



UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

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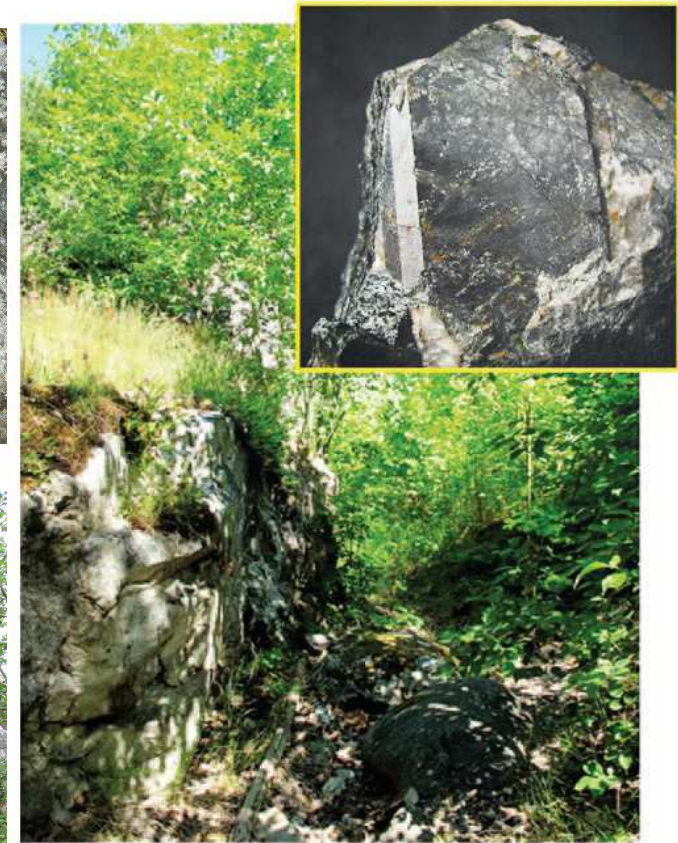
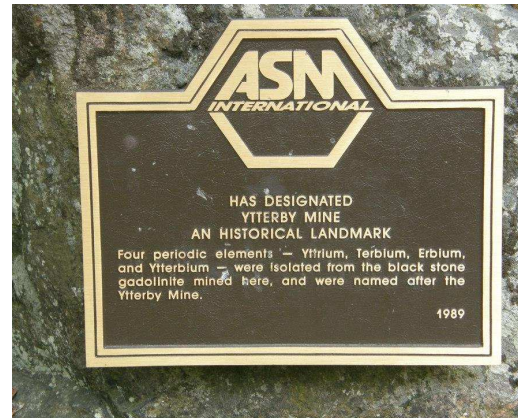
**Terre rare protagoniste nella
transizione ecologica:
aspetti geologici ed economici**

Introduzione

H	Rare Earth Elements by Geology.com																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 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																	

Introduzione - Un po' di storia

Nella seconda metà del 1700, C.A. Arrhenius scopre delle masse nerastre nella miniera di Ytterby vicino a Stoccolma. Queste, in qualche modo, arriveranno a J. Gadolin che scopre che quella massa nerastra è un nuovo minerale (che successivamente prenderà il nome di Gadolinite, $(\text{Ce}, \text{La}, \text{Nd}, \text{Y})_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$) in cui è contenuto una nuova «terra» che verrà chiamata yttria (1794). Nel 1803 venne scoperto il cerio in un minerale proveniente dalla miniera di Bastnäs (Svezia). Solamente nel 1842 si scoprì che la terra denominata yttria era in realtà composta da diversi elementi tra cui l'ittrio vero e proprio, il terbio e l'erbio. Nel 1879 tramite la spettroscopia a fiamma si scoprì il samario e via via gli altri. L'ultima terra rara naturale ad essere scoperta sarà il lutezio nel 1907. Il promezio è radioattivo con un tempo di decadimento molto veloce e venne scoperto solamente negli anni 40 dopo i primi esperimenti nucleari.



Introduzione - Un po' di storia

Table 1.1 Discovery of rare earth elements

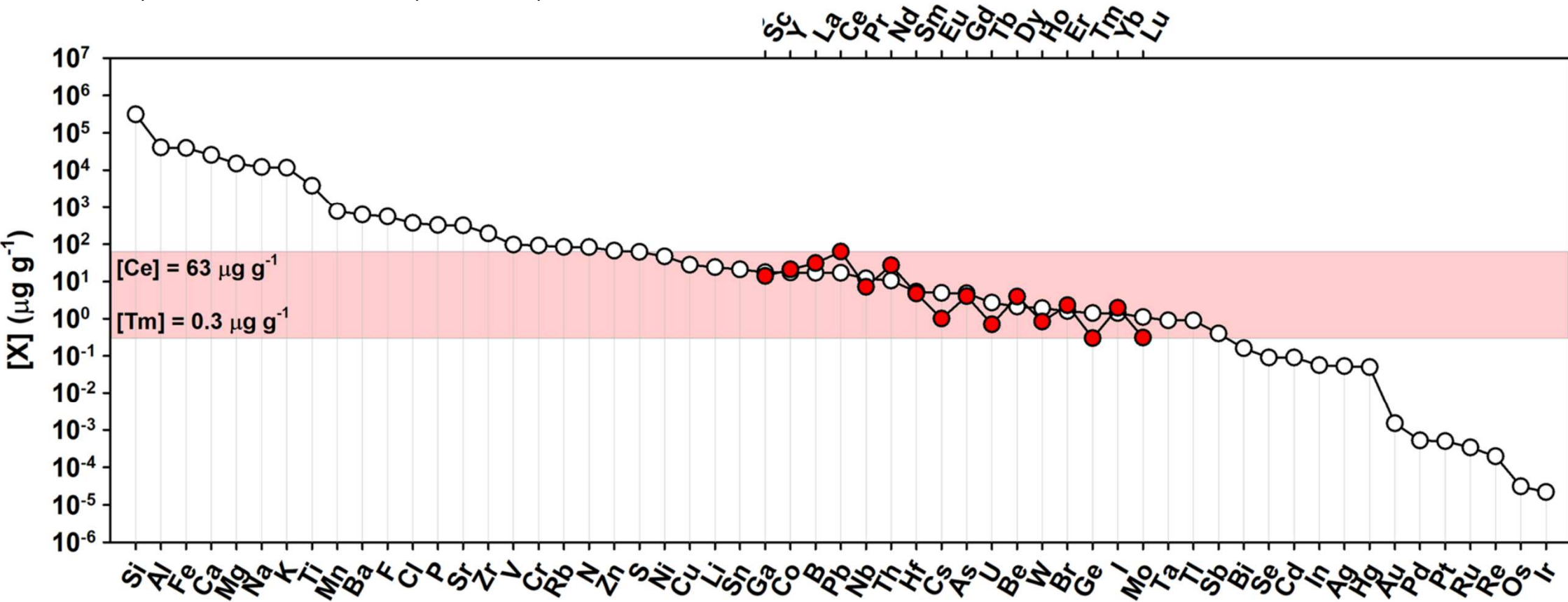
Year	Mineral/element	Discovered by	Named by	Confirmed by	Origin of name
1784	Gadolinite	C.A. Arrhenius	A.G. Ekeberg		Person: J. Gadolin
1794	Yttria	J. Gadolin	A.G. Ekeberg	M. Delafontaine	Place: Ytterby
1751	Cerite	A.F. Cronstedt	J.J. Berzelius, W. Hisinger		Asteroid: Ceres
1804	Cerium	J.J. Berzelius, W. Hisinger	J.J. Berzelius, W. Hisinger		Asteroid: Ceres
1839	Samarskite	M.H. Klaproth, G. Rose			Person: Col. Samarsky
1839	Lanthanum	C.G. Mosander	J.J. Berzelius		Chemical behavior: to escape notice
1842	Didymium	C.G. Mosander	C.G. Mosander		Chemical behavior: twins
1843	Erbium (known as terbium after 1864)	C.G. Mosander	C.G. Mosander	M. Delafontaine, J.L. Soret, H.E. Roscoe, A.J. Schuster, J.G. Marignac, J.L. Smith	Place: Ytterby
1843	Terbium (known as erbium after 1864)	C.G. Mosander	C.G. Mosander	M. Delafontaine, J.L. Smith	Place: Ytterby
1878	Ytterbium	J.C. Marignac	J.C. Marignac	M. Delafontaine, L.F. Nilson	Chemical behavior: between erbium and yttrium

