

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

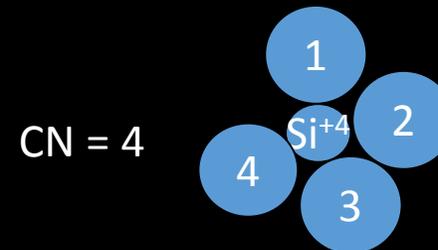
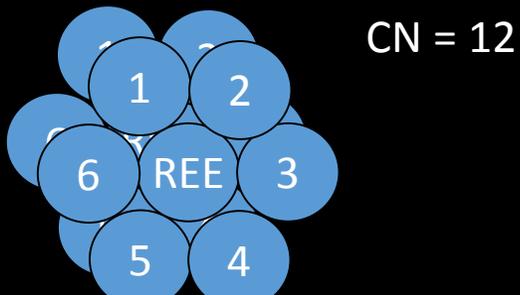
H	Rare Earth Elements																He						
Li	Be	by Geology.com																B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt															
		Lanthanides																					
		LREE																					
		Actinides																					
		HREE																					
		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 $\text{Ca}_5(\text{PO}_4)_3$



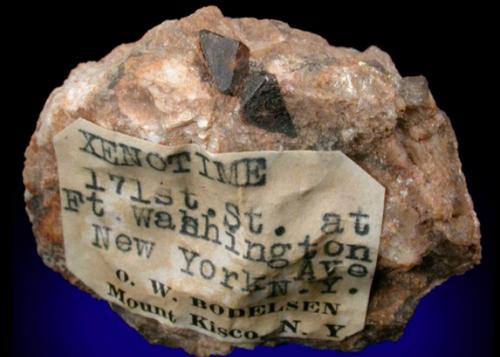
REE-enriched Apatite from Kona Peninsula, Russia
Source credit John H Betts

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

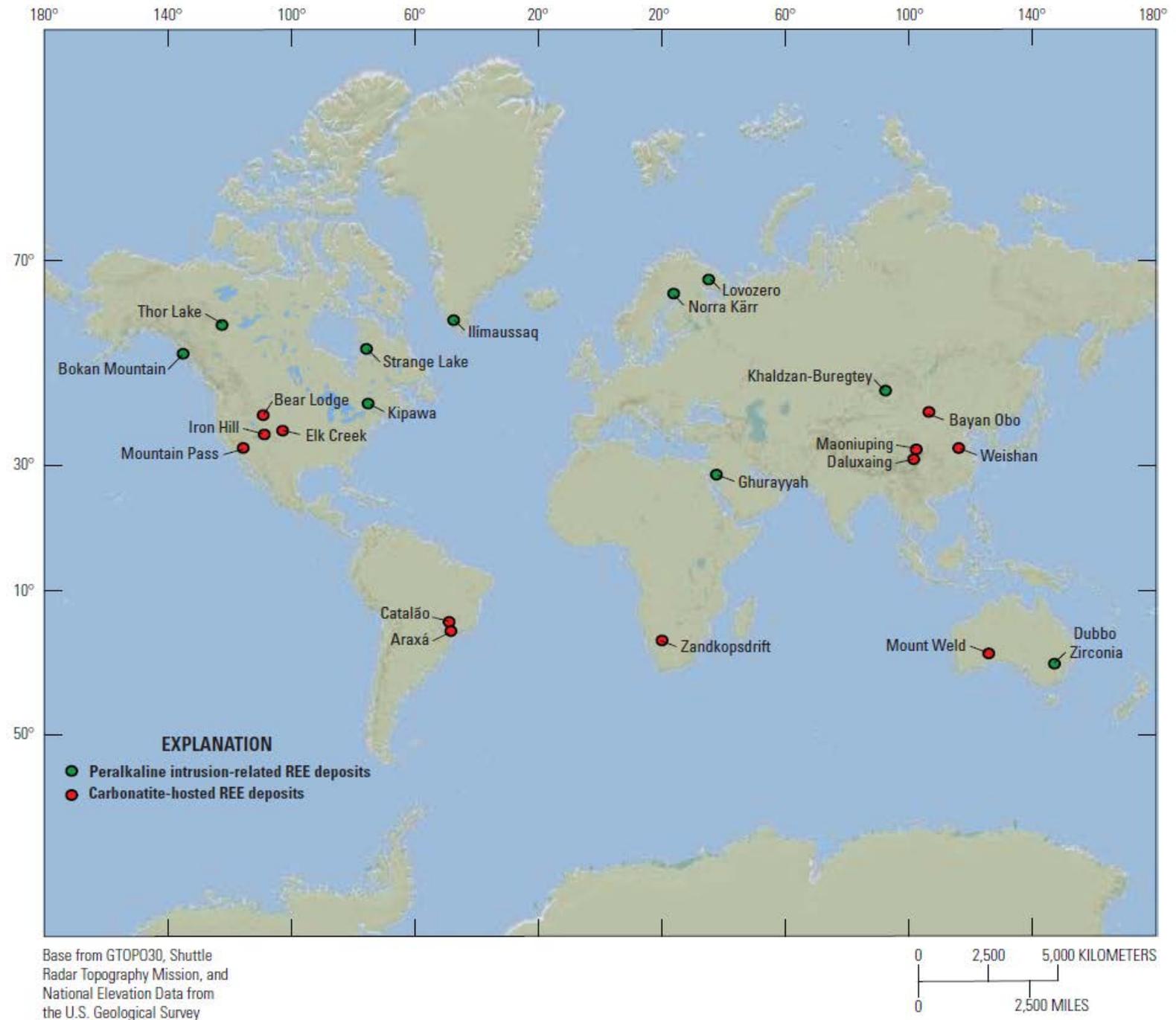
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|-------------------------|------------------------------------|
| a) Carbonatite Deposits | Mountain Pass, CA; Bear Lodge WY |
| b) Peralkaline deposits | Thor Lake, NWT; Bokan Mountain, AK |
| c) Pegmatitic Apatite | Fe-district, Mineville NY |

