Evidence of Mobilization of REE: Geological Aspects of REE Formation in the United States

Tracy Bank[1,2] Elliot Roth[1,2] Bret Howard[1] Phillip Tinker [1,2] William Garber [1,2] Megan Macala [1,2] Evan Granite[1]

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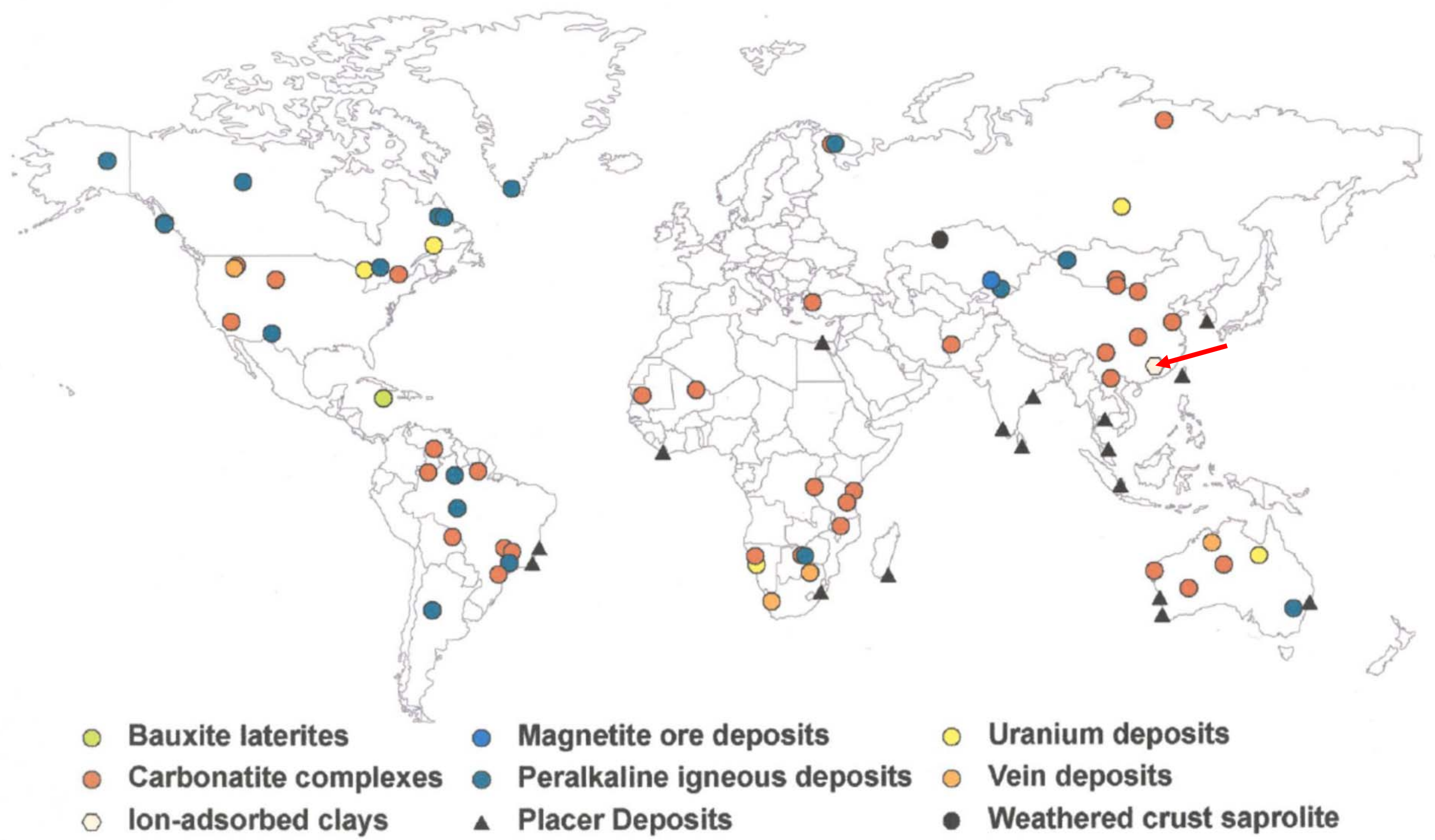
[1]National Energy Technology Laboratory, [2]AEC

Solutions for Today | Options for Tomorrow

REE-Y deposits types

Majority of discovered deposits are carbonatite and peralkaline in origin



Map courtesy of David Lentz, University of New Brunswick

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Carbonatite Deposits

Bayan Obo, China; Mountain Pass, CA; Bear Lodge, WY; Iron Hill, CO;

- Carbonatites are *peculiar* igneous rocks that contain >50 wt % carbonate minerals
- Only a few hundred known locations on Earth
  - Occur mostly in continental rift zones
- Possibly form after primary magma separates into two immiscible carbonate and silicate melts
- Important sources of Cu, Nb, and REE
- Bayan Obo is also the world's largest carbonatite deposit
  - Several wt % REE oxides mainly as bastnaesite REE(CO_3)F
- Mountain Pass is dominated by Ce and other LREE-enriched bastnaesite

Mountain Pass Carbonatite

Peralkaline Deposits

Lovozero, Russia; Bokan Mountain, AK

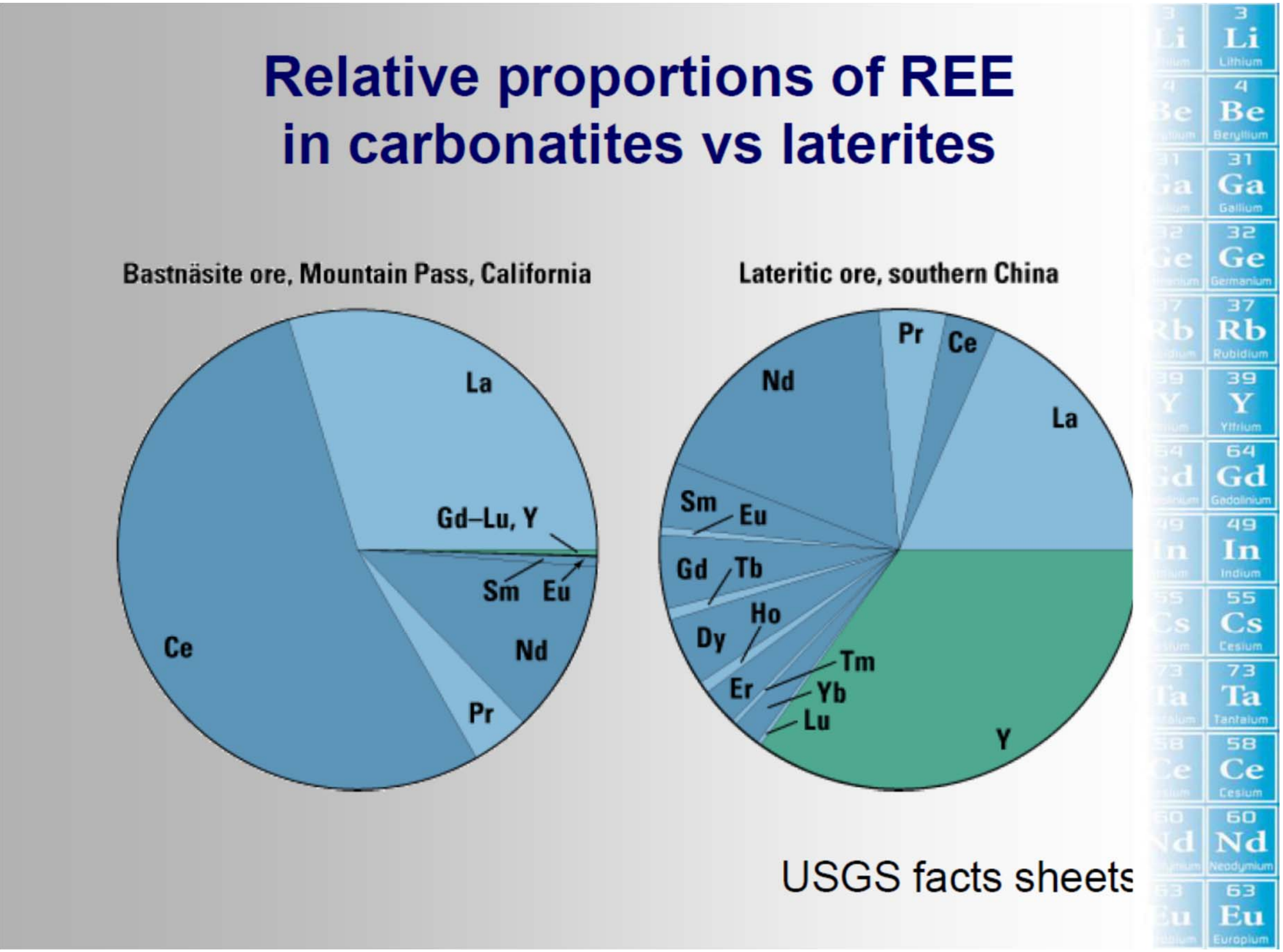
- Peralkaline igneous rocks are oversaturated with Na and K with respect to Al
  - $(Na_2O + K_2O) > Al_2O_3$
- Magma may form from partial melting of metasomatized (hydrothermally altered) mantle
- Peralkaline granites form in island arc and mountain building regions (including Appalachia)
- Sinha et al (1989) identified peralkaline granites in plutonic suites of Appalachia
- REE-bearing minerals include apatite($Ca_5(PO_4)_3$), xenotime (YPO_4), monazite ($LREEPO_4$) and lesser bastnaesite
- Peralkaline and carbonatite deposits often enriched in U and Th

