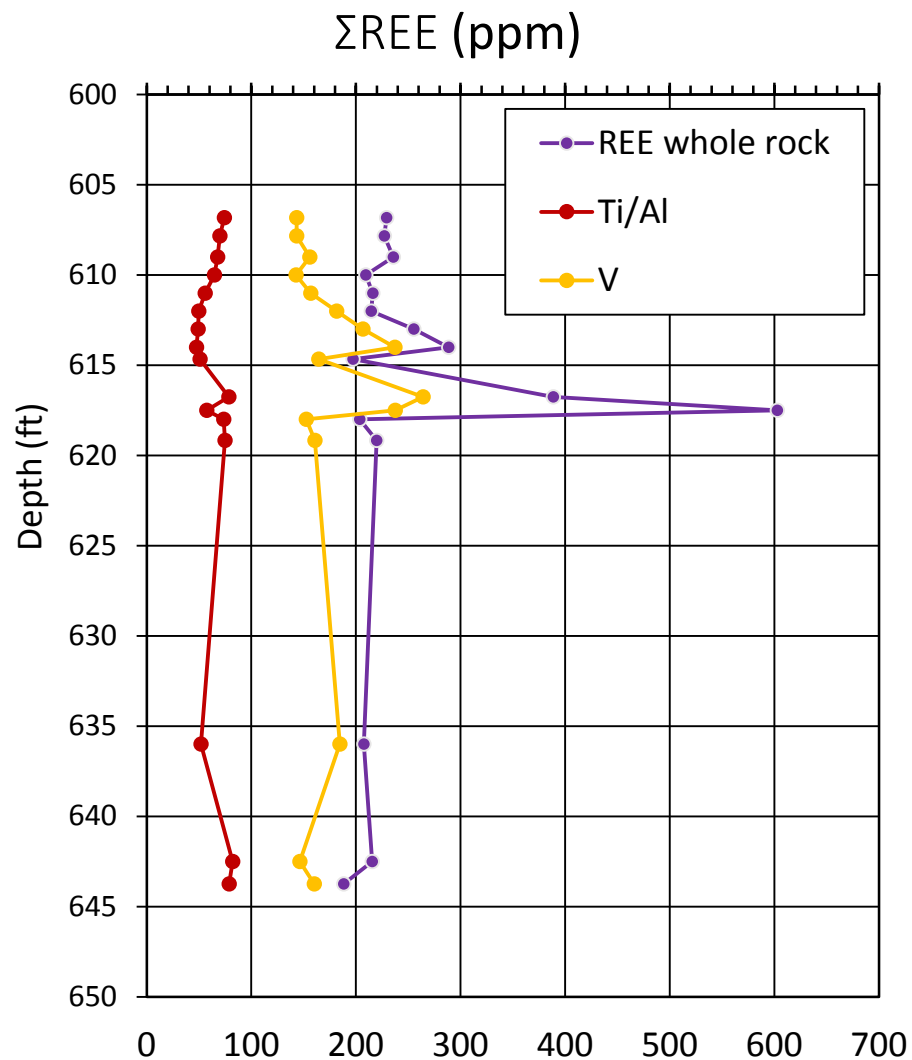
Major Coal Basins in the United States



Ti/Al Geoproxy for erosional rate

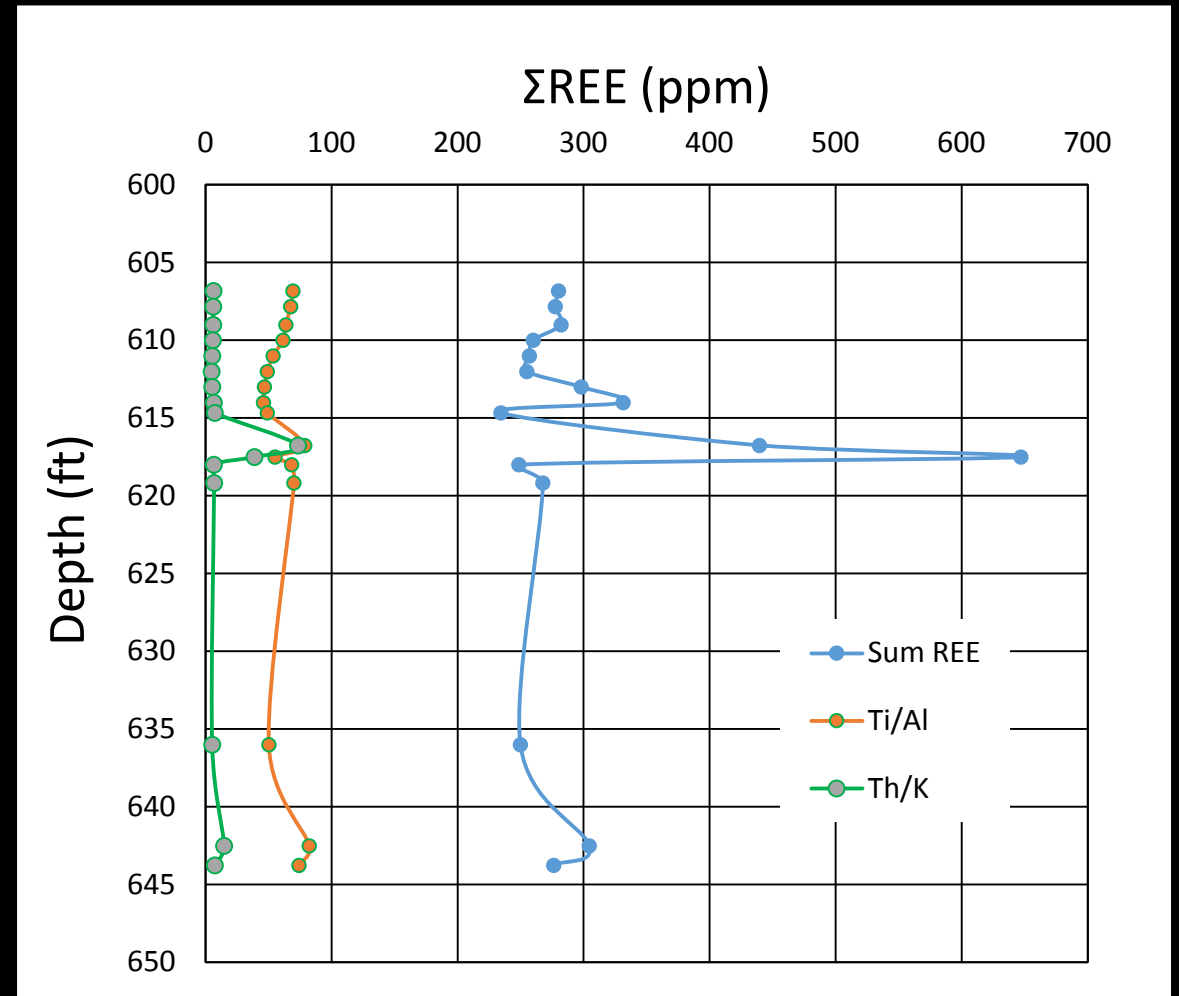
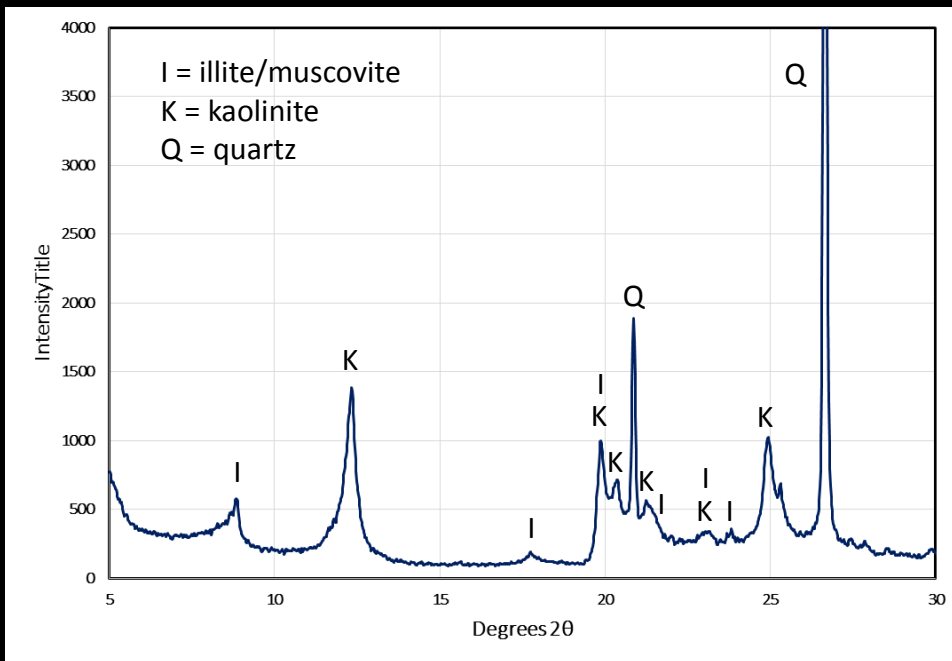
- As erosional rate of source material (granite) increases, Ti/Al increases
- In a given cyclothem, ΣREE correlates positively with Ti/Al
- Suggests that REE in sampled material is physically weathered from Alleghenian granitoids
- Suggests REE was not transported as a dissolved, soluble species but as insoluble and non-reactive mineral grains