Year	Mineral/element	Discovered by	Named by	Confirmed by	Origin of name
1879	Samarium	P.E.L. De Boisbaudran	P.E.L. De Boisbaudran	P.T. Cleve	Mineral: samarskite
1879	Scandium	L.F. Nilson	L.F. Nilson		Place: Scandinavia
1879	Thulium	P.T. Cleve	P.T. Cleve		Place: Scandina- via ("Thule" is her ancient name)
1879	Holmium	P.T. Cleve	P.T. Cleve	J.L. Soret, P.E.L. De Bois- baudran	Place: Stockholm (medieval name)
1886	Dysprosium	P.E.L. De Boisbaudran	P.E.L. De Boisbaudran		Chemical behavior: difficult to access
1886	Gadolinium	J.C. Marignac	J.C. Marignac	M. Delafontaine, J.L. Soret	Person: J. Gadolin
1886	Praseodymium	C.A. von Welsbach	C.A. von Welsbach	A. Bettendorf	Chemical beha- vior: green twin
1886	Neodymium	C.A. von Welsbach	C.A. von Welsbach	A. Bettendorf	Chemical beha- vior: new twin
1901	Europium	E. Demarcay	E. Demarcay	G. Urbain	Place: Europe
1907	Lutetium	G. Urbain, C.A. von Welsbach	G. Urbain		Place: Paris (Roman name of Paris)
1947	Promethium	J.A. Marinsky, L.E. Glendenin, C.D. Coryell	J.A. Marinsky, L.E. Glendenin, C.D. Coryell		Legend: Prometheus

Introduzione - Il perché del nome

La terra rara più comune è il Ce che ha un'abbondanza crostale di 60 ppm ed è il 27° elemento più abbondante nella crosta terrestre (il Pb per fare un esempio ha un'abbondanza di 10 ppm).

Quindi perché terre "rare"? Semplicemente perché è difficile trovarne concentrazioni molto elevate.

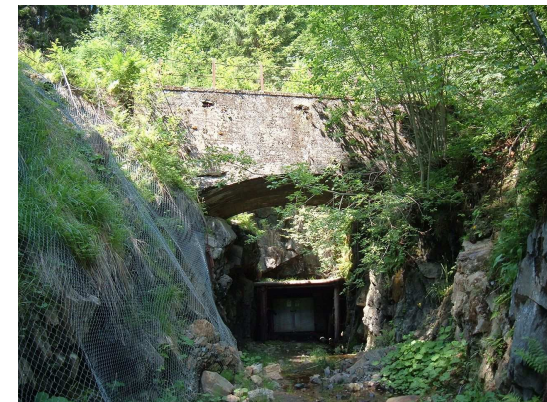


Minerali delle Terre Rare

Esistono tra i 270-290 minerali contenenti Y e REE come componenti essenziali all'interno della struttura, circa il 43% sono silicati, il 23% carbonati, il 14% sia ossidi che fosfati, Meno comuni sono i solfati.