Ion Adsorbed/ Laterite Deposits

Southern China; Eastern USA?

- REE found in soils deposited after weathering of REE-bearing granitic source rocks
- Occur primarily in China
  - sometimes called laterite deposits
- REE were mobilized during weathering and 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

REE-enriched regolith, Virginia
Photo courtesy Nora Foley, USGS



- Laterite deposits contain higher concentrations of HREE
- Adsorption is not as selective as preciptation
- Laterite deposits are more valuable than bastnaesite in current market

Are Ion-Adsorbed deposits in the US?

- Formation of REE laterites dependent on both enriched source material AND chemical weathering conditions
- Similar granitic source rocks in Eastern US (Appalachia) may have weathered to form REE-enriched laterite deposits
- Warm, humid conditions occurred during the Pennsylvanian time period during coal deposition
- Foley and Ayuso (2015) found REE-enriched regolith (2900 ppm) weathered from the mildly peralkaline Robertson River batholith, VA
- Rozelle et al., 2016 reported highly exchangeable sources of REE from PA clay samples
- Efforts are underway to characterize sedimentary overburden and underclay related to coal seams in PA

Sources of REE-enrichment in sedimentary rocks in coal basins

- Enrichment in coal basins of REE can occur due to:
  1) Elevated concentrations in source rock material (ash)
  2) Physical and chemical weathering that selectively concentrates REE-minerals during deposition of ash
  3) Remobilization of REE-bearing minerals during coalification/ diagenesis
  4) Post-deposition enrichment from solution/ waters
  5) REE enrichment from volcanic ash

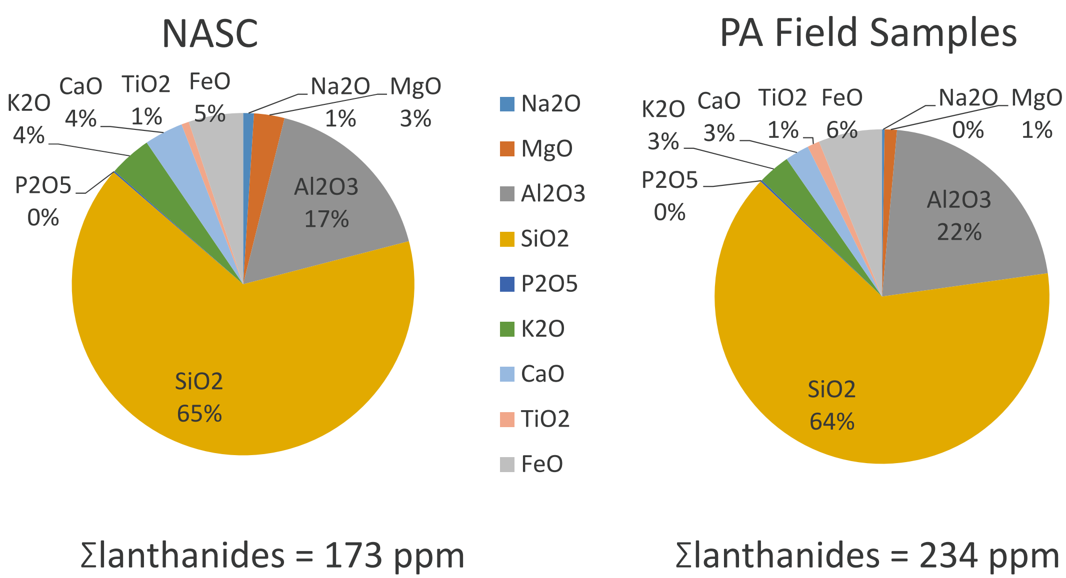
REE Enrichment in Sedimentary Rocks from PA

>700 field samples collected to date

Complete characterization including: moisture %, ash %, CHNS, ICP-MS and ICP-OES after $LiBO_2$ fusion digestion

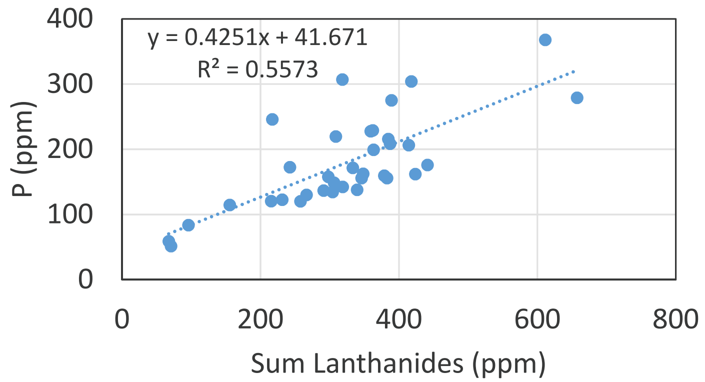
Summary Statistics indicate:

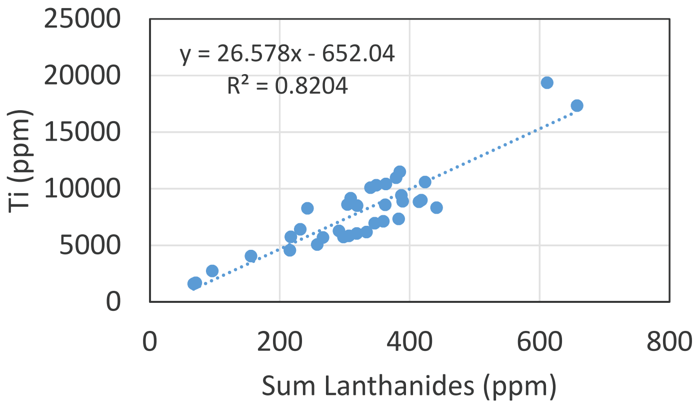
- Field samples are mostly shale
- Ash content nearly identical to NASC (Gromet et al., 1984)
- <0.5 to 86 wt% C
  - Ave 12 wt% C
- Max Σlanthanides = 850 ppm (whole rock), 1135 ppm (dry ash)
- Average Σlanthanides 33% > NASC