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,

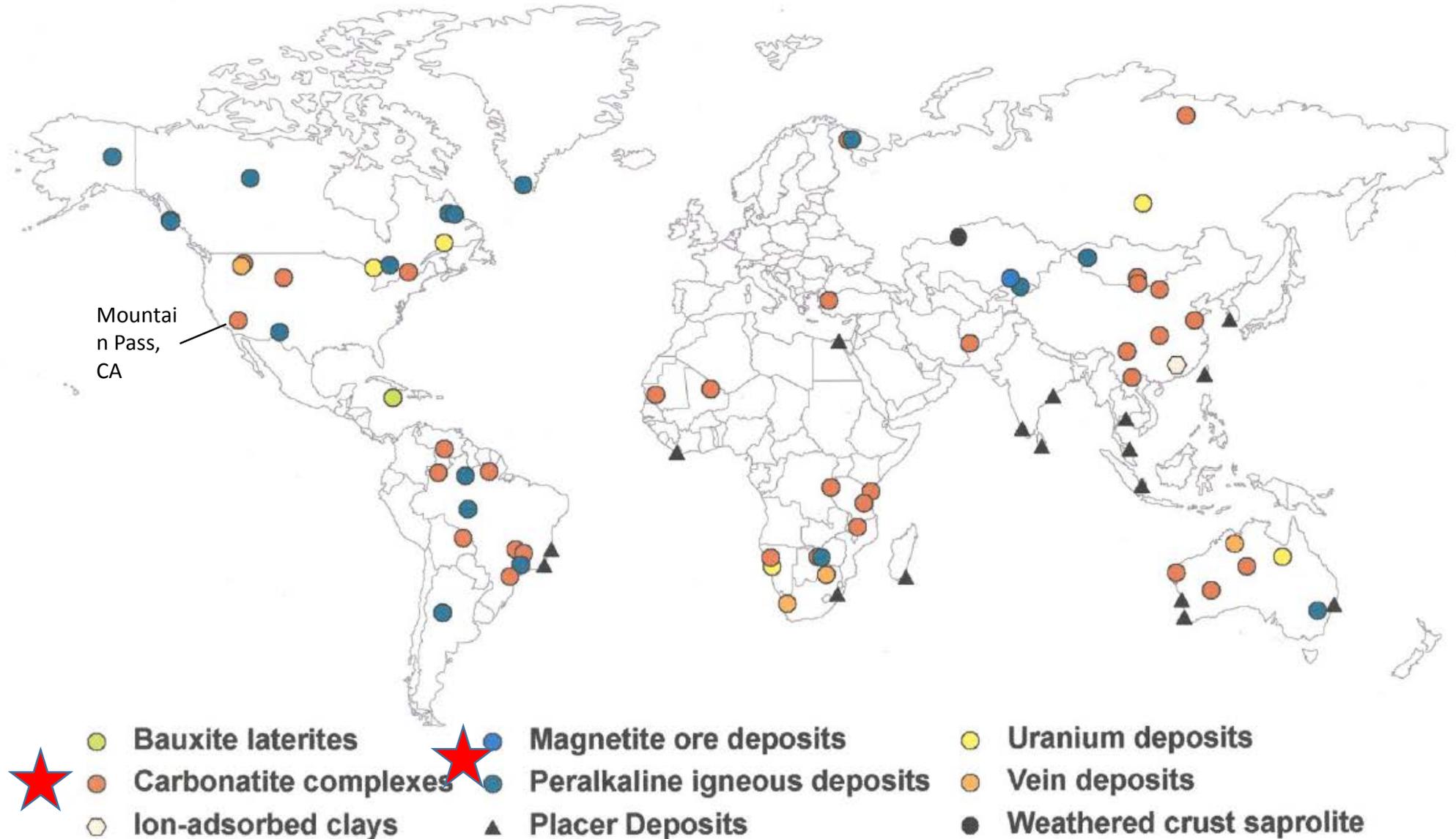
Figure from USGS
Scientific
Investigations
Report 2010-
5070-J



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

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| c) Pegmatitic Apatite | Fe-district, Mineville NY |

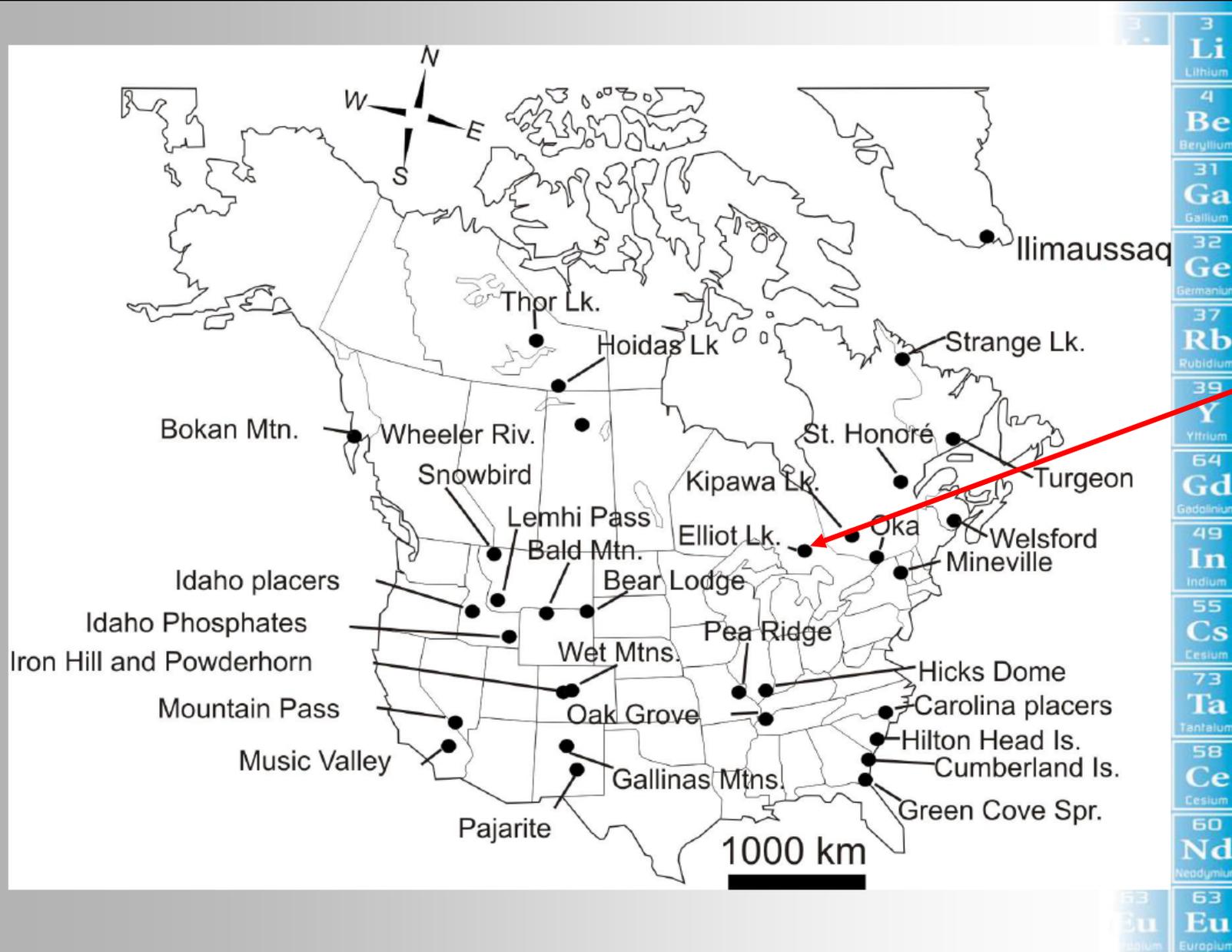
2) Sedimentary rare earth deposits

- | | |
|-------------------------------|----------------------------------|
| 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

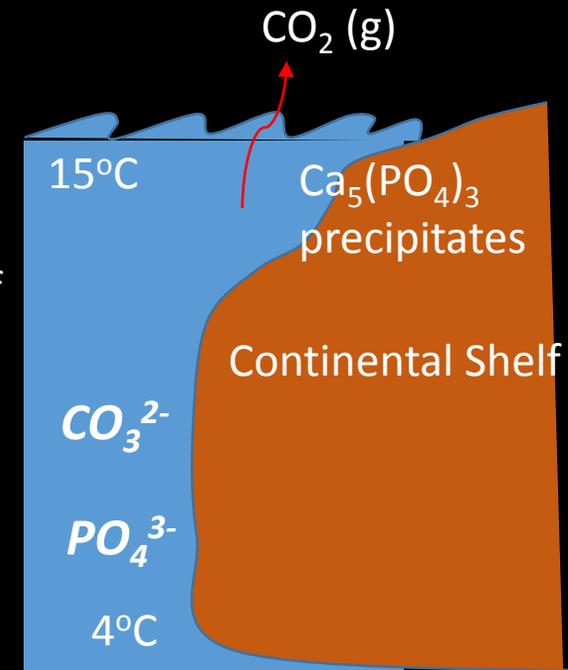
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- Ore is hosted by pyritic quartz-pebble conglomerates formed from intense weathering of an Archean granite source rock ~1.4 Ga
- REE are associated with uranium minerals including: uraninite brannerite, and uranothorite, monazite and zircon is also present
- HREE are more concentrated than LREE
- Average grade ~1600 ppm REE