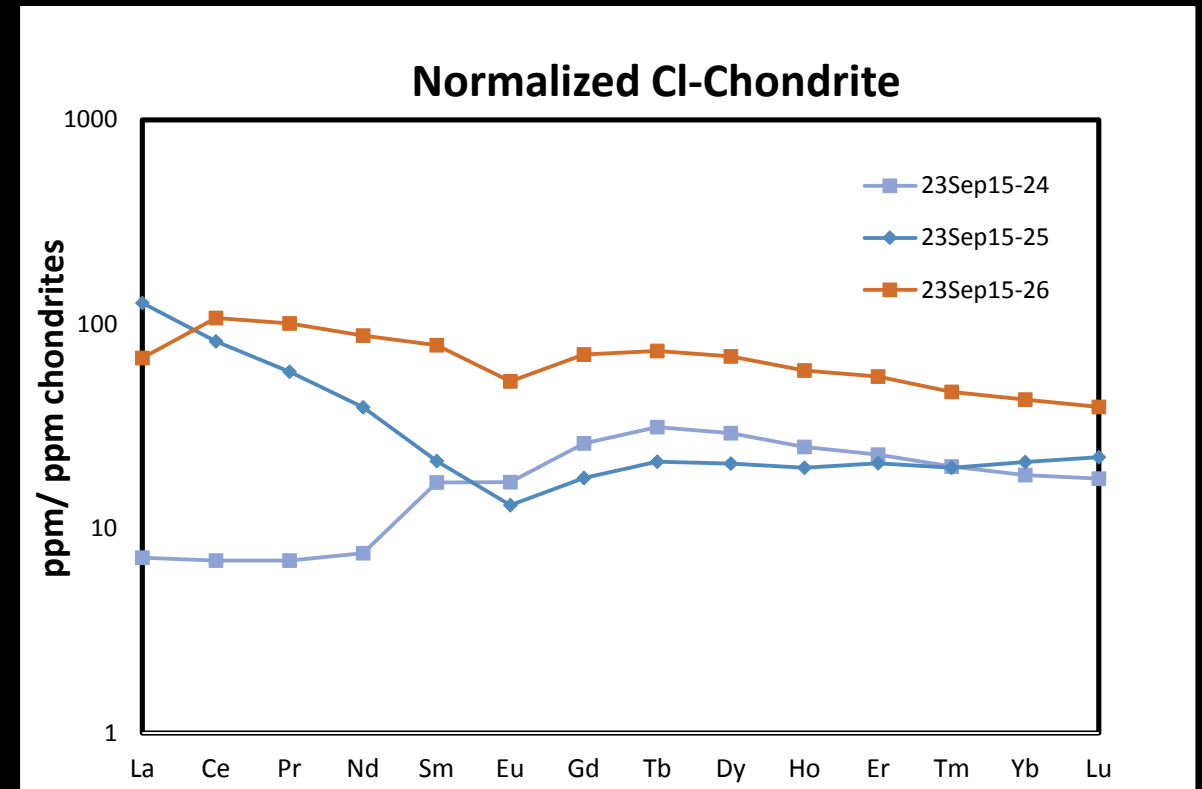