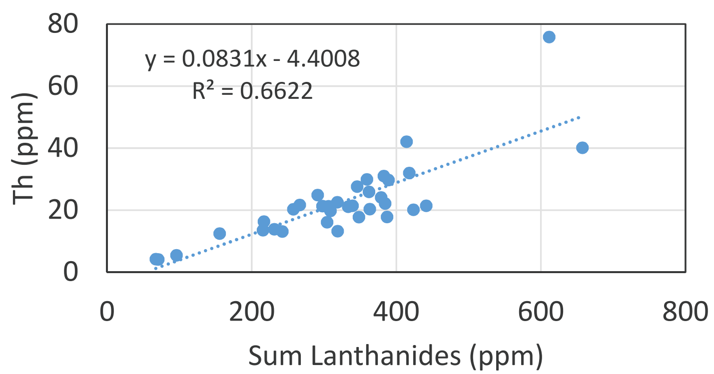


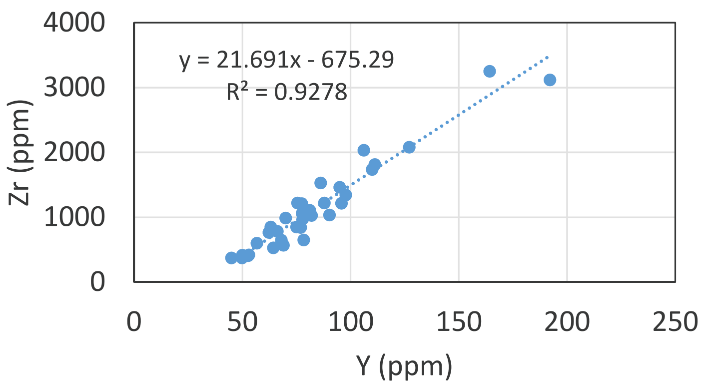
REE Enrichment in Sedimentary Rocks from PA

Element Correlations in Cored Samples N = 35

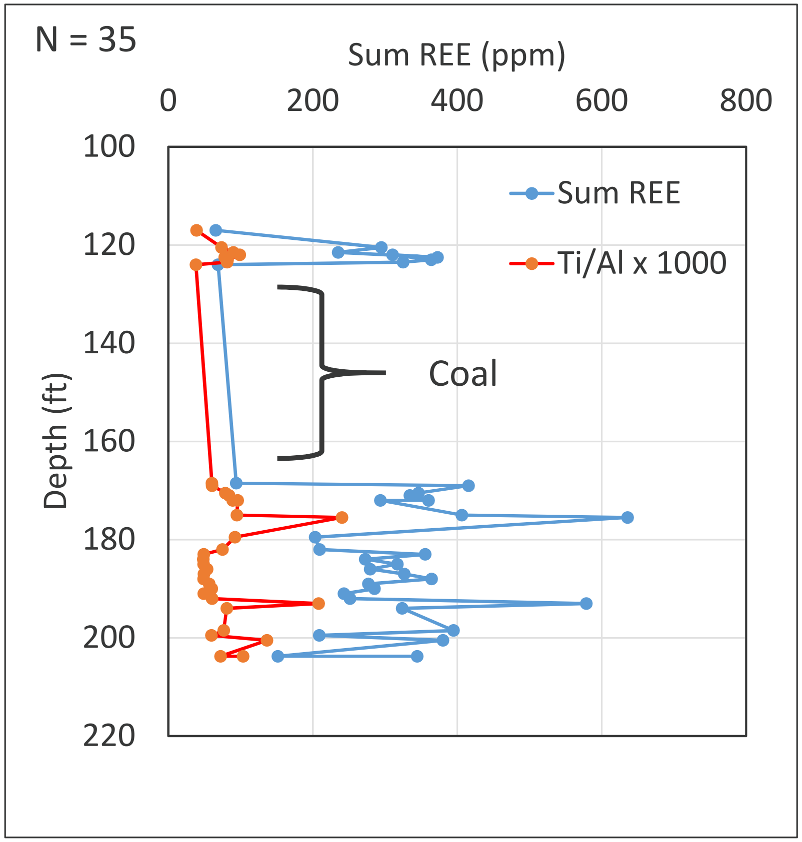








REE Enrichment in Sedimentary Rocks from PA

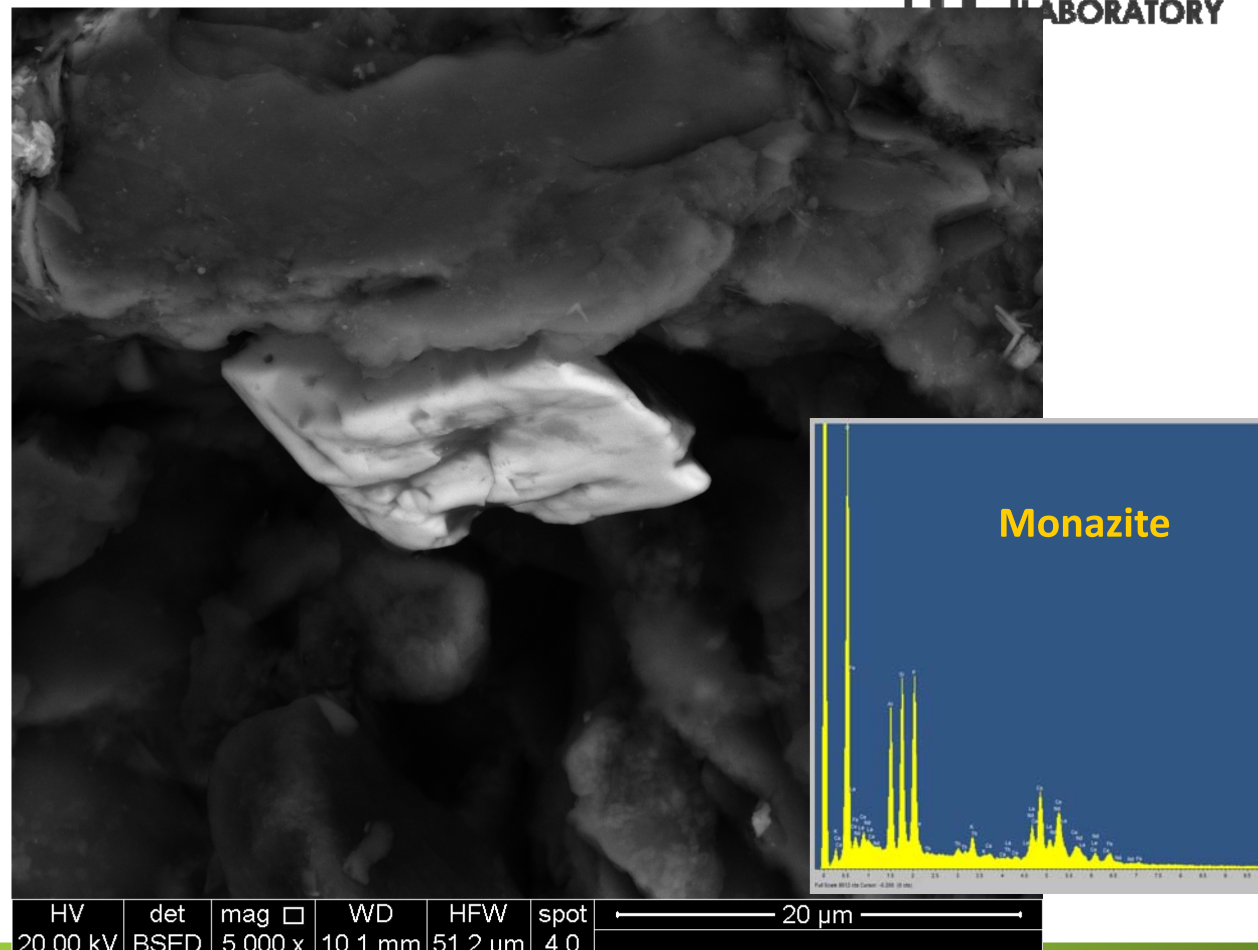


REE correlate with Ti/Al

- As erosional rate of source material (granite/granitoid) increases, Ti/Al increases
- In the studied core, ΣREE correlates positively with Ti/Al (R^2 = .51)
- Suggests that REE in sampled material is physically weathered from source rock
- Suggests REE were transported as non-reactive mineral grains and not as dissolved, soluble species