REE in phosphorite deposits

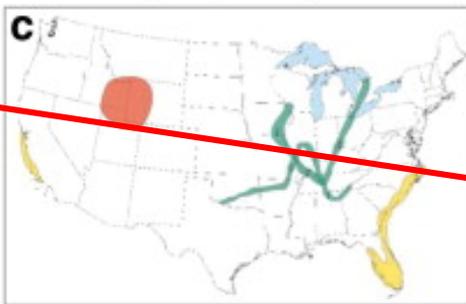
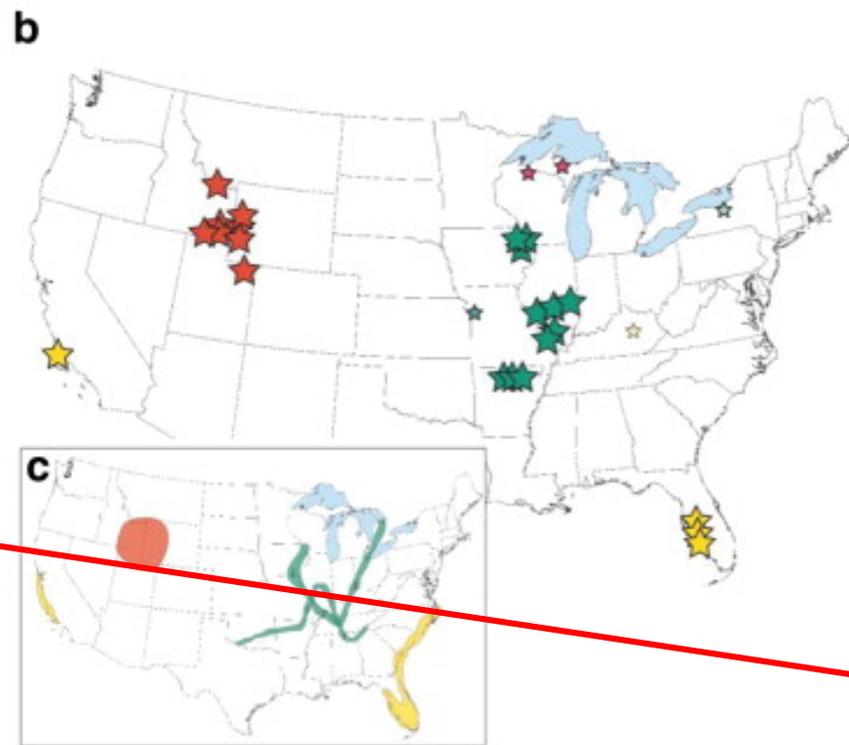
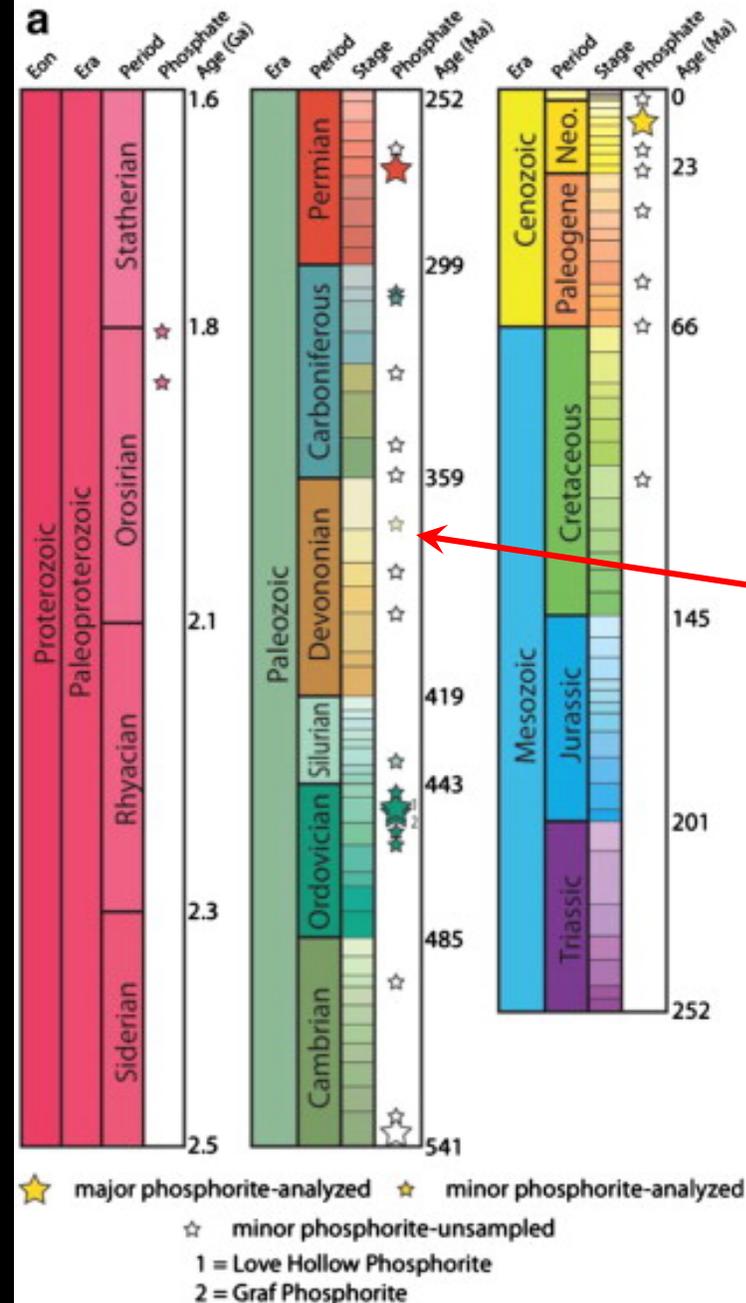
- Phosphorite deposits form as chemical precipitates on continental shelves,
- Upwelling of cold, phosphate rich waters causes warming and decreases in solubility
- REE substitutes for Ca in the mineral francolite $(Ca, Mg, Sr, Na)_{10}(PO_4, SO_4, CO_3)_6F_{2-3}$

