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The Genesis of Rare Earth Element Ore Deposits

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The REE and the Periodic Table

H ¹											n'il			P		100	He ²
Li ³	⁴ Be										~	B ⁵	C 6	N ⁷	08	۹ ه	10 Ne
¹¹ Na	12 Mg								2			13 Al	Si ¹⁴	15 P	S ¹⁶	CI ¹⁷	18 Ar
19 K	²⁰ Ca	21 SC	22 Ti	23 V	Cr ²⁴	²⁵ Mn	²⁶ Fe	27 Co	28 Ni	²⁹ Cu	Zn ³⁰	Ga ³¹	³² Ge	33 As	Se	Br ³⁵	36 Kr
87 Rb	³⁸ Sr	Y ³⁹	Zr ⁴⁰	41 Nb	42 Mo	43 TC	Ru Ru	Rh ⁴⁵	⁴⁶ Pd	Ag ⁴⁷	48 Cd	49 In	Sn	51 Sb	⁵² Te	53 	Xe ⁵⁴
55 Cs	56 Ba	57 La	⁷² Hf	⁷³ Ta	W ⁷⁴	Re ⁷⁵	76 OS	77 Ir	78 Pt	⁷⁹ Au	80 Hg	81 TI	⁸² Pb	83 Bi	⁸⁴ Po	At ⁸⁵	86 Rn
⁸⁷ Fr	⁸⁸ Ra	89 AC	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	114 Uuq					
	Light REE Heavy REE																
		Ce	Pr ⁵⁹	Nd	Pm ⁶¹	Sm	Eu ⁶³	Gd ⁶⁴	Tb ⁶⁵	66 Dy	67 Ho	Er ⁶⁸	Tm ⁶⁹	Yb	⁷¹ Lu		
		Th ⁹⁰	⁾ 91 Pa	U ⁹²	93 Np	³ 94 Pu	Am	Cm ⁹⁶	Bk	Of Of	Es	Fm	¹⁰ Md	1 102 NO	2 103 Lr		

Ytterby and Bastnäs

"Ceria"



Wilhelm Hisinger

Bastnäs



"Yttria"



Johan Gadolin

A Tale of Ceria and Yttria

Bastnäs (Skarn)

Cerite {Ce₉(Fe,Mg)Si₇O₂₇(OH)₄}

Ytterby (Pegmatite)

Gadolinite {Y2FeBe2Si2O10}

Allanite

Cerite

1 cm

Tungsten – heavy stone



The REE and Wind Power



Wind power now supplies 11.4% of the European Union's electricity (128,752 MW); growing at 15.6% /yr.

In the U.S., it supplies 4.4% of electrical energy (65,879 MW); also growing at 15.6%/yr.

In Canada, it supplies 4% of electrical energy (9,694 MW); growing at 19.3%/yr.

Wind turbines are driven by (Nd,Dy) $_2$ Fe₁₄B magnets that require 730 Kg of Nd and Dy per MW.

The REE and Hybrid Cars



Each hybrid / electric car consumes ~28 Kg of REE mainly in magnets and La-Ni-hydride batteries During 2013 hybrid car sales in the US totalled 500,000 units up 14% from 2012, representing 3% of new car sales.

Some Other Uses of the REE



The Strategic Importance of the REE



Rifts, Mantle Plumes and the REE

Peralkaline Granites

Carbonatites, Nepheline Syenites

- 1. A REE/HFSE, volatile rich (H_2O,CO_2, CI, F_2) mantle.
- 2. Low degrees of partial melting, produces F-REE-HFSE-rich peralkaline mafic silicate magmas, carbonatites,
- Crust metasomatised by mantle fluids produces REE/HFSE felsic melts



LREE and HREE – Carbonatites and Peralkaline Silicate Igneous Rocks

LREE are more incompatible (higher Z/r) than HREE and will concentrate in the first partial melts or last residual liquids of crystallisation – carbonatites.



The Mountain Pass LREE Deposit

Reserves: 18.4x10⁶ tons @ 7.98 wt.% TREE₂O₃



Dolomite Carbonatite LREE Ore

Bsn: Bastnäsite-(Ce) {REECO₃F} Mnz: Monazite-(Ce) (REEPO₄)



Castor (2008)

The REE mineralisation is generally thought to be magmatic, e.g., Castor (2008). However, an experimental study by Gysi and Williams-Jones (2015) shows that bastnäsite-(Ce) decomposes at 338 °C!!



The Wicheeda LREE Deposit, British Columbia

Resource: 11.3 million Mt grading 1.95 wt.% TREO





Three Stages of Dolomite

Dolomite 1 (Primary); Dolomite 2 (Hydrothermally altered Dolomite 1); and Dolomite 3 (Hydrothermal dolomite filling vugs)

Bastnäsite-(Ce) {REECO₃F} and parisite-(Ce) {CaREE₂(CO₃)₃F₂}



Isotopic Evolution of the Carbonates

Application of the Raleigh Distillation Model of Ray and Ramesh (2000) assuming that the carbonatite "stewed in its own juices" and that the fluid. contains equal proportions of H_2O and CO_2 .