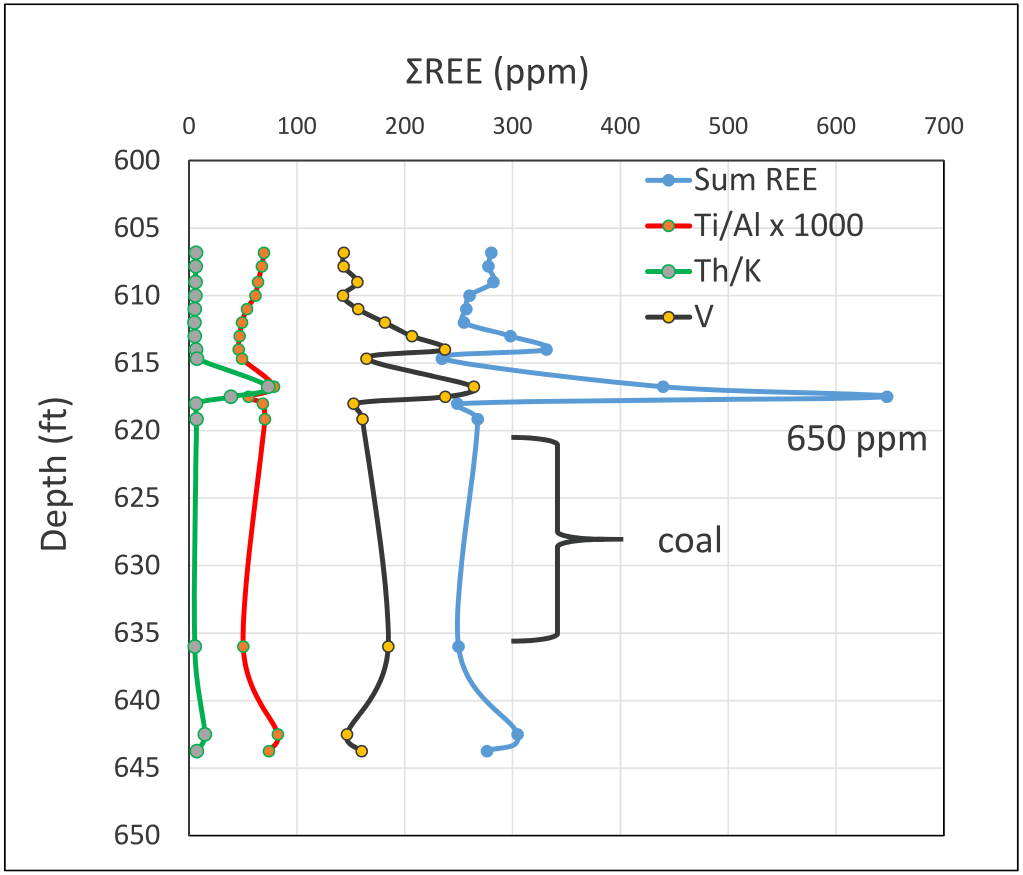
REE Enrichment in Sedimentary Rocks from PA

- Data from SEM support the theory that REE are contained in discrete grains
- REE likely concentrated in small (<20 µm) semi-euhedral monazite grains
- Monazite likely detrital in origin

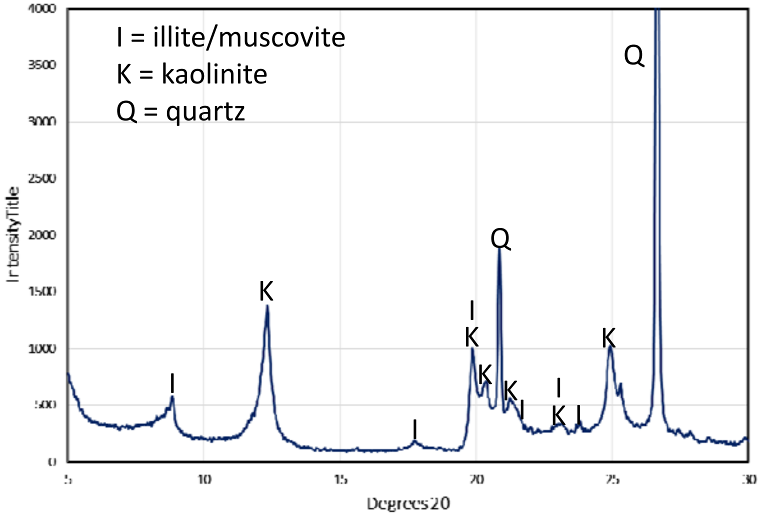


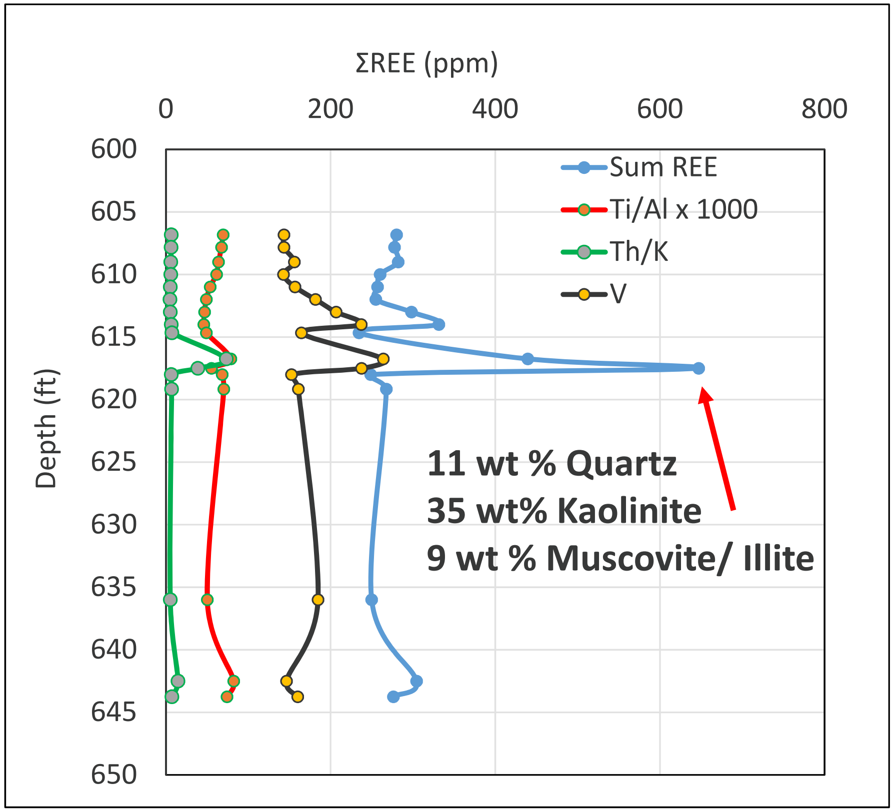
REE Enrichment in Sedimentary Rocks from PA