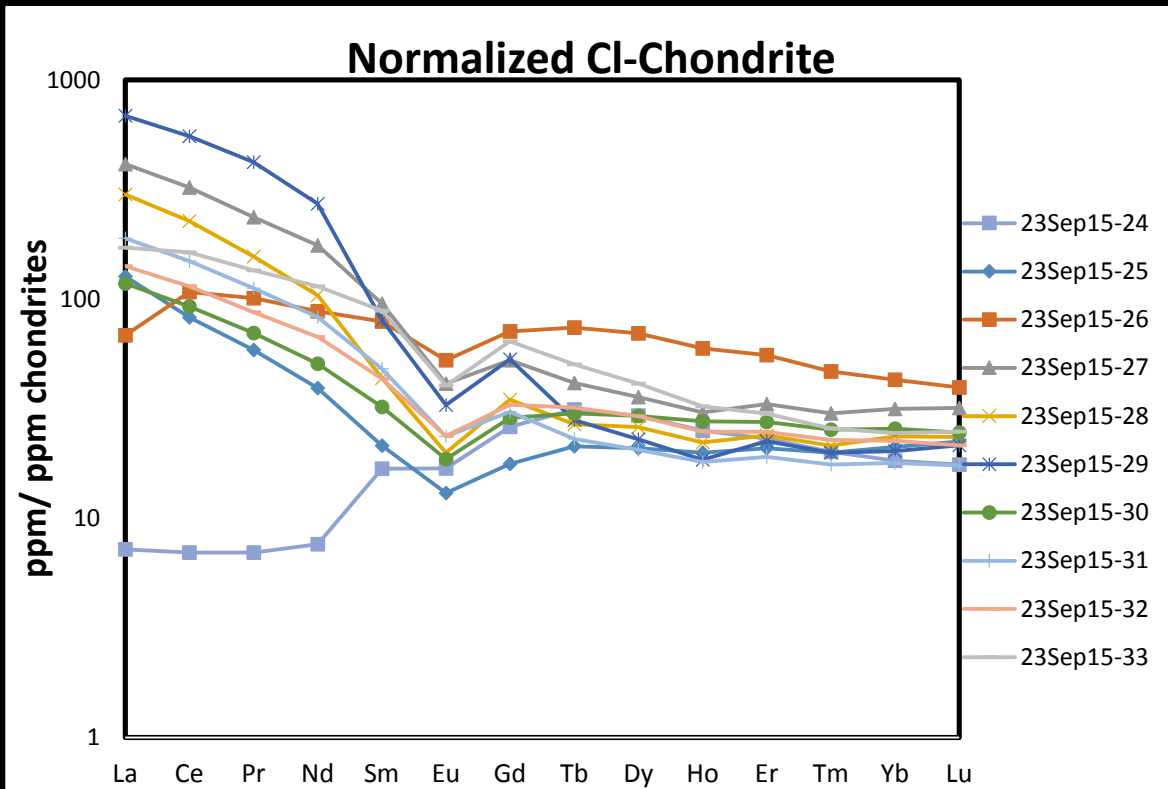