TABLE 1 MAJOR RARE EARTH MINERALS

Mineral name ^a Formula	Relevant rare elements (range or max. value)	Major deposit type(s) ^c	Examples (past, present, and potential producers) ^c
Bastnäsile $\text{REECO}_3(\text{F,OH})$	53–79 wt% $\sum\text{REO}$; ≤ 2.8 wt% ThO_2	CRB; HMD	Bastnäs, SW; Mountain Pass, USA; Maoniuping, Weishan, and Bayan Obo, CH; Karonge Gakara, Burundi
Parisite $\text{CaREE}_2(\text{CO}_3)_3(\text{F,OH})_2$	58–63 wt% $\sum\text{REO}$; ≤ 4.0 wt% ThO_2	CRB; HMD	Mountain Pass, USA; Weishan and Bayan Obo, CH
Synchysite $\text{CaREE}(\text{CO}_3)_2(\text{F,OH})$	48–52 wt% $\sum\text{REO}$; ≤ 5.0 wt% ThO_2	CRB; HMD associated with CRB and granites	Barra do Itapirapuã, BR; Luglin Gol, MN; Kutessay, KR
Ba–REE fluorocarbonates ^b $\text{Ba}_x\text{REE}_y(\text{CO}_3)_{x+y}\text{F}_y$	22–40 wt% $\sum\text{REO}$; ≤ 0.7 wt% ThO_2	HMD; CRB	Bayan Obo, CH
Monazite $(\text{REE,Th,Ca,Sr})(\text{P,Si,S})\text{O}_4$ solid solution to cheralite $(\text{Ca,Th,REE})\text{PO}_4$	38–71 wt% $\sum\text{REO}$; ≤ 27 wt% ThO_2 ; ≤ 0.8 wt% UO_2	CRB; HMD; granitic pegmatites; Fe oxide–phosphate rocks; laterites; placers	Kangankunde, ML; Bayan Obo, CH; Steenkampskraal, SA; Mt. Weld, AU; Tomtor, RU; Tamil Nadu and Kerala, IN; Buena, BR; Nolans Bore and Eneabba, AU; Perak, MA
Xenotime $(\text{REE,Zr})(\text{P,Si})\text{O}_4$	43–65 wt% $\sum\text{REO}$; ≤ 8.4 wt% ThO_2 ; ≤ 5.8 wt% UO_2	Granites and pegmatites; HMD associated with granites; laterites; placers; rarely CRB	Kutessay, KR; Pitinga, BR; Tomtor, RU; Mt. Weld, AU; Kinta and Selangor, MA Lofdal, Namibia
Churchite $\text{REEPO}_4 \cdot 2\text{H}_2\text{O}$	43–56 wt% $\sum\text{REO}$; ≤ 0.3 wt% ThO_2	Laterites	Mt. Weld, AU; Chuktukon, RU
Fergusonite REENbO_4	43–52 wt% $\sum\text{REO}$; ≤ 8.0 wt% ThO_2 ; ≤ 2.4 wt% UO_2	Granites and pegmatites; HMD associated with peralkaline rocks	Bayan Obo, CH; Nechalacho, CA
Loparite $(\text{Na,REE,Ca})(\text{Ti,Nb})\text{O}_3$	28–38 wt% $\sum\text{REO}$; ≤ 1.6 wt% ThO_2	Peralkaline feldspathoidal rocks	Lovozero, RU



Bastnäs Mine – scoperto il Ce come ossido nel 1803, e il La nel 1839.

Abbreviations: CRB = carbonatites, HMD = hydrothermal-metasomatic deposits; AU = Australia, BR = Brazil, CA = Canada, CH = China, IN = India, KR = Kyrgyzstan, MA = Malaysia, ML = Malawi, MN = Mongolia, RU = Russia, SA = South Africa, SW = Sweden; REE = rare earth element(s), REO = rare earth oxide(s)

Minerali delle Terre Rare

Oltre ai minerali delle terre rare veri e propri, esistono molti altri minerali in cui questi elementi possono sostituire anche abbondantemente altri cationi di carica e raggio comparabile.

Tra questi minerali ci sono ad esempio:

- Mosandrite $[(Ca, Na)_{3-x}(Ca, REE)_4Ti(Si_2O_7)_2(OH, F, H_2O)_4 \cdot H_2O]$
- Apatite $[(Ca, REE, Sr, Na)_5(P, Si)_3O_{12}(F, OH, Cl)]$
- Ewaldite $[Ba (Ca, Na, REE)(CO_3)_2 \cdot nH_2O]$
- Perovskite $[(Ca, Na, REE)(Ti, Nb, Fe)O_3]$

In questi minerali il contenuto di REE si aggira su $1-2 \times 10^5$ ppm.

In base alle condizioni di cristallizzazione, contenuti elevati di REE, possono essere presenti anche nella titanite ($CaTiSiO_5$), zirconio $ZrSiO_4$, pirocloro $[Ca, Na)_{2-x}(Nb, Ti)_2O_6(F, OH)]$.

Inoltre esistono le cosiddette ion-adsorption clays ovvero argille ad adsorbimento ionico in cui si hanno contenuti di REE tra lo 0.05 e lo 0.2%. Il 70% di questo contenuto è in forma di cationi adsorbiti sulla superficie dei fillosilicati.