- High REE spike in sample with no correlation to Ti/Al
- Sample contains 650 ppm REE (dry ash)
  - 603 ppm REE (whole rock)
- High V signal indicates calm conditions on deposition
- High Th/K might indicate clay adsorption
  - Th/K > 12 usually indicates kaolinitic clays
  - Spike Th/K = 73, background Th/K = 6



REE Enrichment in Sedimentary Rocks from PA





Average XRD results of field samples

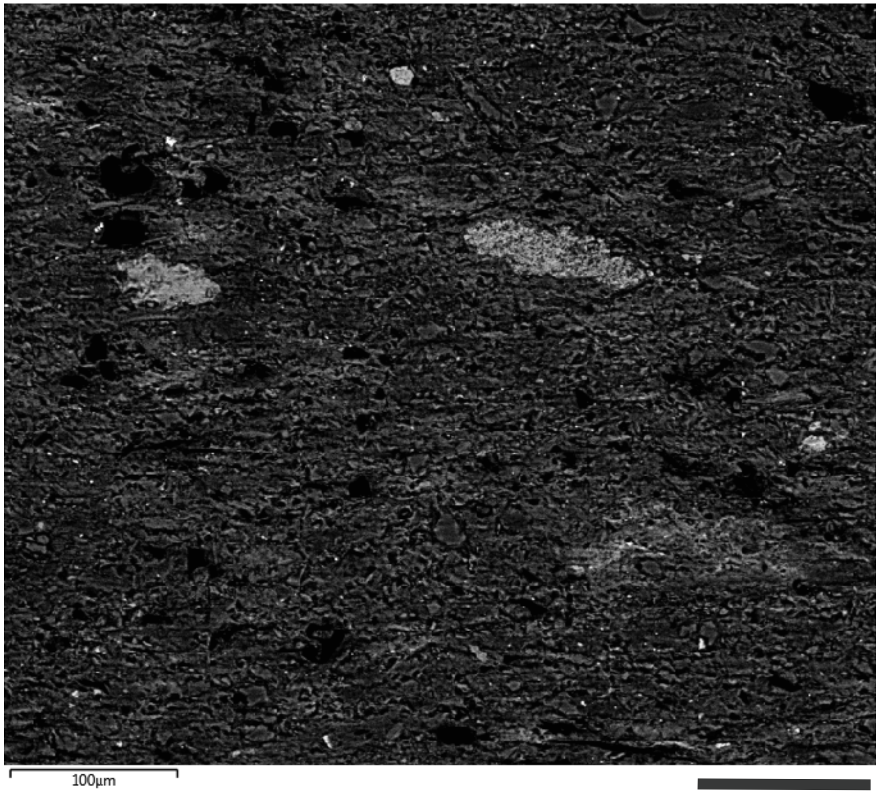
- 34 wt% Quartz
- 26 wt% Muscovite/ Illite
- 13 wt% Kaolinite

REE Enrichment in Sedimentary Rocks from PA

- **Cation Exchange Capacity of sample ~10 meq/100 g**
  - CEC of Chinese laterite deposits 10.8-16.6 meq/100 g (Cocker, 2012)
- **NH_4Cl and $(NH_4)_2SO_4$ extraction experiments were completed to determine % REE occurring as sorbed/exchangeable phases**
  - 10:1 liquid to solid ratio, 1 hour reaction time, ambient temperature
  - Results measured by ICP-MS
- **< 1% of REE extractable using either method**
  - Chinese deposits report 30-90% extractable REE
  - Up to 90% extractable REE from Upper Kittaning Bed, PA (Rozelle et al., 2016)
- **REE are not *currently* ion adsorbed**

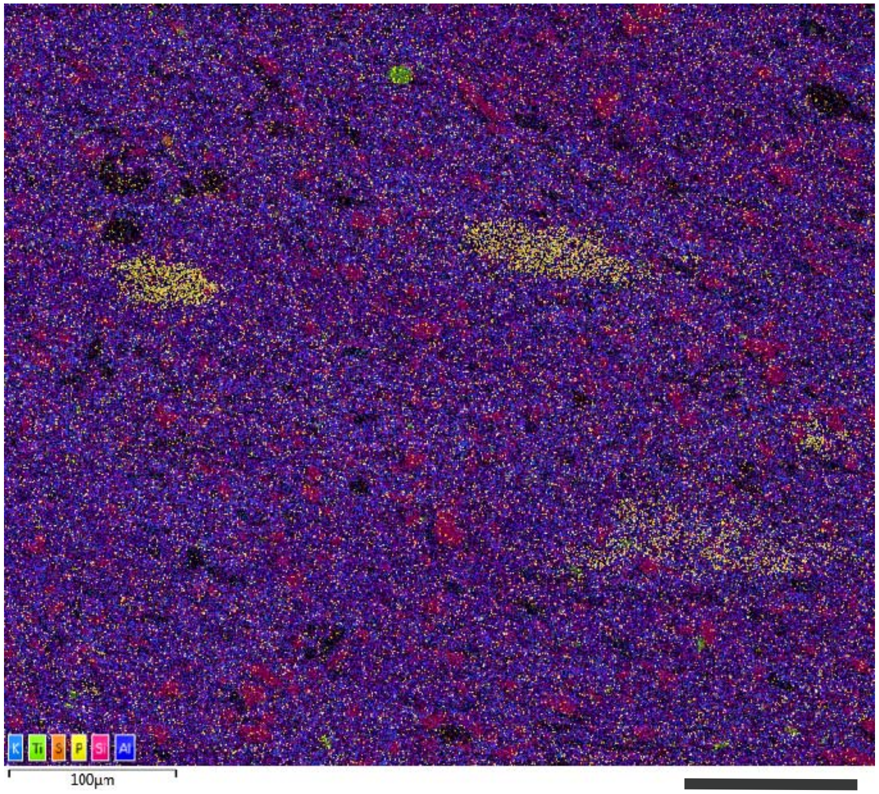
REE Enrichment in Sedimentary Rocks from PA

Backscattered electron image courtesy Bret Howard



100 μm

Stacked EDS maps (yellow zones are P and REE enriched)