- Strong correlation between V and total REE
- REE spike at 617 ft
 - Calm, anoxic conditions (high V)
 - No dramatic change in Ti/Al
 - Is this evidence of ion-exchangeable REE?

- High REE spike in sample with no correlation to Ti/Al
- High Th/K might also indicate clay adsorption
- X-ray Diffraction data support this hypothesis



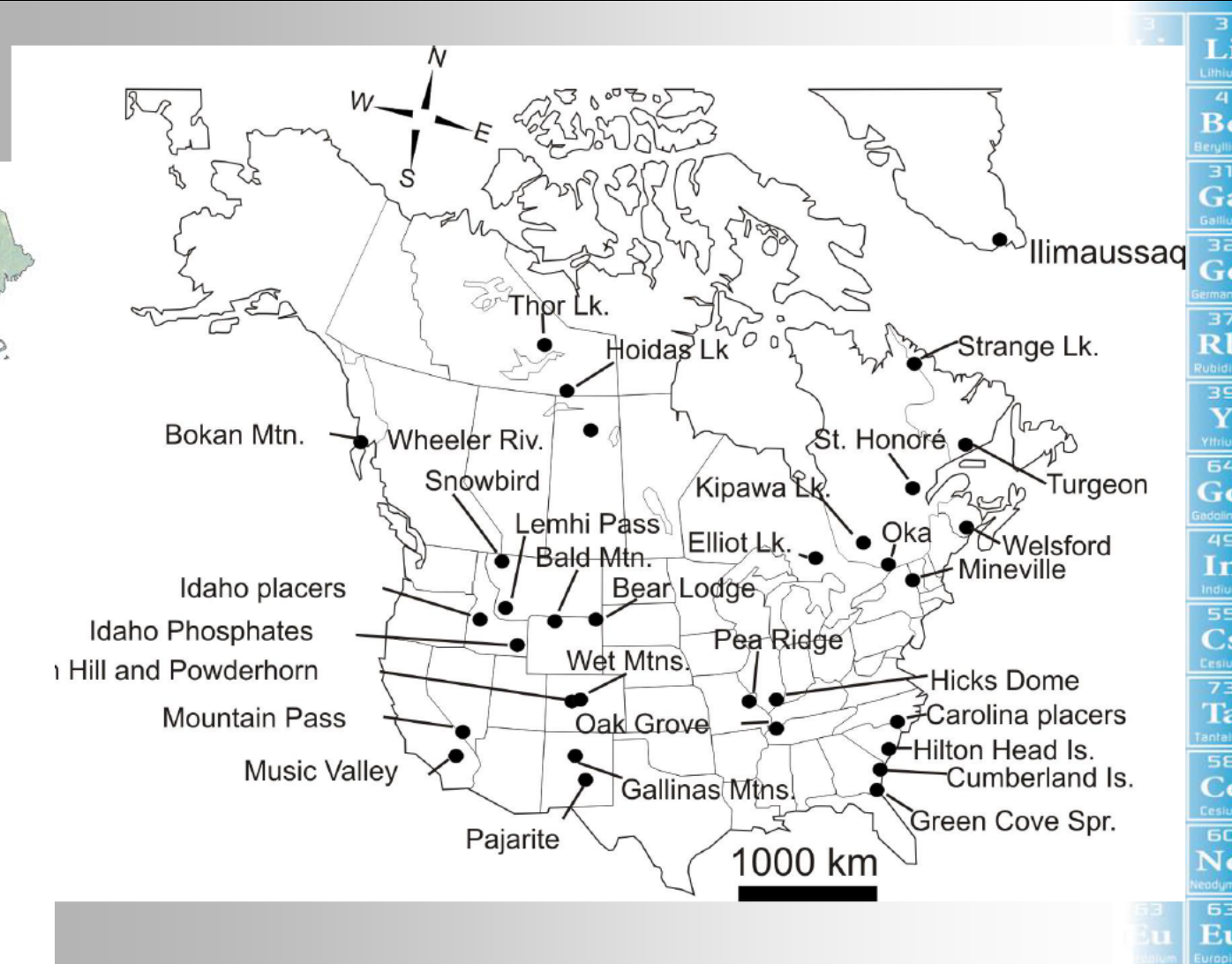
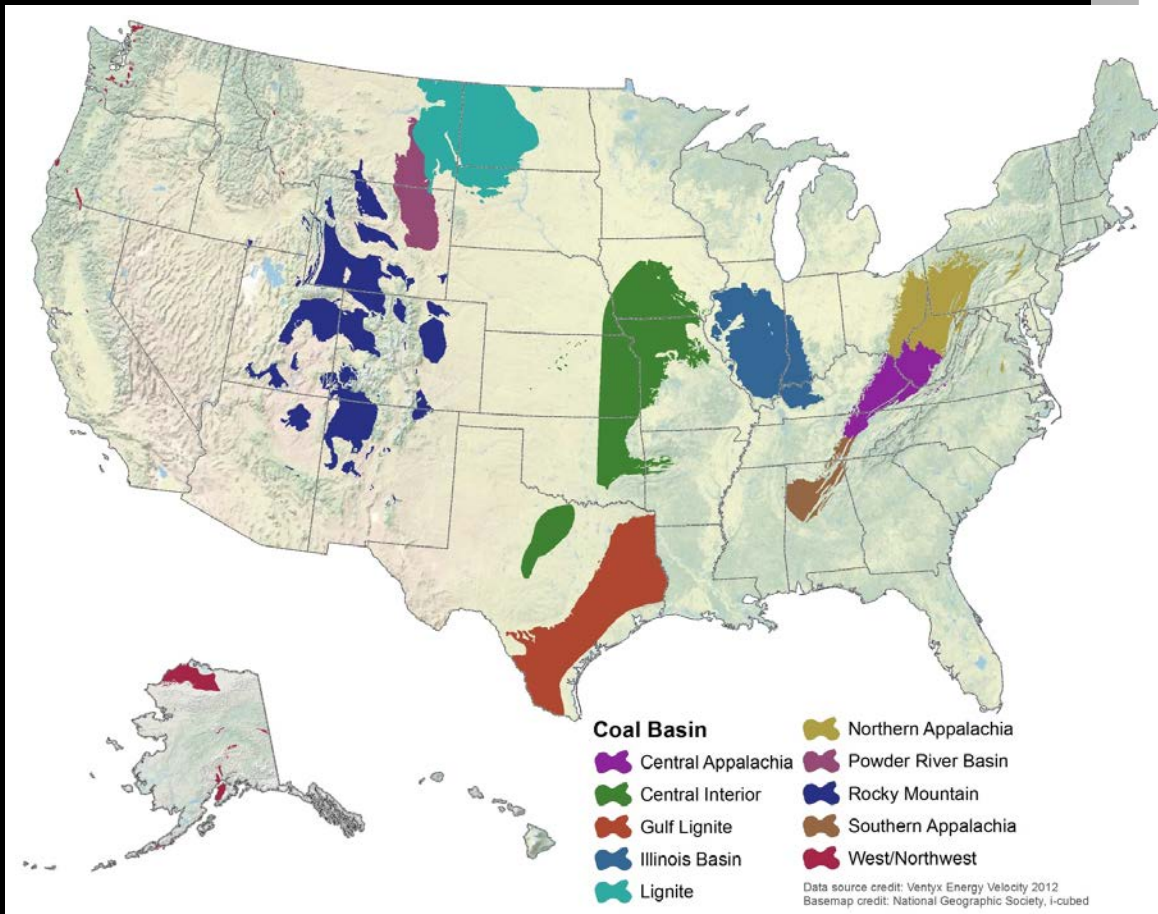
REE distribution in field samples