Minerali delle Terre Rare



Loparite



Parisite



Synchisite

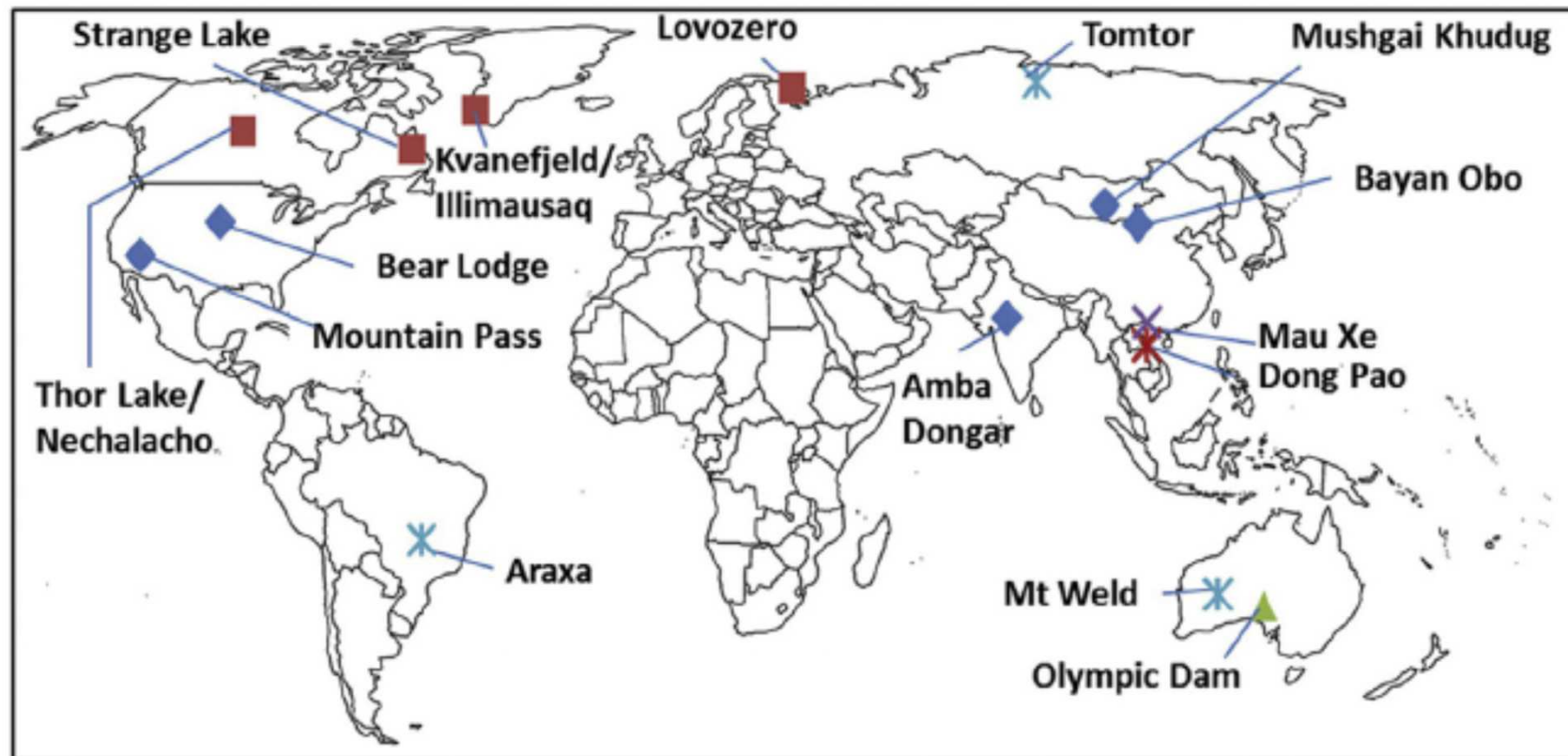


Kainosite

Table 2.4 Minor REE minerals

Mineral name	Formula
Aeschynite	$(\text{Ce, Ca, Fe})(\text{Ti, Nb})_2(\text{O, OH})_6$
Aenigmatite	$(\text{Na, Ca})_4(\text{Fe, Ti, Mg})_{12}\text{Si}_{12}\text{O}_{40}$
Allanite (Orthite)	$(\text{Ca, Ce})(\text{Al, Fe}^{2+})(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$
Ancylite	$\text{SrCe}(\text{CO}_3)_2(\text{OH}) \cdot (\text{H}_2\text{O})$
Apatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$ Apatite is as such not a rare earth mineral, but REEs may concentrate them, in which case they substitute for Ca
Brannerite	$(\text{U, Ca, Ce})(\text{Ti, Fe})_2\text{O}_6$
Britholite	$\text{Ca}_2(\text{Ce, Ca})_3(\text{SiO}_4, \text{PO}_4)_3(\text{OH, F})$
Cerite	$(\text{Ce, La, Ca})_9(\text{Mg, Fe})(\text{SiO}_4)_3(\text{HSiO}_4)_4(\text{OH})_3$
Cerianite	$(\text{Ce, Th})\text{O}_2$
Cheralite	$(\text{Ca, Ce})(\text{Th, Ce})(\text{PO}_4)_2$
Churchite	$\text{YPO}_4 \cdot 2(\text{H}_2\text{O})$
Euxenite	$(\text{Y, Ce, Ca})(\text{Nb, Ta, Ti})_2\text{O}_6$
Fergusonite	$\text{Y}(\text{Nb, Ti})\text{O}_4$
Florencite	$(\text{Ce, La})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$
Gadolinite	$\text{Y}_2\text{Fe}^{2+}\text{Be}_2\text{Si}_2\text{O}_{10}$
Huanghoite	$\text{BaCe}(\text{CO}_3)_2\text{F}$
Hydroxylbastnaesite	$(\text{Ce, La, Nd})\text{CO}_3(\text{F, OH})$
Kainosite	$\text{Ce}_2(\text{Y, Ce})_2(\text{Si}_4\text{O}_{12})(\text{CO}_3) \cdot \text{H}_2\text{O}$
Loparite	$(\text{Na, Ce, Ca, Sr, Th})(\text{Ti, Nb, Fe})\text{O}_3$
Mosandrite	$\text{Na}(\text{Na, Ca})_2(\text{Ca, Ce, Y})_4(\text{Ti, Nb, Zr})(\text{Si}_2\text{O}_7)_2(\text{O, F})_2\text{F}_3$
Parisite	$\text{Ca}(\text{Ce, La})_2(\text{CO}_3)_3\text{F}_2$
Rinkite	$(\text{Na, Ca})_3(\text{Ca, Ce})_4\text{Ti}(\text{Si}_2\text{O}_7)_2\text{OF}_3$
Samarskite	$(\text{Y, Fe}^{3+}, \text{U})(\text{Nb, Ta})_5\text{O}_4$
Synchisite	$\text{Ca}(\text{Ce, Nd, Y})\text{CO}_3\text{F}$
Steenstrupine	$\text{Na}_{14}\text{Ce}_6\text{Mn}^{2+}\text{Mn}^{3+}\text{Fe}_2^{2+}(\text{Zr, Th})(\text{Si}_6\text{O}_{18})_2(\text{PO}_4)_7 \cdot 3(\text{H}_2\text{O})$
Tengerite	$\text{Y}_2(\text{CO}_3)_3 \cdot 2-3(\text{H}_2\text{O})$
Thalenite	$\text{Y}_3\text{Si}_3\text{O}_{10}(\text{OH})$
Yttrotantalite	$(\text{Y, U, Fe})(\text{Ta, Nb})\text{O}_4$
Zircon	ZrSiO_4 . Zircon also is not a rare earth mineral as such, but like apatite, it may concentrate REEs, in which case they substitute for Zr

Depositi delle Terre Rare



◆ Carbonatite and related
 ■ Alkaline igneous (silicate)

✕ Metamorphism
 ✱ Laterite (carbonatite)

