Rare Earth Minerals
In the World and in Missouri

Missouri Geological Survey
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Rare Earth Elements (REEs)

Rare earths are not rare
However, the number of currently known economic concentrations are limited

They are metals, rather than earths
Discovered in 1794 by Finnish chemist Johan Gadolin
At time, term “earths” used for oxide compounds

First very impure REE metal was made in 1826

REE concentrates
Rare Earths Elements (REEs)

Defined as group of 17 elements comprising scandium, yttrium and the lanthanides

Lanthanides: lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium
Rare Earth Elements (REEs)

Light-group rare-earth elements (LREE) defined as lanthanum through gadolinium

Heavy-group rare-earth elements (HREE) defined as terbium through lutetium, yttrium
Major Rare Earth Ore Minerals

Bastnaesite \((\text{Ce, La, Nd, Pr})(\text{CO}_3)\text{F}\)

Monazite \((\text{Ce, La, Nd, Th})\text{PO}_4\)

Xenotime \(\text{YPO}_4\)

Loparite \((\text{Ce, Na, Ca})(\text{Ti, Nb})\text{O}_3\)

Ion adsorption type (IAT) REE ions adsorbed on clay

Y-rich and La-Nd-rich
REE Mineral Reserves

121 million tons of known rare-earth oxide (REO) reserves (USGS estimated for 2012)

REE World Mineral Production

140,000 tons of REO produced
(USGS estimated for 2012)

REE Metal Properties

Lower toxicity than many metals they replace
  Rechargeable batteries
High melting and boiling points
Lower metal density while adding strength
High luster
High conductivity
Strong reducing agents
Compounds are generally ionic
Often strongly paramagnetic
React to form wide range of compounds
Rare Earth Element Applications
Wind Turbines (Nd, Pr, Dy, Tb)

Rare-earth based permanent magnet generator
  Gearless generator
  Fewer moving parts
  Significantly increased reliability
  Reduce maintenance costs
  Higher efficiency at low wind speeds
  Lower weight

Large wind turbine generator requires ~1,300 lbs of REE

Source: Jim Hedrick – USGS (retired)
Rare Earth Batteries (La, Nd, Pr, Dy, Tb)

Pure La metal or REE metals and Fe (mischmetal)

Hybrid vehicles, mobile phones, laptops, rechargeable power tools, cameras

Other REEs in hybrid vehicles:

Electric motor, regenerative braking system

Typical hybrid vehicle contains 62 lbs of REE

Almost 200,000 tons worldwide (March 2013)

~78,000 tons for hybrids in the US (October 2012)

Source: Jim Hedrick – USGS (retired)
Oil Refining

REEs used to produce fluid cracking catalysts (La)
Used to “crack” crude oil to diesel, kerosene, gasoline, propane, natural gas
“Crack” better than other catalysts
Improve yield of “light” fraction
More gasoline from heavier oils

Source: Jim Hedrick – USGS (retired)
Compact Fluorescent Bulbs, LEDs
   Use Y, Ce, Eu, Tb to make natural white light

Hard Disk Drives (Nd, Pr, Dy, Tb)
   REE magnet provides greater hard drive stability
   More information storage space

Flat Panel Screen Displays, CRTs
   (Y, Eu, Tb, Gd, Pr, Ce)
   Required for red color
   Make other colors brighter
   Screens last longer

Source: Jim Hedrick – USGS (retired)
Defense Applications

REEs used in:
- Missile motors (Sm)
- Missile counter-measures
- Tail-control fins
- Smart bombs
- Laser targeting systems
- Coatings in jet engines – alloy protection (Y)
- REE phosphors in avionics – screens
- Sonar (Tb, Dy)
- Radar, satellite communication (Y, Gd)
- Electronic surveillance
- Missile tracking (Y)
- Early warning systems (Y)
- Drones
- Targeting systems
- Etc.

Source: Jim Hedrick – USGS (retired)
Other Uses

Clean industrial pollution
Medical imaging, tracers
Communication systems
Anti-lock brakes
Metal alloys
Ceramics, coatings
Microwaves, refrigeration
Water treatment
UV resistant glass
Glass polishing

And thousands more....