100 μm

REE Enrichment in Sedimentary Rocks from PA

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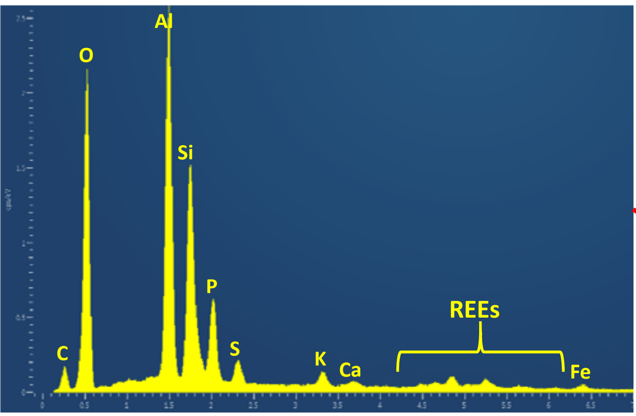
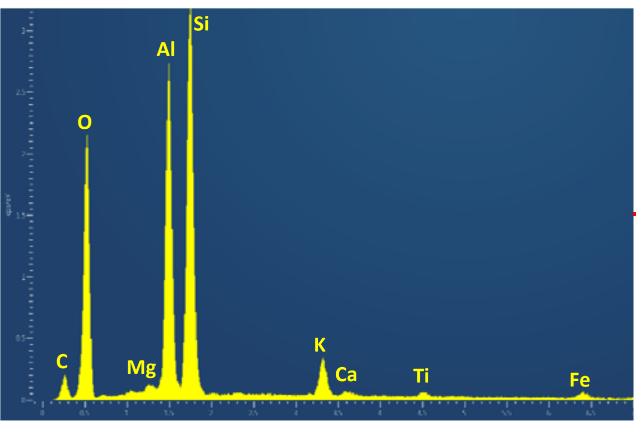
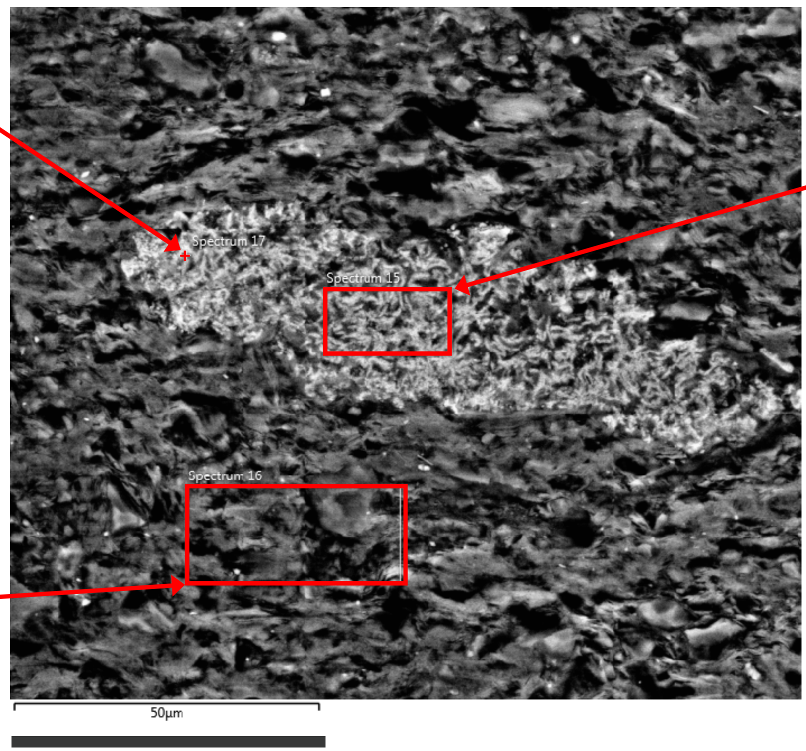
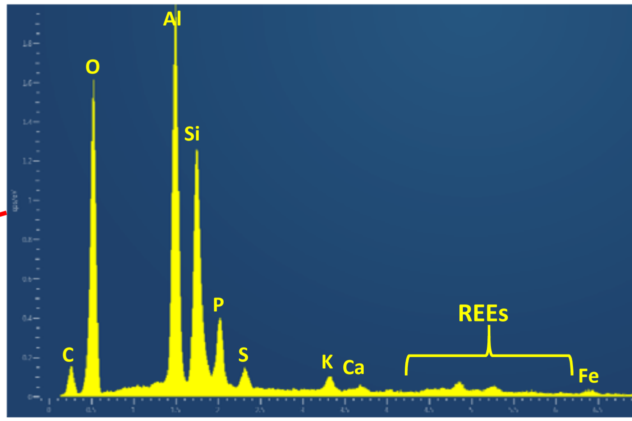