✕ Laterite (syenite)
 ▲ IOCG Iron Oxide Copper Gold mineralization

Depositi delle Terre Rare

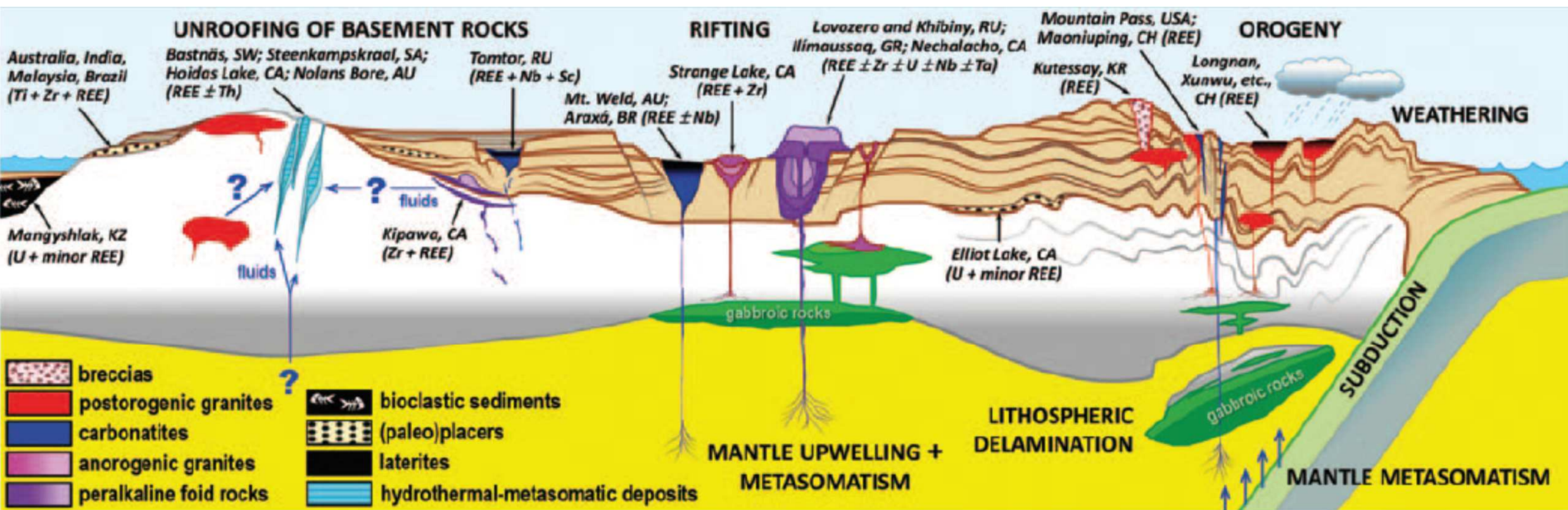


FIGURE 5 Major REE deposit types in a tectonic context. Rock types are given in the legend; processes are shown in capital letters; and past, present, and potential producers are in italics (KZ = Kazakhstan; for other abbreviations, see TABLE 1). Bayan Obo, although the world's largest REE deposit, is one of the least well understood (Kynicky et al. 2012) and is not indicated on this diagram.

Depositi delle Terre Rare - Rocce Ignee

Fondamentalmente le rocce ignee in cui si possono trovare depositi di REE sono:

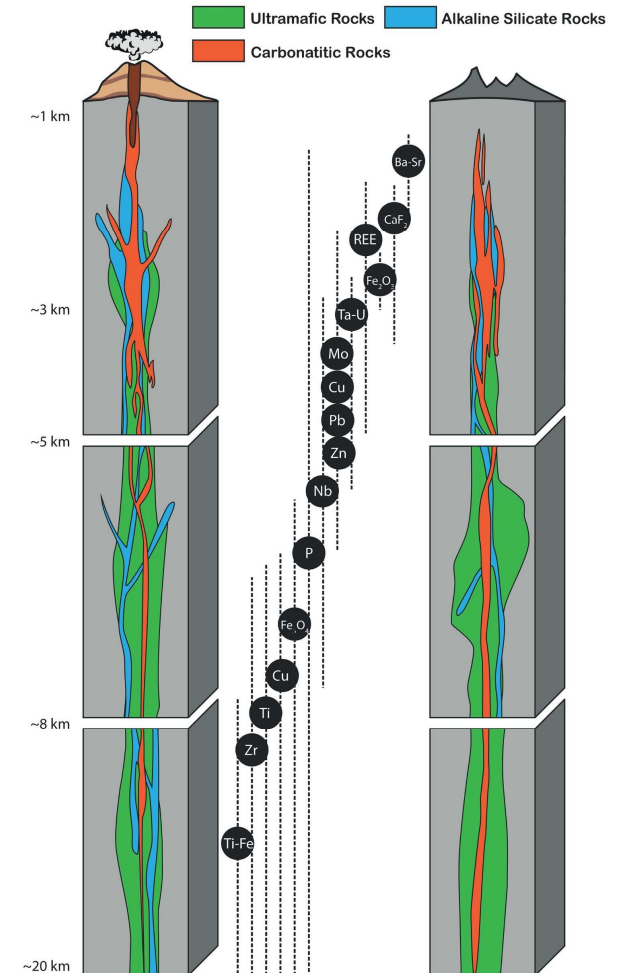
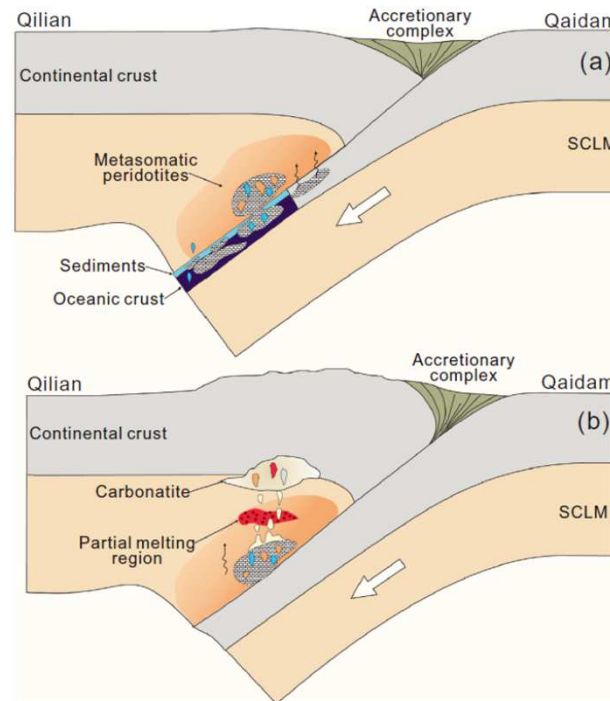
- Carbonatiti
- Rocce peralcaline sottosature in silice
- Graniti peralcalini e pegmatiti
- Pegmatiti associate a graniti sub- e meta- alluminiferi
- Depositi di ossidi di Fe e fosfati

Depositi delle Terre Rare - Carbonatiti

Con il termine carbonatite si fa riferimento ad una roccia magmatica (intrusiva, o effusiva) in cui le fasi minerali carbonatiche sono pari o superiori al 50%.