Lofdal, a HREE-rich Deposit Classified as Carbonatite-Hosted

Cut-Off	Tonnes	LREO	HREO	TREO	REO	HREO
%TREO	million	%	%	%	Tonnes	Proportion
0.1	2.88	0.08	0.24	0.32	9,234	76.3%
0.2	1.62	0.09	0.37	0.45	7,358	80.9%
0.3	0.90	0.09	0.53	0.62	5,594	85.6%
0.4	0.58	0.09	0.69	0.78	4,477	88.3%
0.5	0.39	0.09	0.84	0.93	3,673	90.3%
0.6	0.28	0.09	1.00	1.09	3,039	91.8%
0.7	0.20	0.08	1.18	1.26	2,524	93.5%

In-situ Indicated Mineral Resource

In-situ Inferred Mineral Resource

Cut-Off	Tonnes	LREO	HREO	TREO	REO	HREO
%TREO	million	%	%	%	Tonnes	Proportion
0.1	3.28	0.07	0.20	0.27	8,973	74.7%
0.2	1.80	0.08	0.30	0.37	6,748	79.3%
0.3	0.75	0.08	0.47	0.56	4,180	85.1%
0.4	0.42	0.08	0.64	0.72	3,071	88.8%
0.5	0.27	0.08	0.81	0.89	2,377	90.9%
0.6	0.21	0.08	0.91	0.99	2,049	92.1%
0.7	0.16	0.07	1.03	1.10	1,717	93.5%

Lofdal Geology



Sovite Dykes Intruding Nepheline Syenite in the Main Intrusion



REE-Mineralised Structures

The REE mineralised structures give the appearance of ferrocarbonatite dykes but are instead fault-controlled sodic fenites (albitites) that have been altered to calcite and/or ankerite. The red colour reflects pyrite oxidation.





Lithogeochemical Survey

Structure with zones of strong fenitisation and carbonate alteration (dark grey); weaker fenitisation (light grey). Coloured dots show distribution of Dy. Xenotime-(Y) concentrates in the structure and monazite-(Ce) distally from it.



Xenotime-(Y) Mineralisation

Albitite cut by xenotime-(Y)-zircon-biotite veins and then replaced by calcite. Xenotime-(Y) {HREEPO₄}



The Bayan Obo LREE Deposit, China

The world's richest REE deposit with reserves of 48 million tonnes grading 6 wt.% REE_2O_3 , Bayan Obo, is responsible for 70% of global REE production





Monazite (LREEPO₄) and bastnäsite (LREECO₃F), together with magnetite, hematite and fluorite replaced H8 dolomite . Fluids 5 – 15 wt% NaCl eq., T ~ 400 °C.

Smith and Henderson (2000)



The Nechalacho Deposit: Potential HREE Producer

Measured and Indicated Resources in the Basal Zone at Various NMR Cut-offs

(August 2013)

Basal Zone	Tonnes (millions)	% TREO	% HREO	% HREO/ TREO	% ZrO ₂	% Nb₂O₅	% Ta₂O₅				
US\$345 NMR Cut-Off (Reflects entire Basal Zone)											
Measured	12.56	1.71	0.38	22.50	3.20	0.405	0.0404				
Indicated	49.33	1.62	0.35	21.27	3.07	0.405	0.0398				
US\$800 NMR Cut-Off (Approximately Reflects High Grade "Basin")											
Measured	5.11	2.20	0.58	26.17	4.23	0.52	0.0544				
Indicated	16.15	2.20	0.55	24.87	4.13	0.52	0.0542				
and the second											

Geological Setting of the Nechalacho Layered Suite, Blachford Lake Complex





The Blachford Lake Complex is interpreted to be part of a large alkaline igneous province produced by an equally large mantle plume associated with the break-up of the Archean Supercontinent.

Sheard et al. (2012); Möller and Williams-Jones (2014)

Cross-Section through part of the Nechalacho Layered Suite



Hydrothermal Alteration

The upper 250-300 m of the layered suite has been intensely altered, largely obliterating primary igneous textures

Biotite-magnetite alteration - early

Albitisation - late



The Ore Zones

Zircon cumulates





Pseudomorphs after Eudialyte cumulates



Basal Zone REE Mineralization

Pseudomorphs after eudialyte Na₁₅(Ca, REE)₆(Fe,Mn)₃Zr₃NbSi₂₅O₇₂(O,OH,H₂O)₃ Pseudomorph after eudialyte in plane polarised light



Mnz - monazite (LREEPO₄)

Hydrothermally unlocking and concentrating the REE

Progressive alteration of zircon to fergusonite-(Y) (HREENbO₄)



Magmatic concentration of the REE in the Nechalacho Layered Suite



Residual, volatileand HFSE-rich magma(s) saturates with REE-bearing zirconosilicates (zircon, eudialyte); soon afterwards it exsolves a hydrothermal fluid

The Stability of REE F & CI Complexes



Log K REEF²⁺

Stability of REEF²⁺ complexes high, decreases with increasing atomic number.

Log K REECI²⁺

Stability of REECl²⁺ complexes, moderate, decreases with increasing atomic number.

Solid lines – experimental data of Migdisov et al. (2009) Dashed lines – theoretical predictions of Haas et al. (1995)

Migdisov et al. (2009)

Modelling REE Mineral Solubility in a F-Bearing Brine



The REE are transported dominantly as chloride complexes despite the greater stability of REE fluoride complexes, because HF is a weak acid and REE fluoride is relatively insoluble.

Migdisov and Williams-Jones (2014)

Simplified Model for the Hydrothermal Transport and Deposition of REE

Mixing of magmatic and external fluids

Fluid/rock interaction

REE Mineral Deposition

Mobilisation of REE as acidic REE-CI complexes complexes at high T.



Deposition of REE minerals, due to increasing pH, decreasing temperature and high activity of a depositional ligand. "These elements [the rare earths] perplex us in our researches, baffle us in our speculations and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying and murmuring strange revelations and possibilities."

(Sír William Crookes, February 16th, 1887)