Backscattered electron image and data courtesy of Bret Howard, NETL

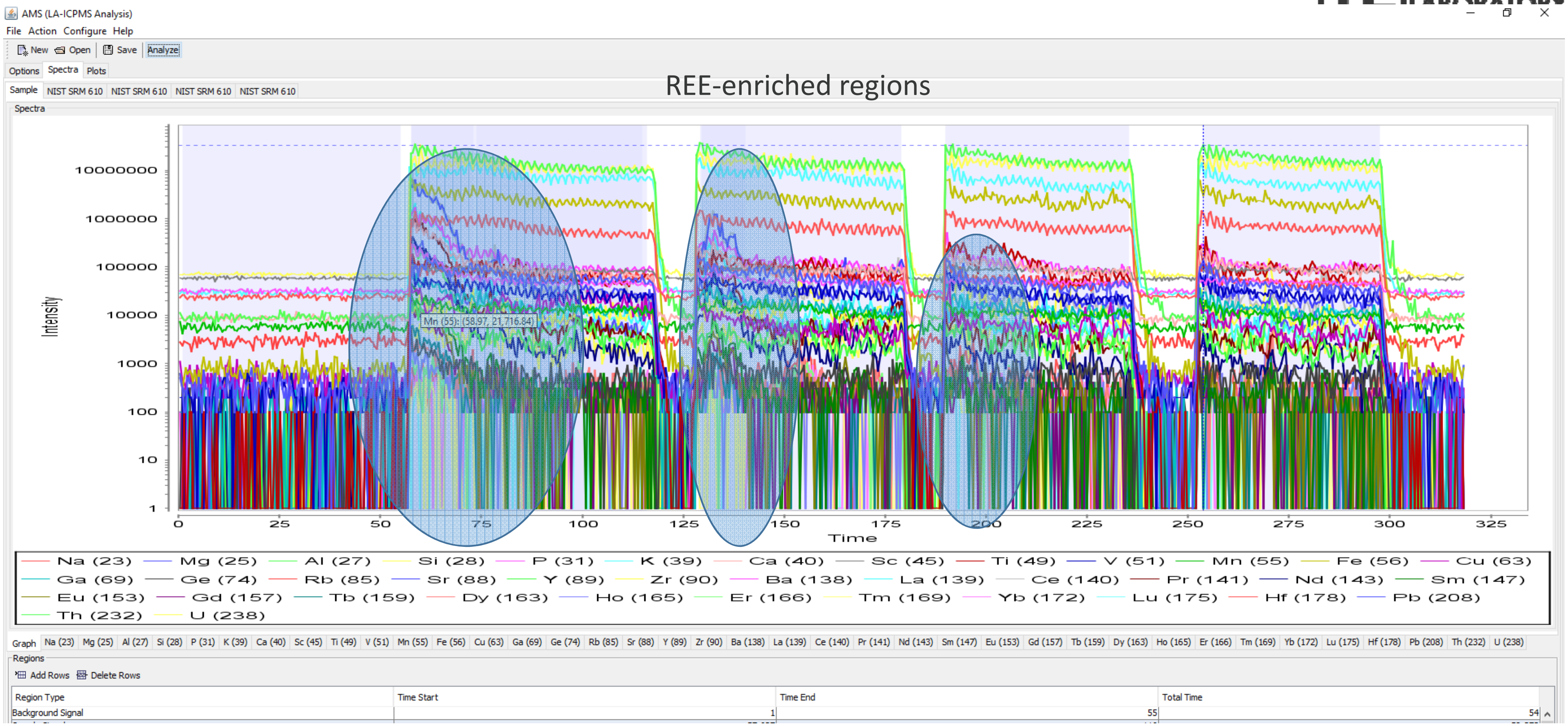


50µm

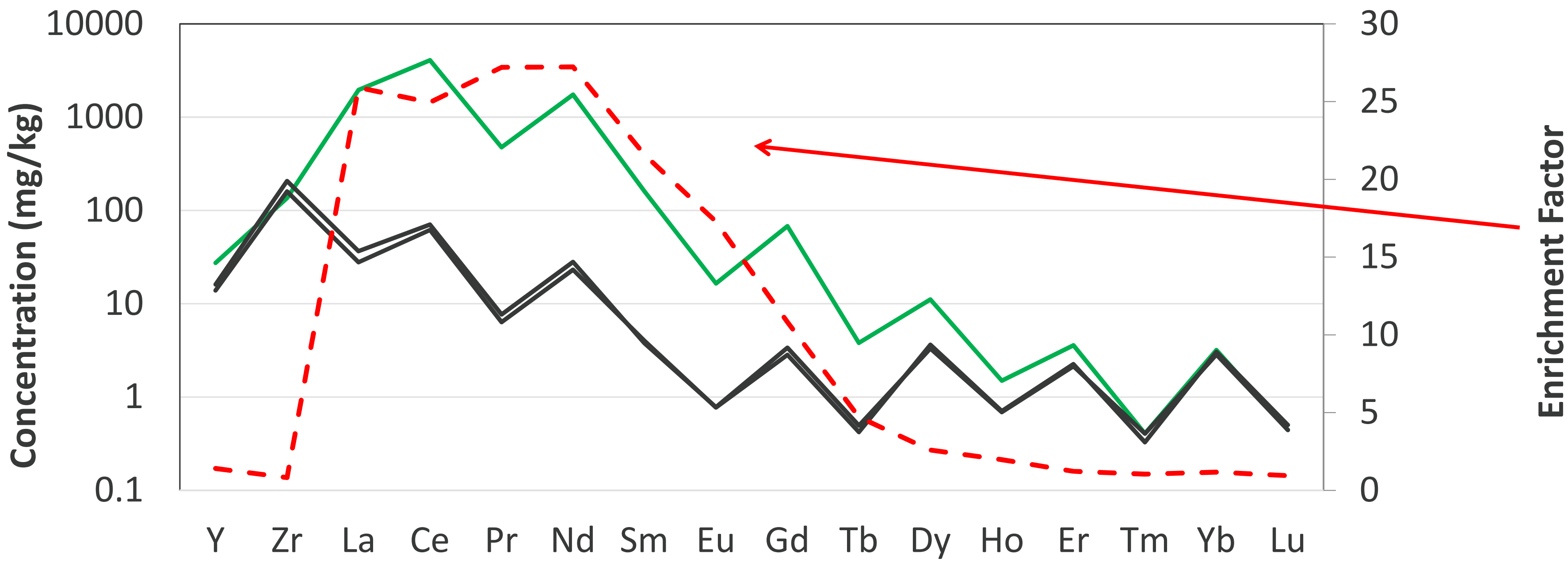


Fine crystals of REE-bearing phosphate in aluminosilicate matrix

LA- ICPMS Data

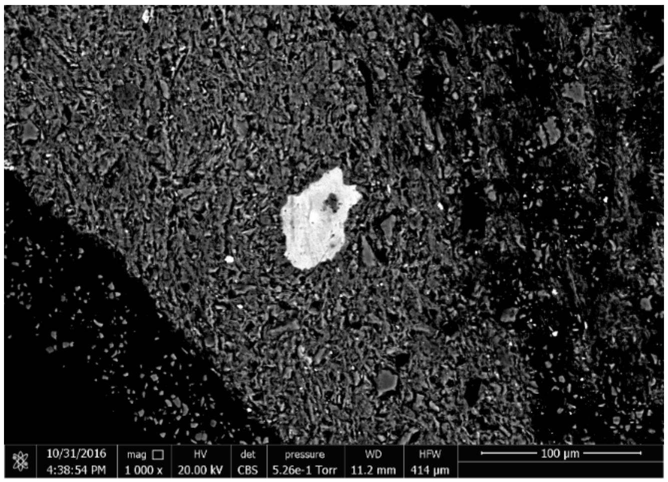


30 x REE enrichment in fine crystals

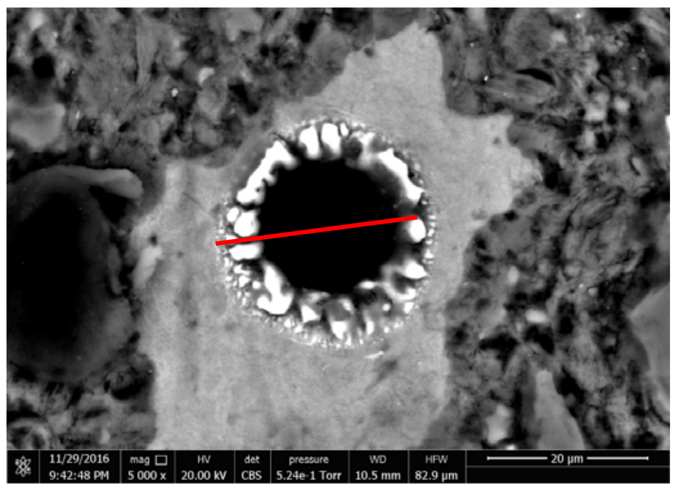


Re-crystallized Diagenetic Monazite

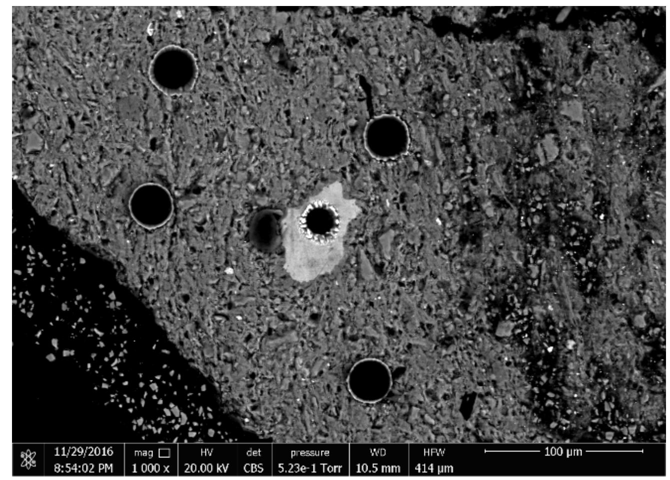
Before LA



Bret Howard SEM images

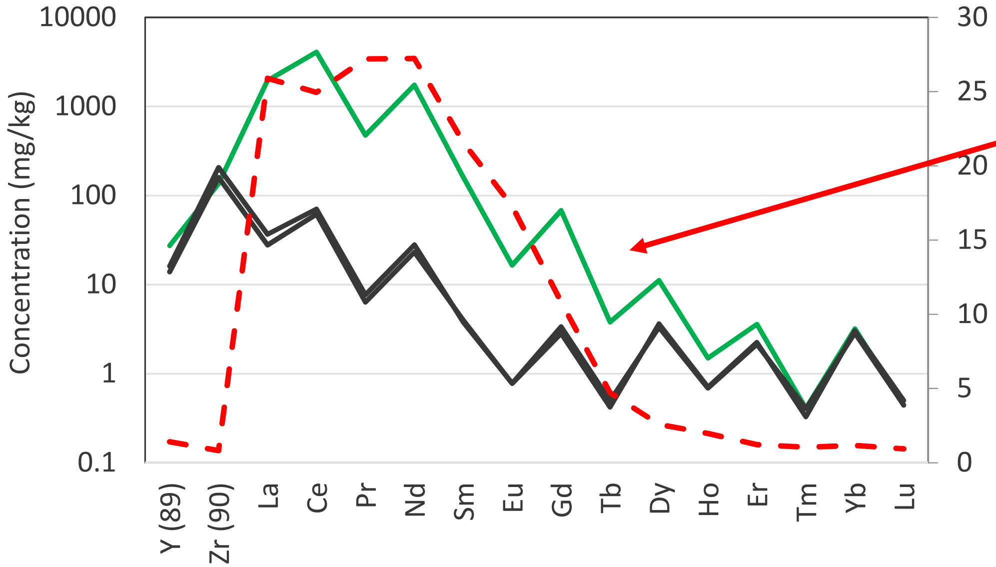


After



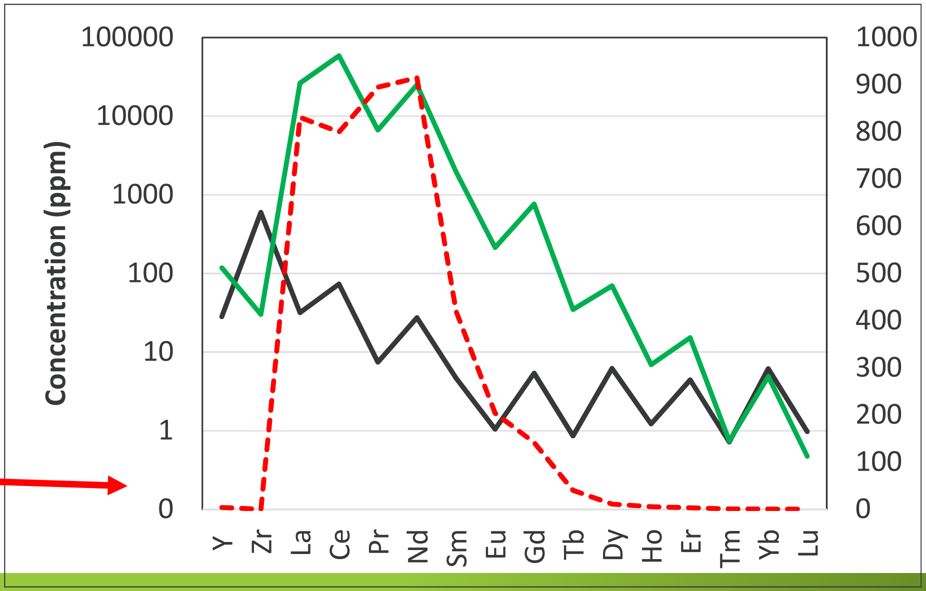
24 µm spot

Slow recrystallization of ion adsorbed REE



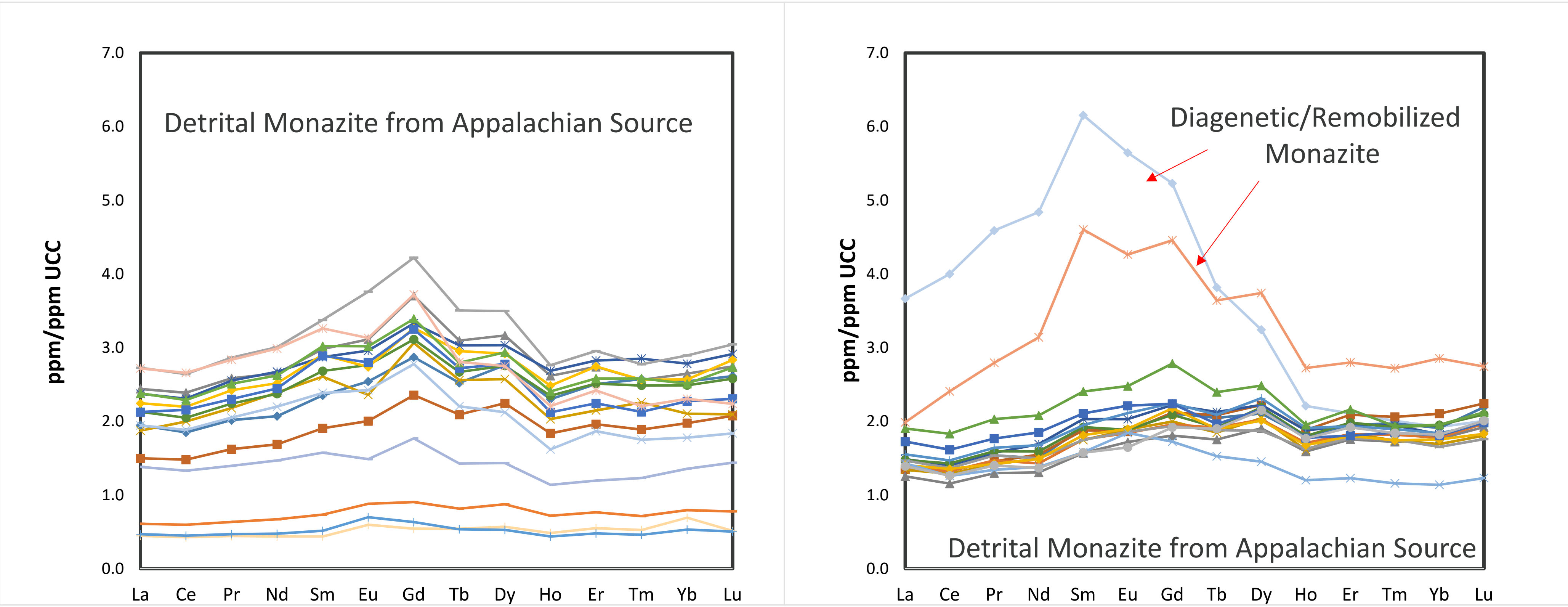
Finely crystalline diagenetic monazite is MREE- HREE enriched

Diagenetic monazite becomes more LREE enriched over time as it slowly recrystallizes and pulls in more LREE from matrix



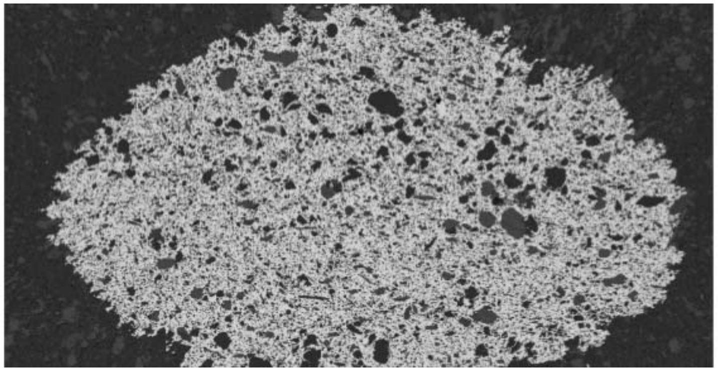
Comparison of Diagenetic and Detrital REE

Normalized to Upper Continental Crust courtesy Elliot Roth, NETL



Significance of Diagenetic Monazite

- **Diagenetic monazites have been reported in literature**
  - Milodowski and Zalasiewicz, 1991; Kryza, 2004; Alipour-Asll, et al., 2012
- **Crystals form after clay-adsorbed REE precipitate during diagenesis**
- **Clay adsorbed REE may be from weathered detrital grains or possibly a second source of REE**
- **Marine limestones surrounding the coal seam indicate seawater may have been a secondary source of REE**



Diagenetic Monazite Source: Bruker

REE Enrichment in Sedimentary Rocks from PA

Conclusions

- **Field samples with high ΣREE (>600 ppm) have been collected in Pennsylvania**
- **Most samples with high REE contain physically weathered monazite grains probably from an Appalachian granitoid source**
  - Ti/Al correlates strongly with REE and indicates REE were concentrated during periods of high erosion
  - Some of these granitoids may be peralkaline and REE-enriched
- **High REE in clay-rich regions are geochemically distinct**
- **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)**
- **Diagenetic monazite crystals indicate that the adsorbed REE have been re-precipitated and are no longer extractable**

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