Nel caso il contenuto in silice sia inferiore al 20% in peso si parlerà di carbonatite s.s. mentre per tenori superiori al 20%, le rocce vanno identificate come SILICO CARBONATITI.

Nel caso la silice superi il 50% in peso, la nomenclatura di riferimento è quella delle rocce magmatiche silicatiche, ma la frazione carbonatitica "obbligatoriamente" aggettiva la roccia studiata.



Depositi delle Terre Rare - Carbonatiti

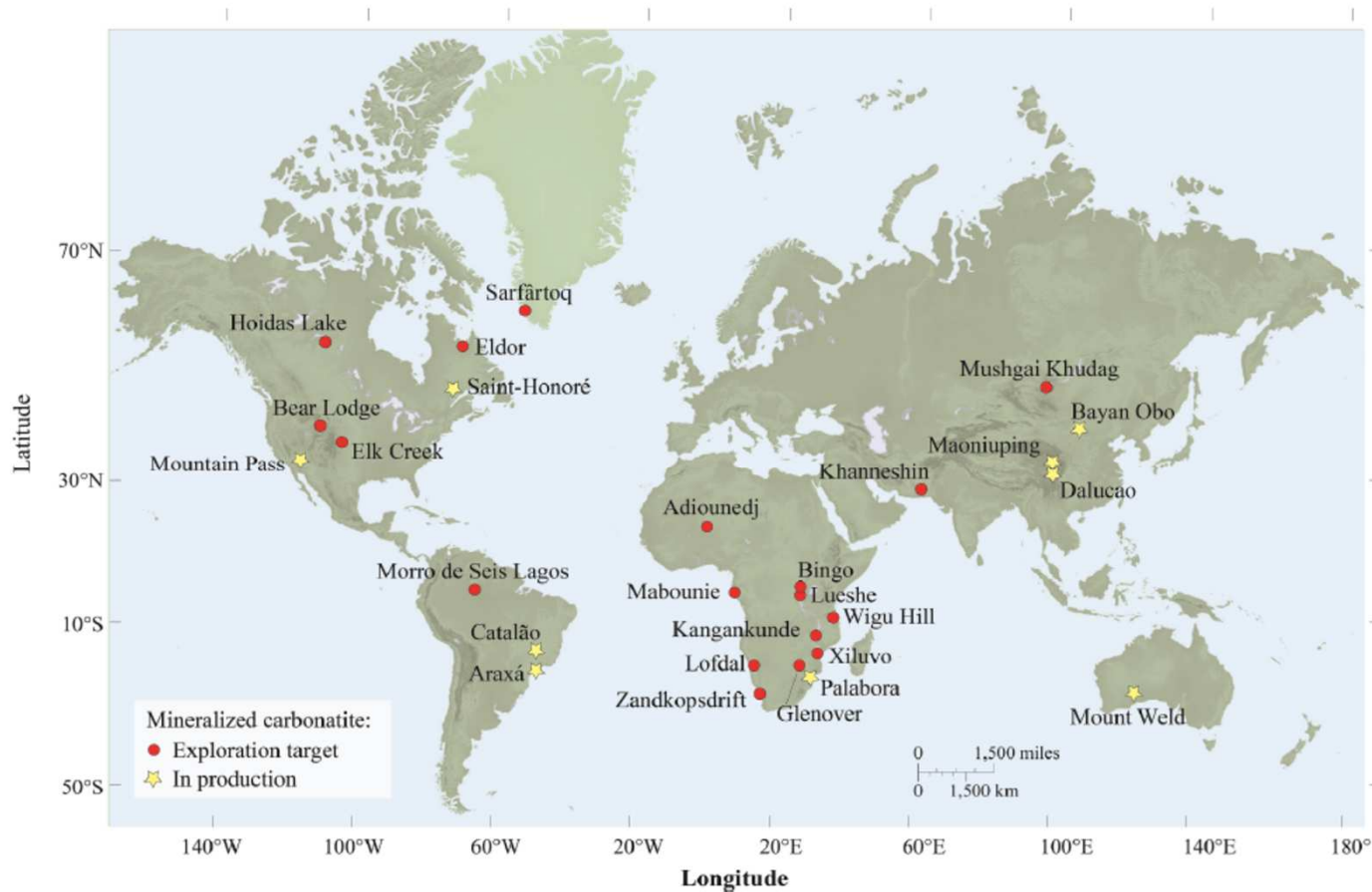
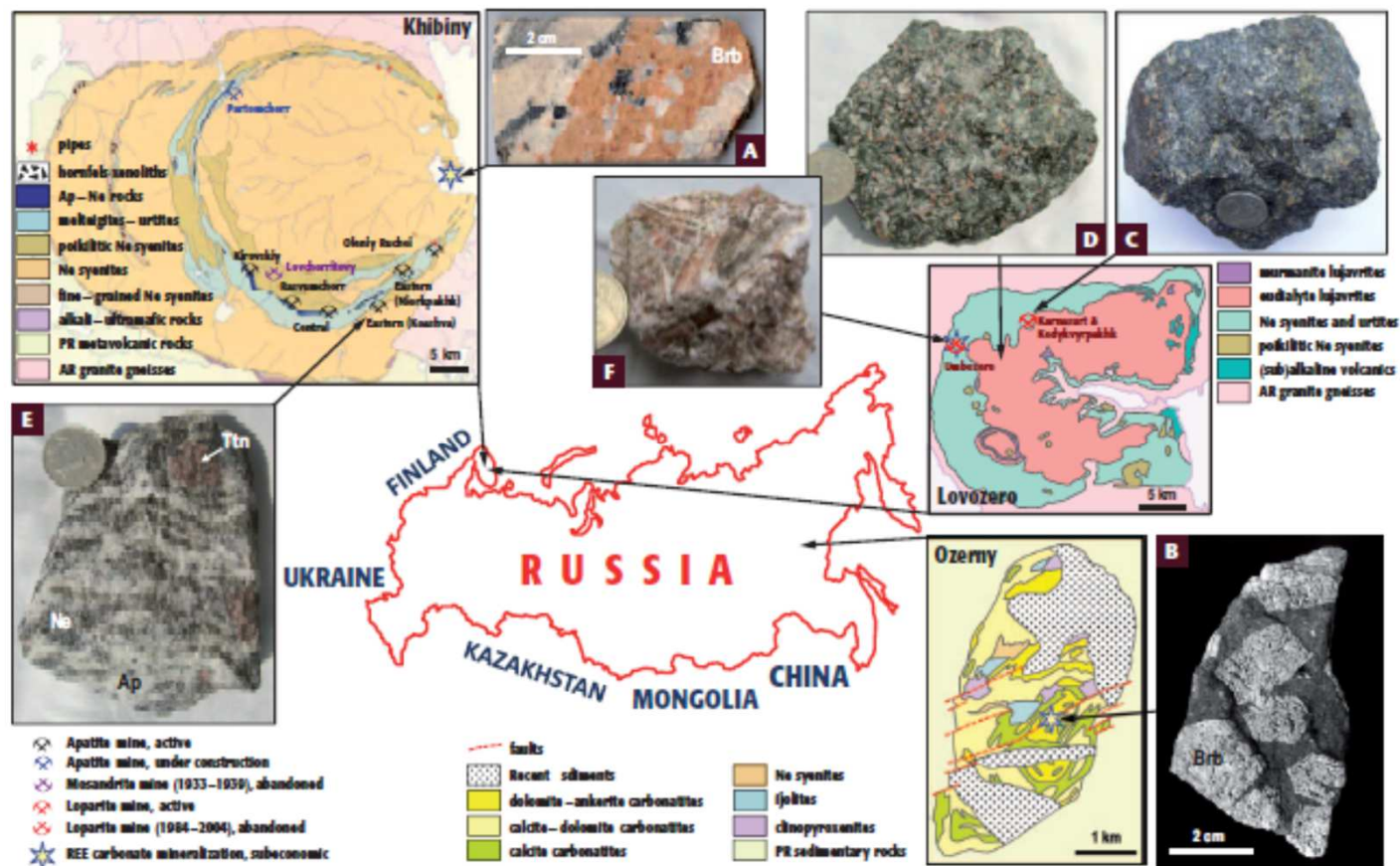