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

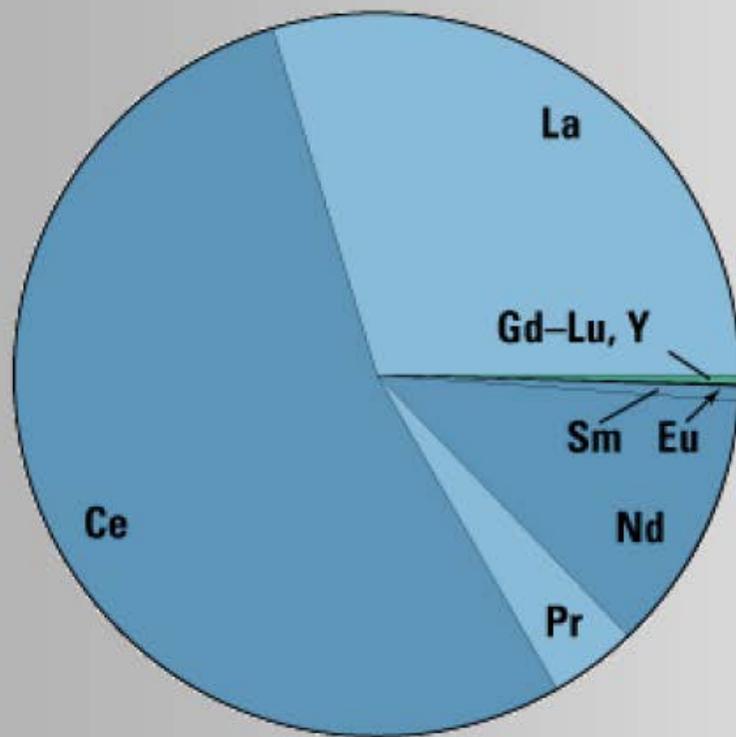
- Up to 5000 ppm REE, mean value of ~1000 ppm
- Enriched in HREE, mean ~500 ppm
- Upper Devonian and Mississippian Phosphorites (>380 Ma) up to 18000 ppm REE
- Nearly 100% extractable with dilute acid

Ion Exchangeable REE in Clay Deposits

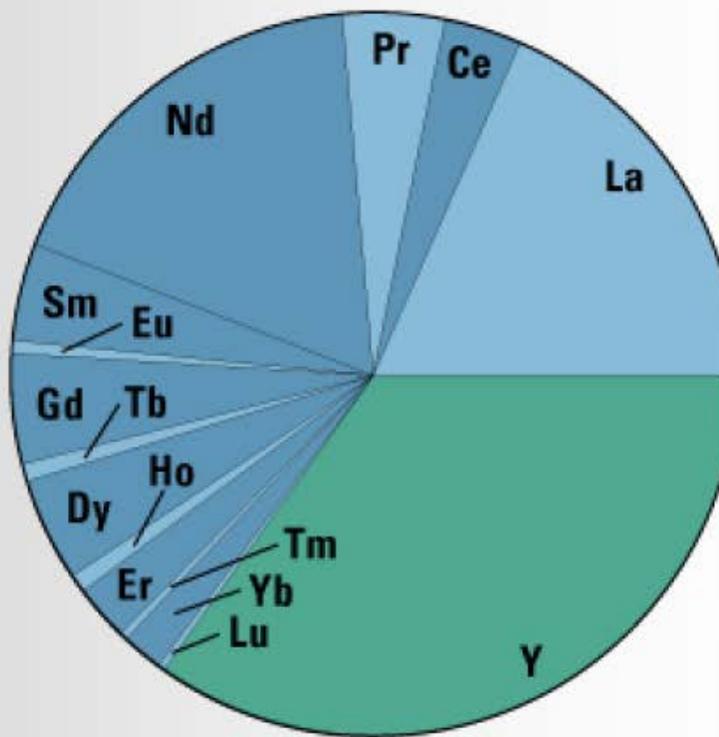
- REE found in soils deposited after weathering of granitic source rocks
- Occur primarily in China, sometimes called laterite deposits
- REE adsorbed to kaolinite, halloysite and illite clay minerals
- Ore is relatively low-grade, generally only 0.05% to 0.5% REO, with high heavy REE
- Easily extractable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

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

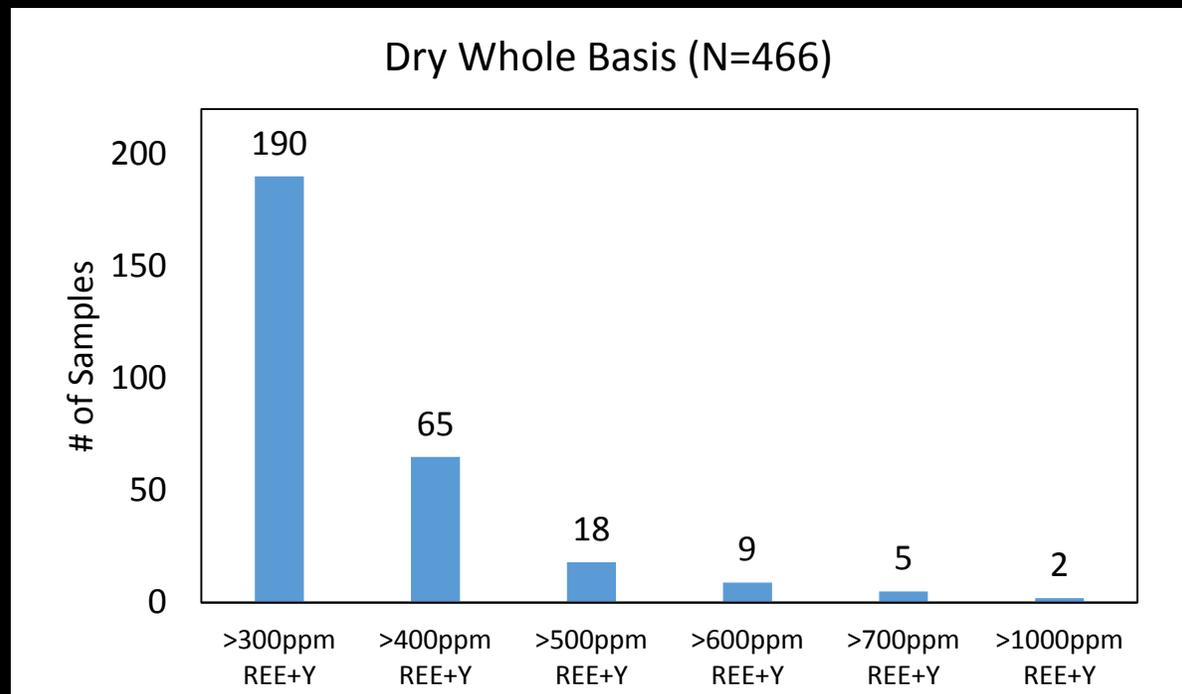
- Laterite deposits contain higher concentrations of HREE

Are REE Laterite deposits in the US?