Source: Jim Hedrick – USGS (retired)
Strategic/Critical Classification Criteria

U.S. Department of Energy
Critical or essential for Clean Energy Technology
Dy, Eu, Tb, Nd, Y, Ce, La

U.S. Department of Defense
Required for defense and national security
Import dependent
No viable substitute
Geopolitical concern over source
All REEs

U.S. Geological Survey
Import reliance – percentage of material imported
REEs – essentially 100% net import reliance

Source: Jim Hedrick – USGS (retired)
The Principal Rare Earth Elements Deposits of the United States - A Summary of Domestic Deposits and a Global Perspective

Keith R. Long, Bradley S. Van Gosen, Nora K. Foley, and Daniel Cordier
Southeast Missouri Iron Metallogenic Province

Seven major iron deposits

Numerous minor deposits

Pea Ridge is only deposit in Province with confirmed rare earth element concentrations
Granite central pluton
Trachyte porphyry ring intrusion
Granite porphyry ring intrusion
Subvolcanic granite massif
Rhyolite volcanic rocks
Inactive mine
Undeveloped deposit
Town
Missouri
Pea Ridge

In production from 1964 - 2001

Primary product was magnetite for steel production
  Also coal desulfurization, concrete densification, high power magnets, iron pigments

Pyrite sold for sulfuric acid

Waste rock sold as road metal

REE not produced
  Potential ore was stockpiled underground
Steeply dipping, discordant tabular orebody
Host rocks are rhyolites, ash-flow tuffs
400m of overlying Paleozoic sedimentary cover
188+ million tons of 59% iron
(measured + indicated)
Economically significant REE reserves
Lithologic Zones

Rhyolite host rock
Amphibole-quartz zone
Magnetite zone
Hematite zone
Silicified zone
REE- and Au-bearing breccia pipes

Zonation outward from massive magnetite core to FeOx-cemented breccias
Magnetite

Forms core of deposit

Only iron oxide mineral recovered during mining

Interstitial apatite and monazite

Fine-grained and massive to fine-crystalline and granular
Magnetite

Known vertical extent of ore – 670 m

Drilling to depth of 1040 m from surface

Deposit widens at depth

Geophysical work (USGS) indicates deposit extends to greater depth

The bottom of the deposit has not been intersected
Magnetite

Assays from past operating levels
50-67% magnetic iron
Average 57% iron (77% magnetite)

Assays at greater depths –
66% magnetic iron (85% magnetite)

Assays in 5 holes at depth:

<table>
<thead>
<tr>
<th>Depth (feet)</th>
<th>Fe content</th>
</tr>
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<tbody>
<tr>
<td>2765-3105</td>
<td>63%</td>
</tr>
<tr>
<td>2785-2955</td>
<td>68%</td>
</tr>
<tr>
<td>2725-3005</td>
<td>66%</td>
</tr>
<tr>
<td>2935-3287</td>
<td>67%</td>
</tr>
<tr>
<td>3035-3180</td>
<td>65%</td>
</tr>
</tbody>
</table>

Individual assays as high as 70% iron
94% magnetite
Pea Ridge contains high-quality, high-purity FeOx mineralization

Chemical-quality and specialty iron oxide products

- Water purification
- Air emission “green” catalysts
- Coal desulfurization
- Heavy media
- Concrete densification
- Iron pigments
REE-Bearing Breccia Pipes

Elongate to ovoid in plan view
Horizontal length as much as 60 m; widths reach 15 m
Steeply dipping (>60°)
Minimum vertical extent of 120 m
Maximum vertical extents unknown

Located on footwall and eastern edge of orebody
At contact between iron oxide and host rock
Located along faults and at faulted contacts
Suggests structural control on emplacement
REE-Bearing Breccia Pipes

Clasts of rhyolite, actinolite, iron oxide, silicified rock

Clasts are subrounded to rounded
< 1 mm to several meters

Matrix of rock flour, k-spar, chlorite, quartz, calcite, apatite
REE-bearing minerals
Cemented by barite, orthoclase
REE-Bearing Minerals