Fig. 1. Global carbonatite distribution including deposit in production and exploration targets (Sources: Eggert et al., 2016; Verplanck et al., 2016).

- Le carbonatiti hanno un contenuto in REE maggiore rispetto alle altre rocce dove possono essere contenuti questi elementi.
- I tenori di REE vanno da 250 a 8000 ppm.
- In genere le LREE sono più abbondanti delle HREE.
- A parte i minerali di REE, le REE sono distribuite tra carbonati, fosfati, ossidi e fasi silicatiche.

Depositi delle Terre Rare - Rocce Peralcaline Sottosature

Le serie peralcaline sono rappresentate da rocce alte in potassio ($K_2O > 3\%$ wt.; $MgO > 3\%$ wt) con rapporti $K_2O/Na_2O > 2$ e alte in sodio.



Depositi delle Terre Rare - Rocce Peralcaline Sottosature

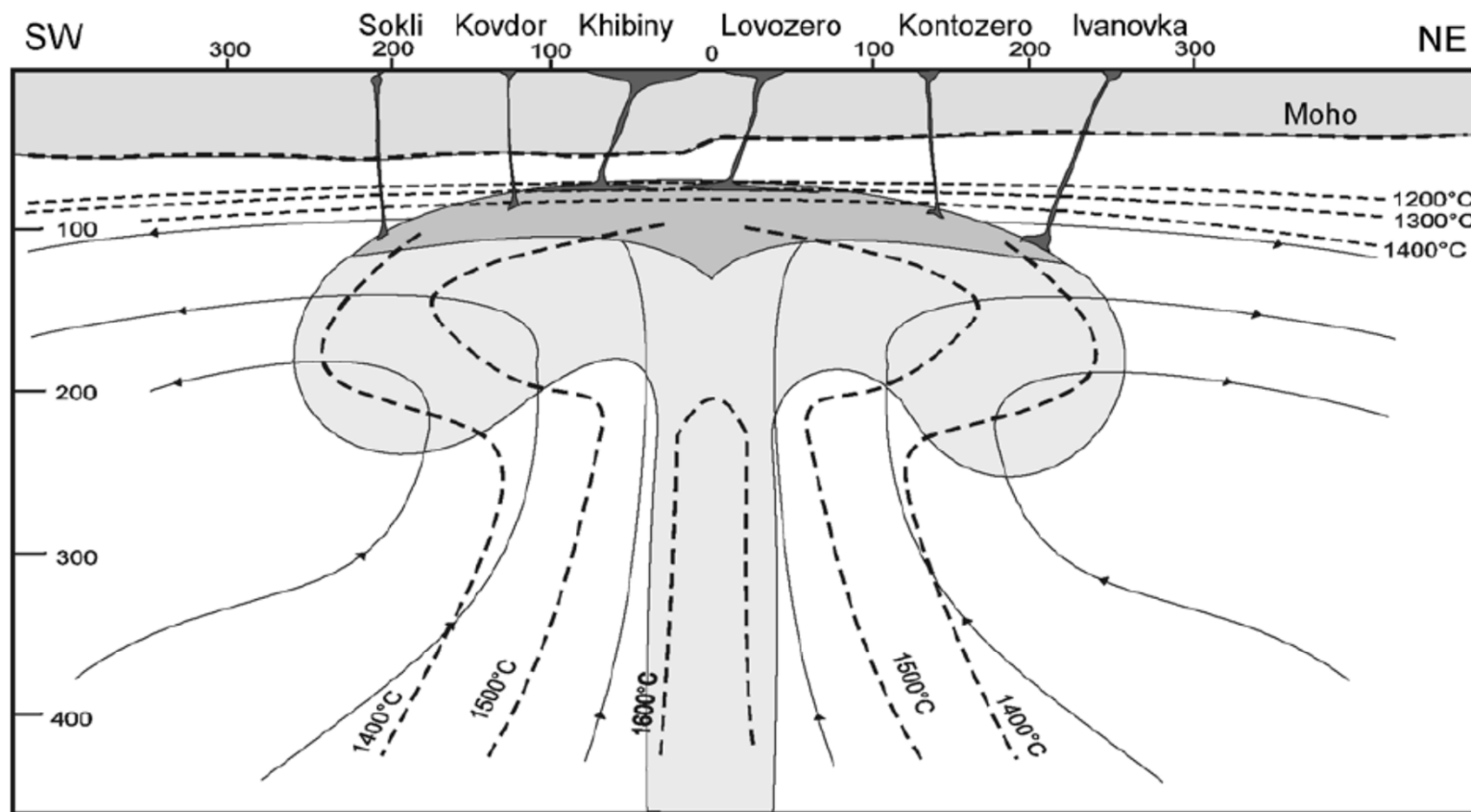


Figure 13. A hypothetical model for the mantle plume–lithosphere interaction in the zone of the Paleozoic alkaline magmatism in the northeastern part of the Baltic Shield, based on the data of *Leitch et al.* [1998], *McKenzie and Bickle* [1988], *Thompson and Gibson* [1991], and *White and McKenzie* [1989].