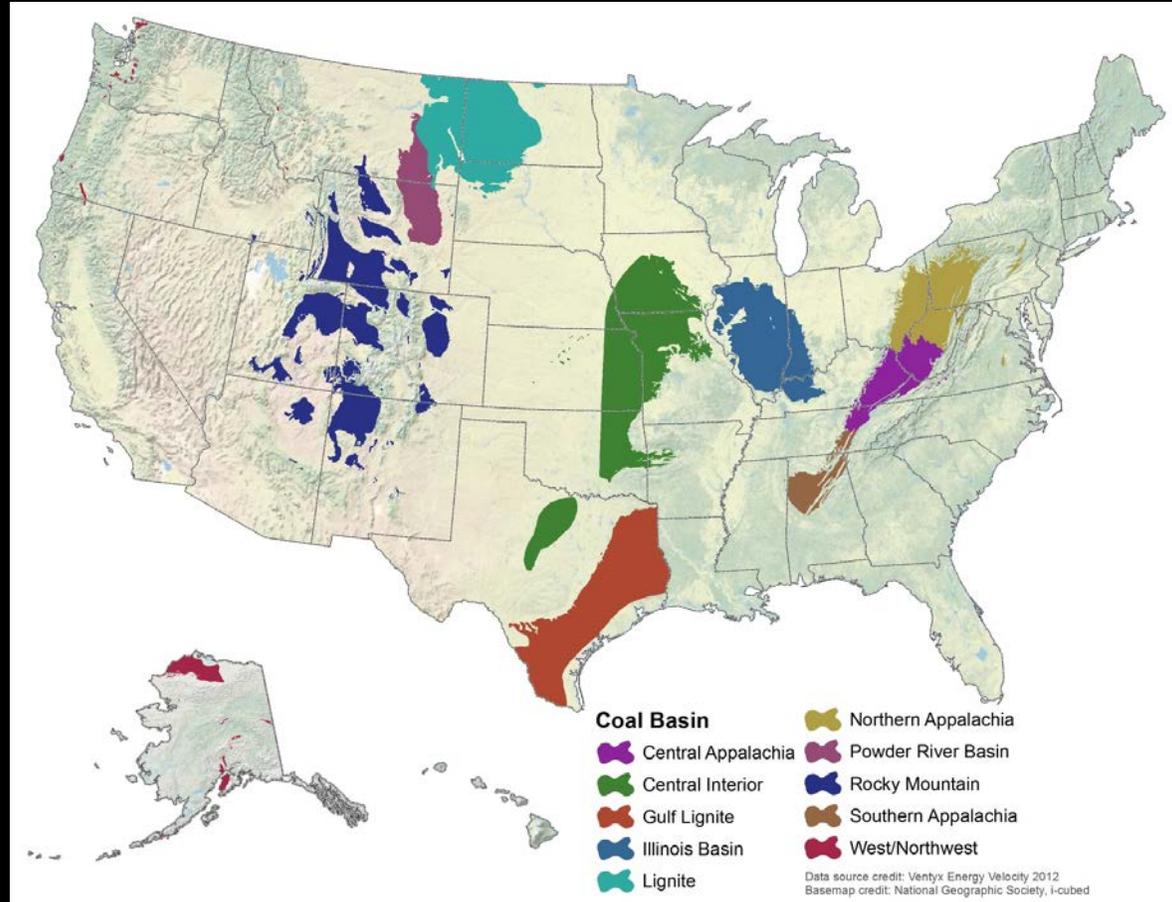
- Similar granitic source rocks in Eastern US (Appalachia) may have weathered to form REE-enriched laterite deposits
- Rozelle et al., 2016 reported highly exchangeable sources of REE from PA clay samples
- Foley and Ayuso (2015) found REE-enriched regolith (2900 ppm) weathered from the mildly peralkaline 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
 - 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