Primary:
- Monazite \((\text{Ce,La,Nd,Th})\text{PO}_4\)
- Xenotime \(\text{YPO}_4\)

Rare:
- Bastnaesite \((\text{Ce,La,Nd,Pr})\text{CO}_3(\text{OH,F})\)
- Britholite \((\text{Ca,Ce})_5(\text{SiO}_4,\text{PO}_4)_3(\text{OH,F})\)
- Allanite \([\text{Ca(Ce,La,Y)}](\text{Al}_2\text{Fe}^{2+})\text{O(OH)}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\)

Tentative:
- Tengerite \((\text{CaY}_3(\text{CO}_3)_4(\text{OH})_3\cdot3\text{H}_2\text{O}\)
- Synchisite \((\text{Y,Ce})\text{Ca(}\text{CO}_3\text{)}\text{F}_2\)
REE-Bearing Breccia Pipes

0.5-1.0 mm crystals with granular texture
Some euhedral crystals
Discrete grains segregated in pipe matrix
Radial crystal aggregates

Monazite and xenotime replacing rhyolite fragment
Disseminated to nearly total
Also replaced matrix

Monazite and xenotime fracture fill in brecciated barite and feldspar crystals
Irregular grains
Some grains appear abraded
Larger grains than replacement
REE Concentrations

Total REO concentrations:

Grab samples -
4.9 to 37.8 weight %
avg of 20.3 weight %

U.S. Bureau of Mines bulk samples -
7 to 25 weight %
avg 12 weight %

Proven reserves: 200,000 tons REO
72,000 tons REO in X-11 pipe
(600,000 tons 12% REO)

Pipes are open at top and at depth
Other Sources – REE

Abundant inclusions of monazite, xenotime and possible britholite in interstitial apatite

Inclusions of monazite in apatite common at greater depths in mine

Apatite recovered during magnetite beneficiation

Photo courtesy of Kevin Conroy

USGS photo
Other Sources – REE

Pea Ridge Mine Tailings

USBM testing on reprocessing of mine tailings

Flotation of phosphate minerals in tailings
  Primarily apatite
  Monazite, xenotime, britholite

Resulted in 70%+ recovery of available phosphate minerals

Up to 95% recovery of rare earth-bearing minerals from concentrate
  Gravity separation
  Average size REE grains - 10 µ

Recovered Ce, La, Y
  Significant Dy, Sm, Nd
  Also Er, Eu, Ga, Gd, Pr, Yb, Ge, Hf, Ho

2012 drilling evaluation
  2.7 million tons of apatite in tailings lake
  Apatite separate: 3.0% REE
Pea Ridge Genesis

Intrusion of Fe- and Si-rich magma into shallow subvolcanic chamber

Lowered temperature and pressure lead to liquid immiscibility

Early Fe-rich fluid altered rhyolite to actinolite and quartz

Magnetite emplacement, formation of magnetite-cemented breccias

Later oxidation to hematite

Emplacement of Si-rich fluid – silicification

Breccia pipe emplacement
Breccia Pipe Genesis

Remaining fluid in subvolcanic chamber underwent further cooling
  Fluid enriched in K, Ba, REE, U, Th, P, F, Cl, Au

Exsolution of vapor phase from fluid lead to second boiling event

Increase in volume caused rapid expulsion of fluid from chamber
  Expansion reopened fractures/faults

Resulted in brecciation and mixing of clasts

REE-bearing minerals precipitated in breccia
Summary

188+ million tons of iron reserves remain at Pea Ridge
  Additional probable reserves
  Chemical quality and specialty products
  Base of deposit not intercepted

High-grade chemical quality ores fill strategic needs
  Currently imported from Sweden

Proven market for waste rock

REEs are potential by-products
  Pea Ridge has 15 of 17 REEs, including HREEs

Reserves in breccia pipes, as inclusions in apatite

Potential REE resource in mine tailings
Thank you!

Questions?