REE in Coal-related Sedimentary Rocks

- Field samples with high REE (>600 ppm) have been collected
- Data support an Alleghenian granitoid source
 - Some of these granitoids may be peralkaline and REE-enriched
- Weathering of granites has concentrated some REE in sedimentary rocks near coal seams (Ti/Al correlates strongly with REE)
- Chemical leaching may have created regionally minor deposits similar to the ion-adsorbed clay deposits in China (high Th/K and no correlation to Ti/Al)
- Variations in chondrite normalized patterns indicate no single deposit type in field samples collected to date

Major Coal basins and REE enrichments in NA



Summary

- Carbonatite and peralkaline igneous deposits contain the highest REE concentrations but are exceedingly rare, especially in PA
- Co-recovery with other elements or recovery of REE from waste streams may increase economic potential
- Abandoned tailings piles from some coal and iron mines may be important resources of REE
- Although ion adsorbed REE in clays from South China provide the bulk of HREE to the market place, economics may render similar deposits uneconomical in the US

| Name | Country | State/Province | REO (Mt) | REO (%) | Source | Comments |
|--------------------------|---------|--------------------|----------|---------|-------------------------------------|--|
| Carbonatite | | | | | | |
| Iron Hill | USA | Colorado | 2.600 | 0.42 | Jackson and Christiansen (1993) | By-product of Nb |
| Mountain Pass | USA | California | 1.800 | 8.9 | Castor and Nason (2004) | 5% REO cut-off |
| Bear Lodge | USA | Wyoming | 0.380 | 3.3 | Meyer (2002) | Carbonatite dikes |
| Oka | Canada | Quebec | 0.221 | 0.1 | Orris and Grauch (2002) | By-product of Nb |
| Wet Mountains | USA | Colorado | 0.140 | 1.0 | Orris and Grauch (2002) | Dike deposits, high Th |
| Hicks Dome | USA | Illinois | 0.062 | 0.42 | Jackson and Christiansen (1993) | By-product of Nb |
| Alkaline rock | | | | | | |
| Thor Lake | Canada | NW Territories | 1.547 | 0.41 | Orris and Grauch (2002) | REO = Y ₂ O ₃ only |
| Strange Lake | Canada | Labrador-Quebec | 0.440 | 0.85 | Richardson and Birkett (1996) | REO = Y ₂ O ₃ only |
| Lackner Lake | Canada | Ontario | 0.130 | 2.72 | Orris and Grauch (2002) | |
| Pajarito Mountain | USA | New Mexico | 0.004 | 0.18 | Jackson and Christiansen (1993) | |
| Kipawa Lake | Canada | Quebec | ND | ≥0.10 | Richardson and Birkett (1996) | |
| Iron oxide-REE | | | | | | |
| Mineville | USA | New York | 0.160 | 1.04 | Jackson and Christiansen (1993) | Apatite in mine tails |
| Pea Ridge | USA | Missouri | 0.072 | 12.0 | Orris and Grauch (2002) | |
| Vein Powerderhorn | | | | | | |
| Lemhi Pass | USA | Colorado | 0.886 | 0.36 | Jackson and Christiansen (1993) | Stockwork veins |
| Hoidas Lake | USA | Idaho | 0.199 | 0.51 | Jackson and Christiansen (1993) | Allanite and apatite |
| Diamond Creek | Canada | Saskatchewan | 0.035 | 2.56 | Great Western Minerals Group (2007) | |
| | USA | Idaho | 0.003 | 1.22 | Jackson and Christiansen (1993) | |
| Placer | | | | | | |
| Oak Grove | USA | Tennessee | 0.157 | 0.09 | Jackson and Christiansen (1993) | Monazite |
| Idaho placers | USA | Idaho | 0.150 | 0.01 | Jackson and Christiansen (1993) | Mostly Monazite |
| Hilton Head Island | USA | South Carolina | 0.061 | 0.01 | Jackson and Christiansen (1993) | Monazite |
| Carolina placers | USA | N. and S. Carolina | 0.057 | ND | Jackson and Christiansen (1993) | Monazite |
| Cumberland Island | USA | Georgia | 0.027 | 0.01 | Jackson and Christiansen (1993) | Monazite |
| Green Cove Spring | USA | Florida | 0.005 | 0.005 | Jackson and Christiansen (1993) | Monazite |
| Paleoplacer | | | | | | |
| Elliott Lake | Canada | Ontario | 0.020 | 0.009 | Jackson and Christiansen (1993) | Monazite |
| Bald Mountain | USA | Wyoming | 0.014 | 0.12 | Jackson and Christiansen (1993) | Monazite |
| Phosphodiorite | | | | | | |
| Idaho deposits | USA | Idaho | 0.100 | 0.1 | Jackson and Christiansen (1993) | Several deposits |
| Fluorite | | | | | | |
| Gallinas Mountains | USA | New Mexico | 0.001 | 2.95 | Orris and Grauch (2002) | |

- Documented occurrences of REE minerals in North America from Castor, 2008

Acknowledgements/References

- David Lentz, University of New Brunswick
- Steve Wilson, USGS
- USGS Scientific Investigations Report 2010-5070J
- Stephen Castor, Rare Earth Deposits of North America, Resource Geology V58, 337-347.
- Rozelle, P.L., et al., 2016, A Study on Removal of Rare Earth Elements from U.S. Coal Byproducts by Ion Exchange, Metallurgical and Materials Transactions E, V3, 6-17.
- Foley and Ayuso, 2015, REE enrichment in granite-derived regolith deposits of the Southeastern United States: Prospective source rocks and accumulation processes, British Columbia Geological Survey Paper 2015-3