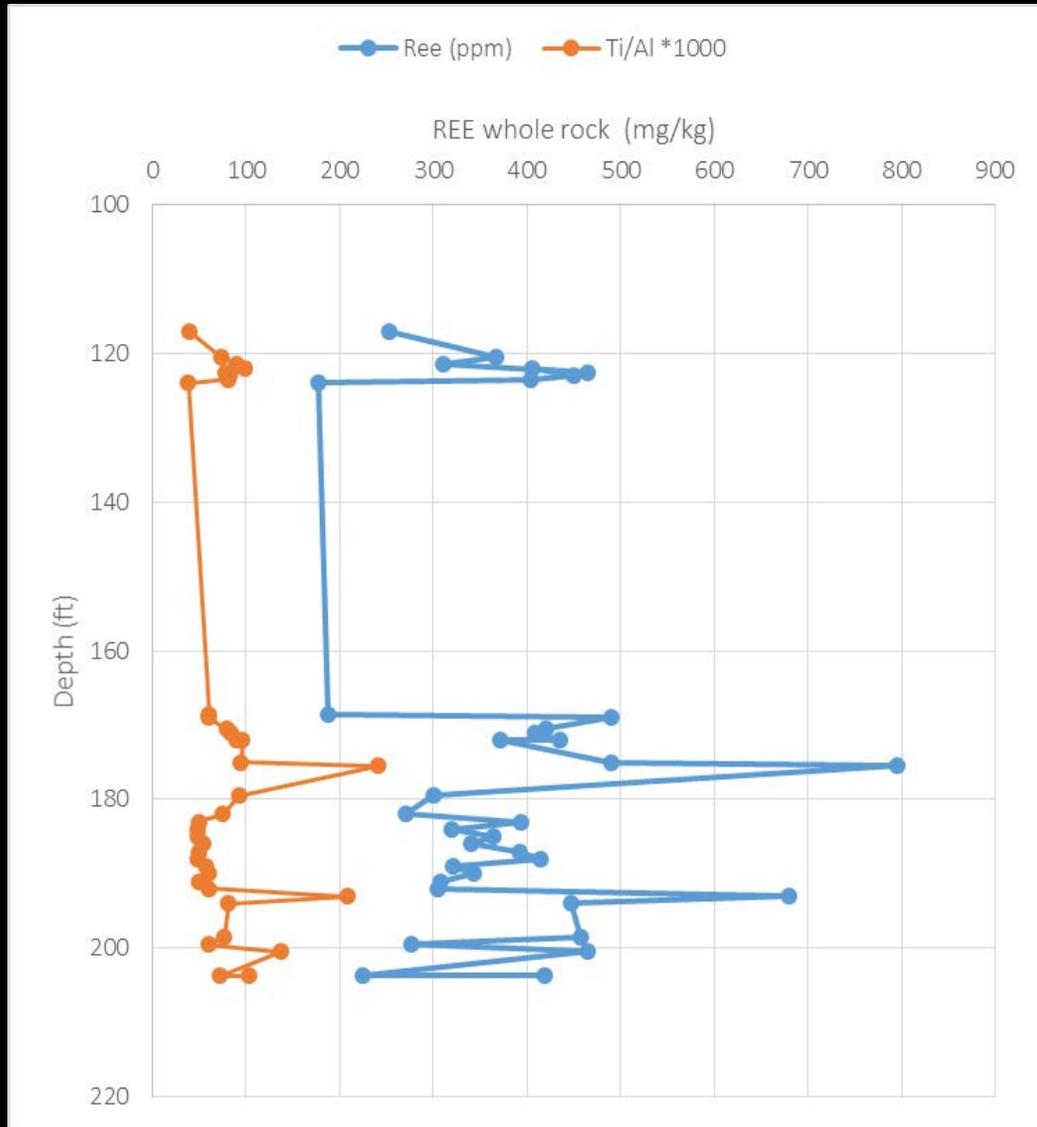


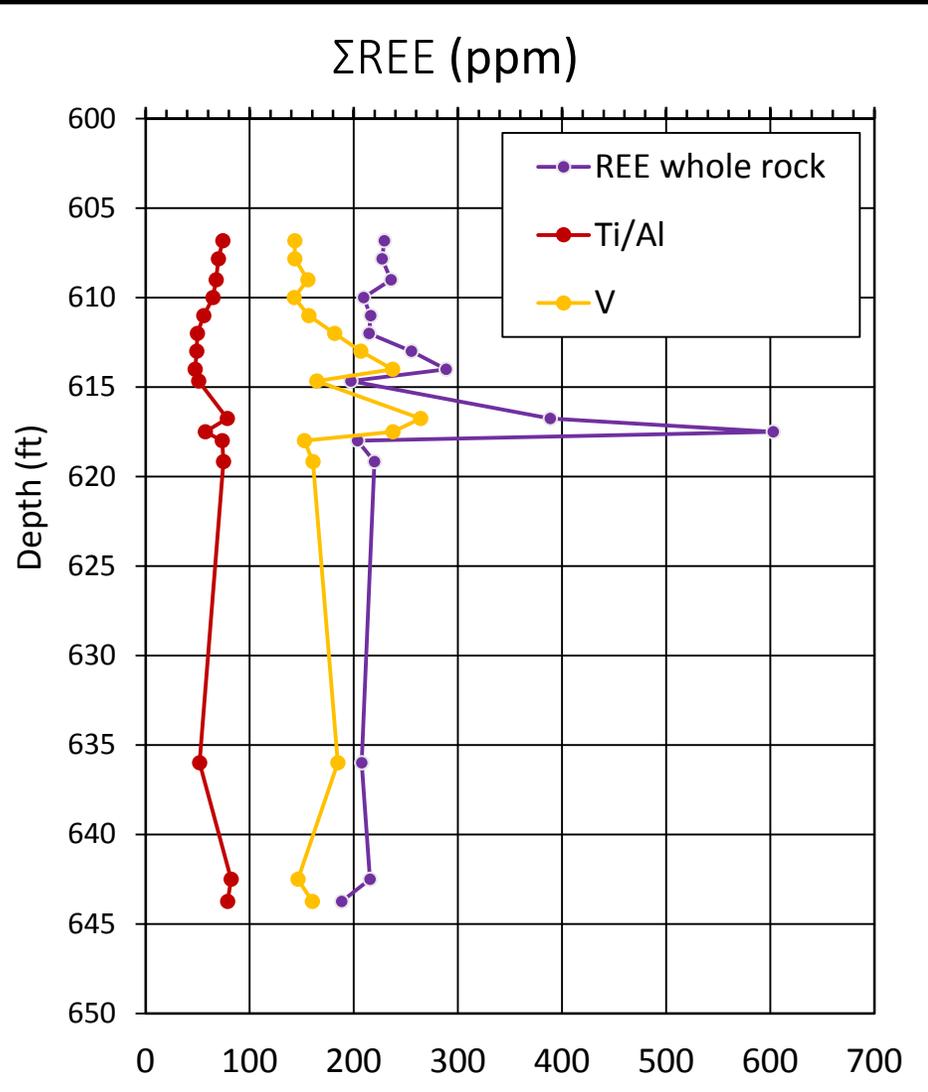
Major Coal Basins in the United States



Ti/Al Geoproxy for erosional rate

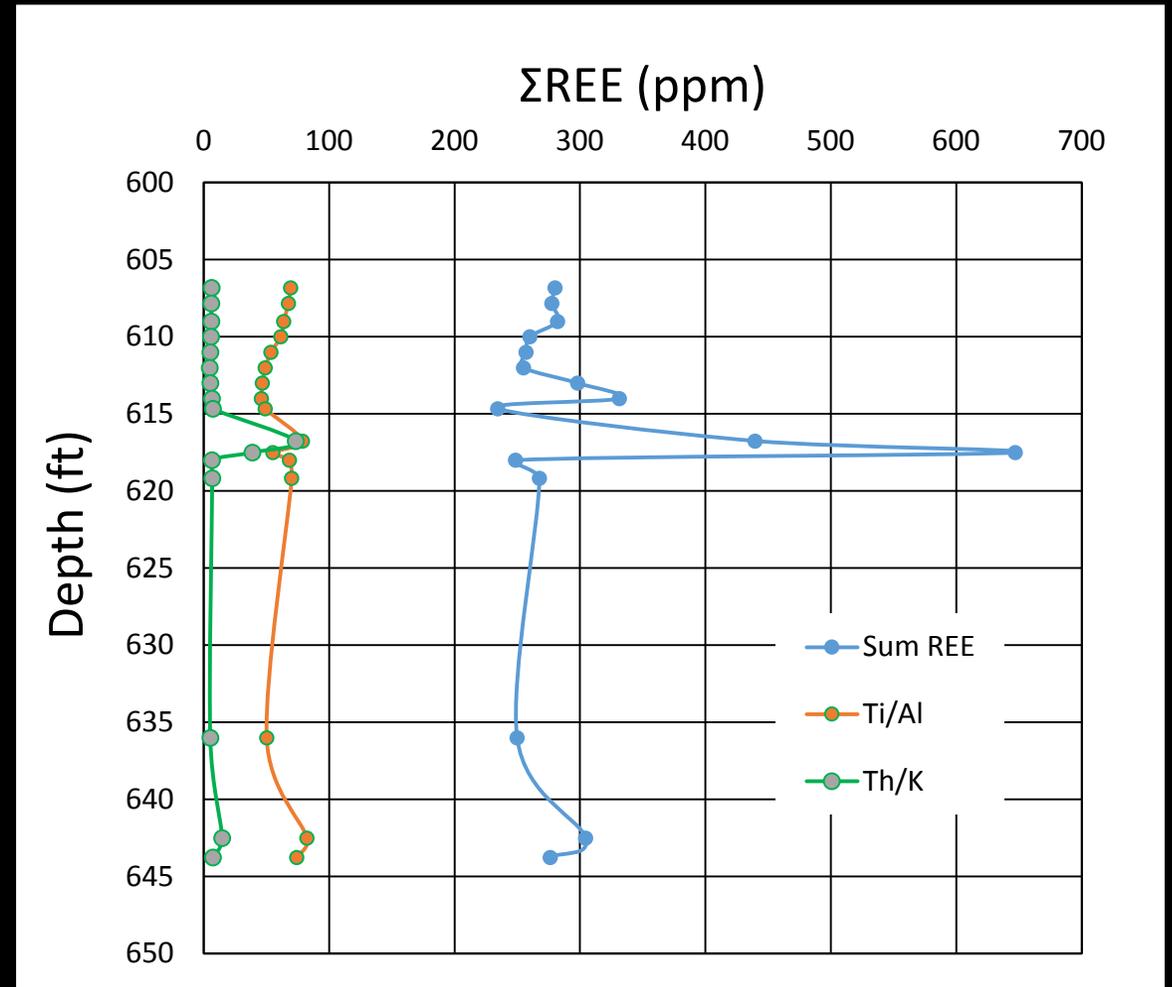
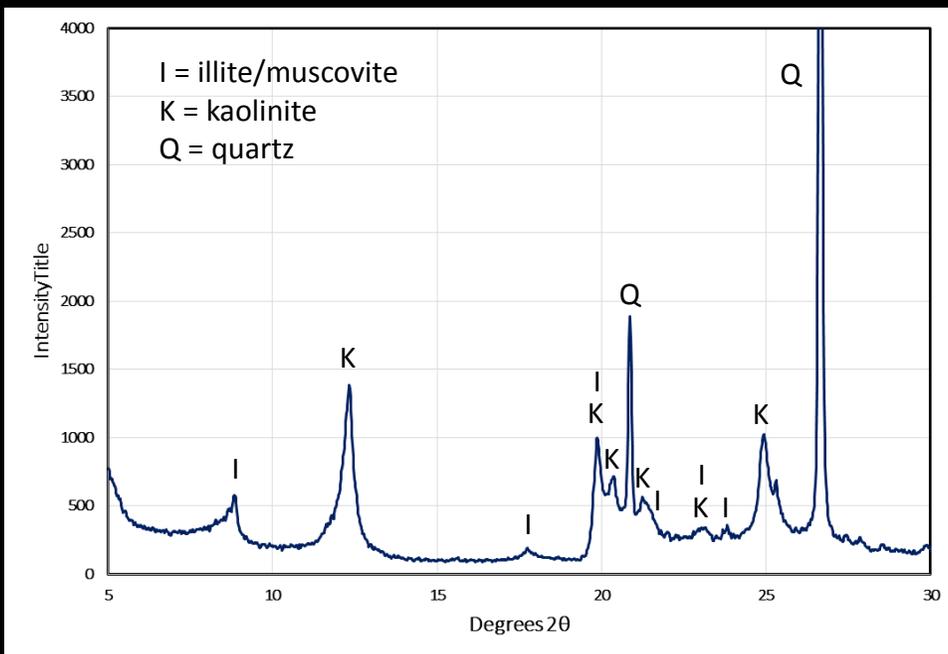
- As erosional rate of source material (granite) increases, Ti/Al increases
- In a given cyclothem, Σ REE correlates positively with Ti/Al
- Suggests that REE in sampled material is physically weathered from Alleghenian granitoids
- Suggests REE was not transported as a dissolved, soluble species but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



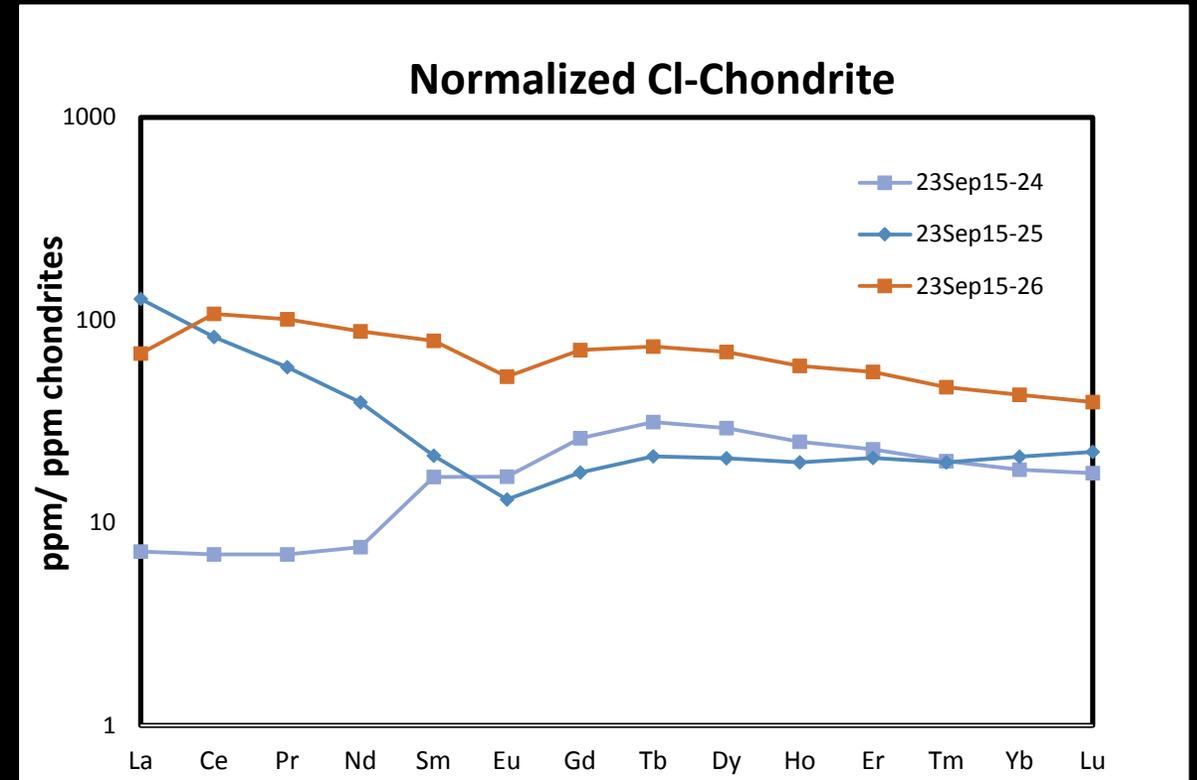
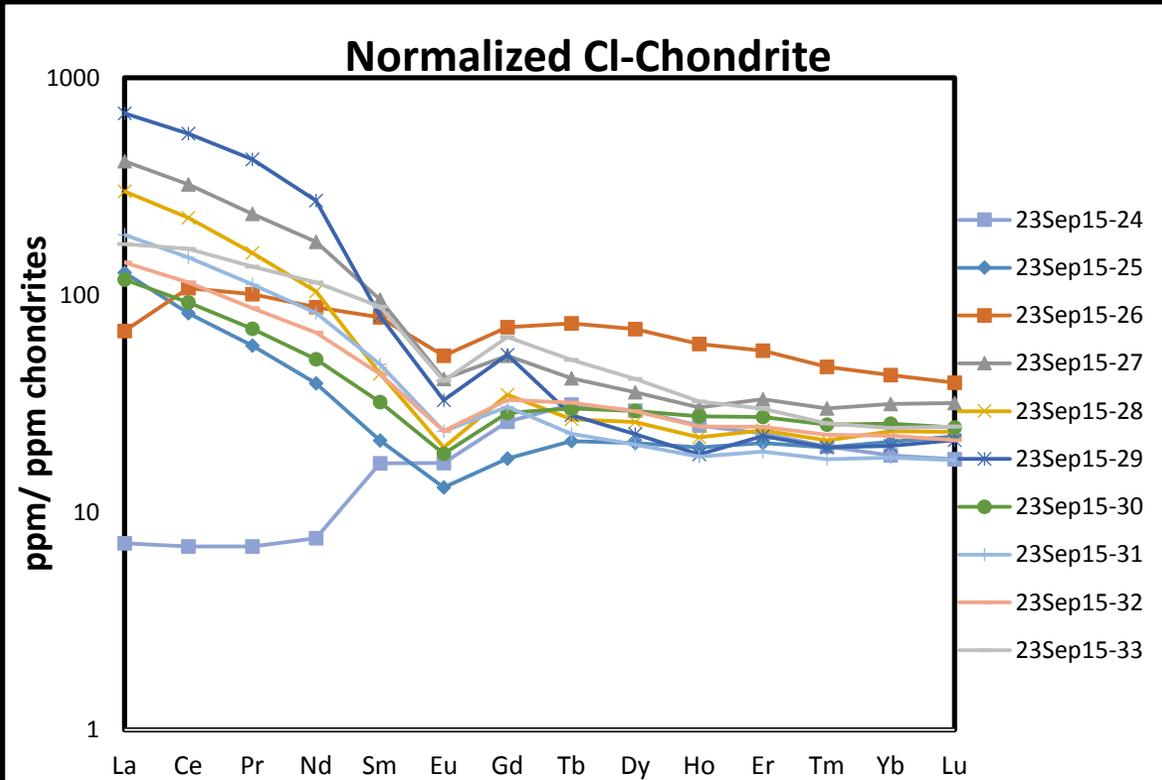


- Strong correlation between V and total REE
- REE spike at 617 ft
 - Calm, anoxic conditions (high V)
 - No dramatic change in Ti/Al
 - Is this evidence of ion-exchangeable REE?

- 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



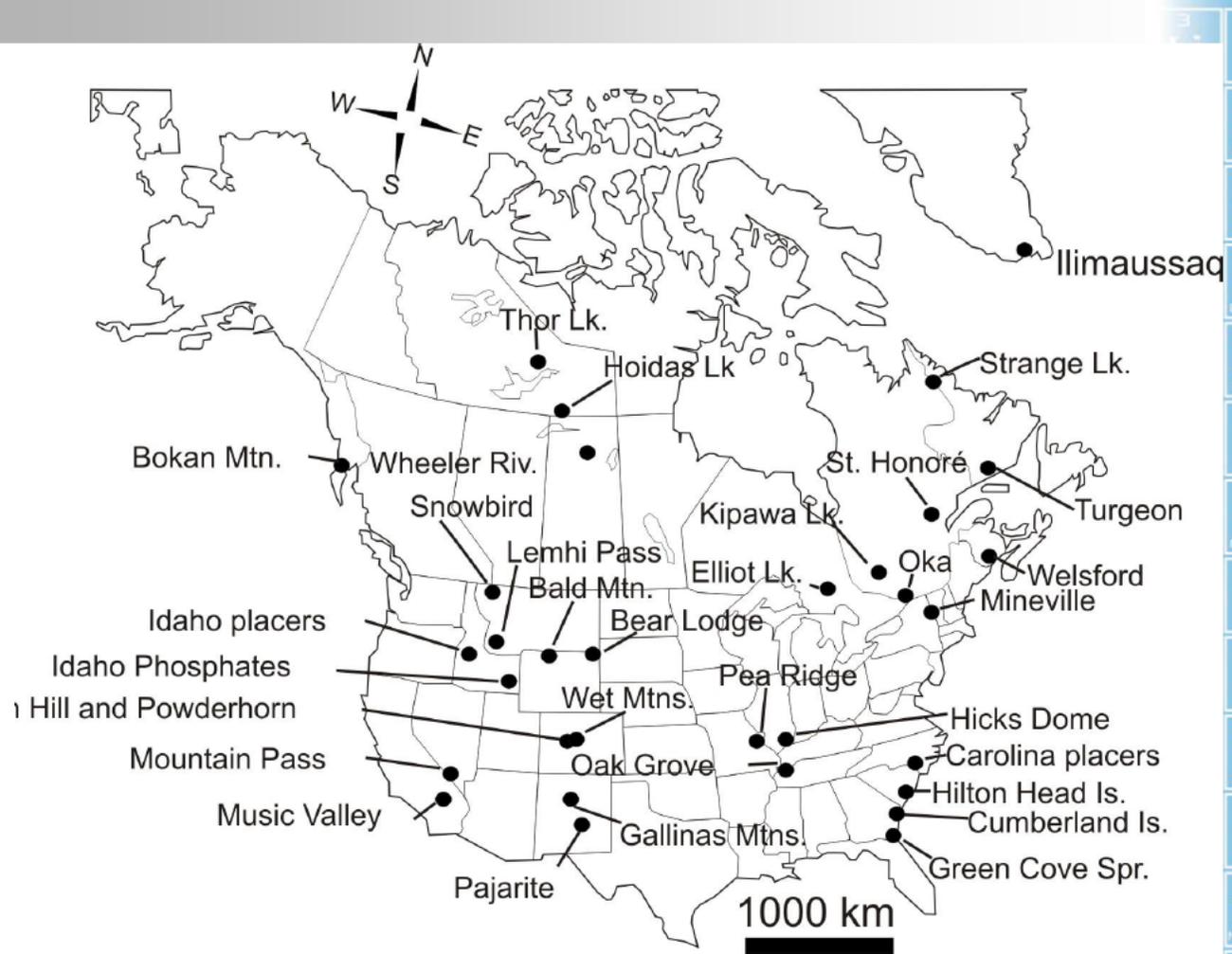
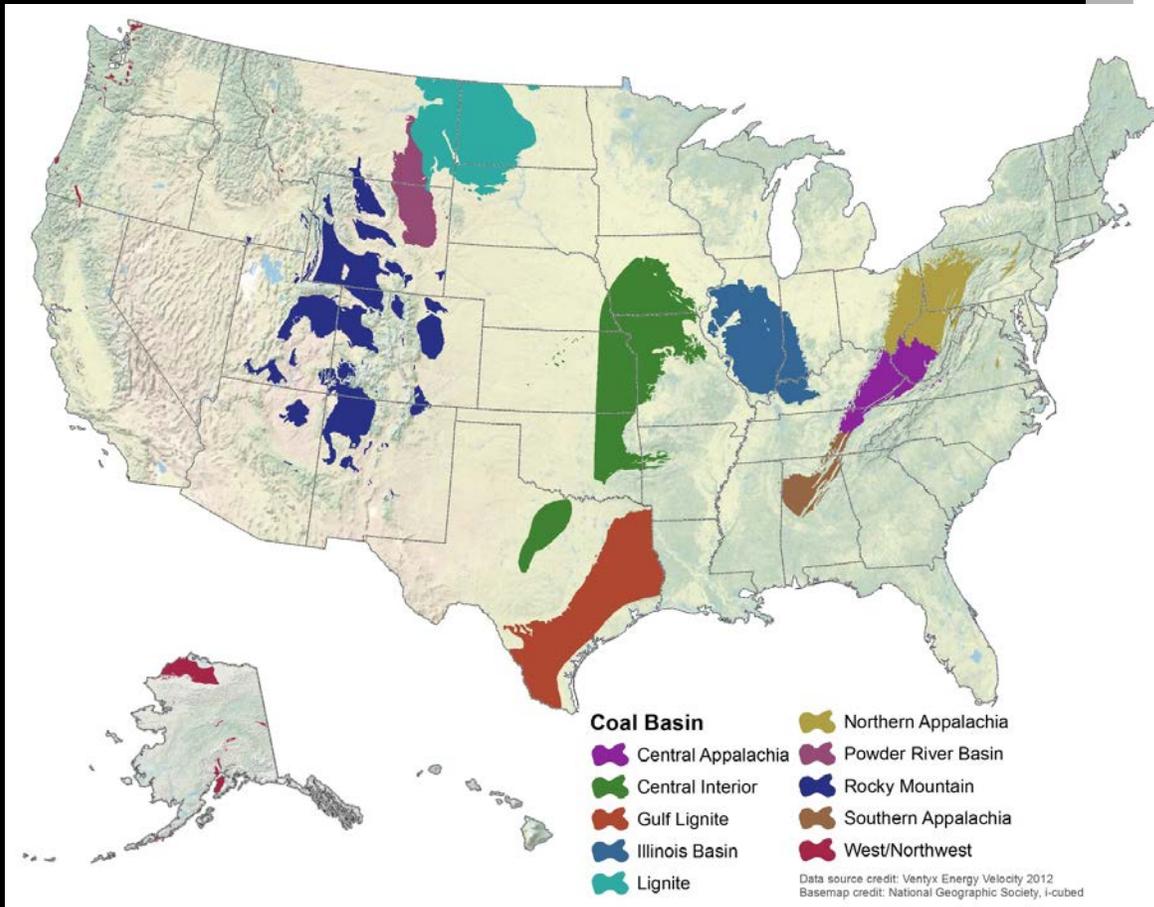
REE distribution in field samples



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



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

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
Phosphodorite						
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