Depositi delle Terre Rare - Rocce Peralcaline Sottosature

Rispetto alle carbonatiti in queste rocce mancano la monazite e gli REE-carbonati

La maggior parte delle terre rare è contenuta in fosfati del gruppo della apatite, silicati a Zr e Ti (gruppo dell'eudialite, $[\text{Na}_{15}\text{Ca}_6(\text{Fe},\text{Mn})_3\text{Zr}_3(\text{Si},\text{Nb})(\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH},\text{H}_2\text{O})_3(\text{Cl},\text{OH})_2])$ mentre fasi tipo perovskite e pirocloro sono più rare.

La loparite $(\text{Ce},\text{Na},\text{Ca})_2(\text{Ti},\text{Nb})_2\text{O}_6$ è stata la maggior sorgente di LREE, Nb e Ta dell'industria dell'Unione Sovietica dal 1951.



Depositi delle Terre Rare - Graniti peralcalini e pegmatiti associate

Esistono diversi tipi di rocce granitoidi che differiscono per contenuto di Al, alcali e calcio. Le concentrazioni più alte (300-800 ppm) si trovano in graniti peralcalini anorogenici e nelle pegmatiti associate. In genere queste rocce sono arricchite in HREE. I minerali che contengono REE in queste rocce sono monazite, allanite, xenotime, fergusonite, samarskite, gagarinite oltre a zirconosilicati (da zircone a eudialite) e pirocloro. I giacimenti più importanti di questo tipo sono Strange Lake e la miniera a Sn-Nb-Ta di Pitinga in Brasile

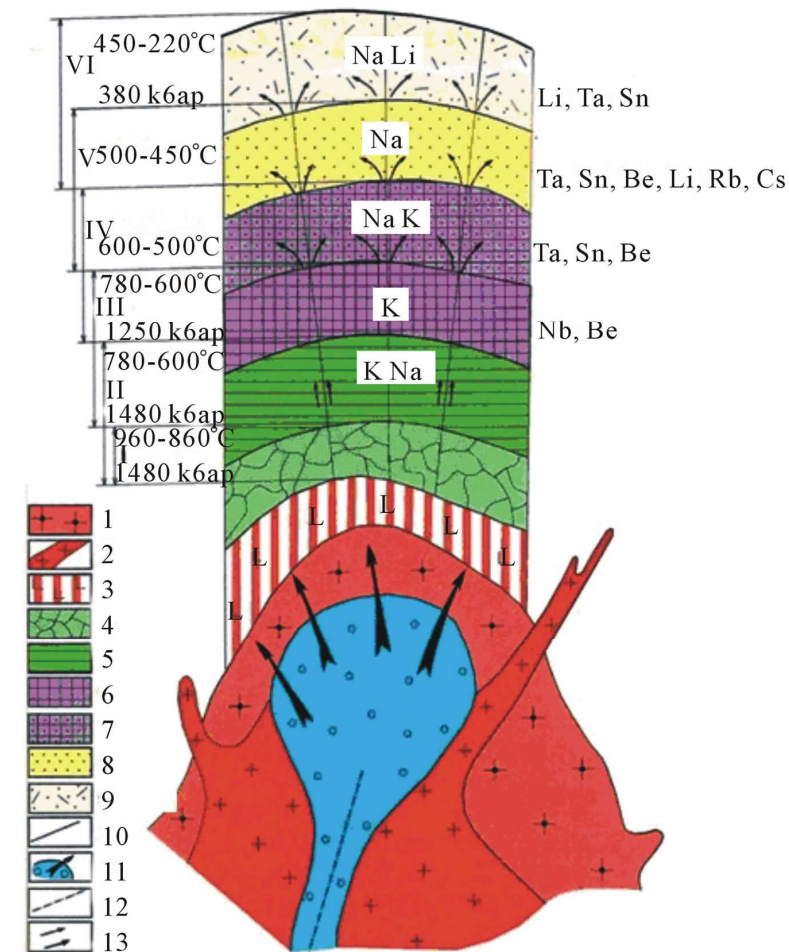


Depositi delle Terre Rare - Graniti peralcalini e pegmatiti associate

In ambiente acquoso le REE tenderanno a formare i complessi più stabili secondo $F^- > OH^- > NO_3^- > Cl^- > Br^-$ se consideriamo specie monovalenti. Altrimenti potranno seguire quest'ordine $CO_3^{2-} > SO_4^{2-} > P_2O_5^{2-}$. In un ambiente acquoso ricco in F oppure in Cl, il comportamento degli REE è sostanzialmente simile con gli LREE più stabili rispetto agli HREE.

Qualsiasi meccanismo che aumenti il pH e/o l'attività dei carbonati o porti ad una diminuzione dell'attività del Cl porterà alla deposizione del minerale.

A model formation pegmatite rare deposits. 1— coarse-and medium-biotite granite; 2—fine-and medium-grained muscovitized granite; 3—aplite-like, aplite; 4 - 10—pegmatites (4— oligoclase-microcline barren, 5—grafic, 6— microcline in blocks with beryl and columbite 7—microcline-albite with tantalite, cassiterite, beryl (rarely spodumene), 8—albitic (productive) with tantalite, cassiterite, beryl, pollucite, spodumene, lepidolite; 9—albite (cleavelandite)-spodumene, with tantalite, amblygonite, petalite, polychromatic tourmaline; 10—faults; 11, 13— direction of the fluid movement; 12 —ore-controlling deep fault.



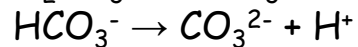
Depositi delle Terre Rare - Depositi di ossidi di ferro e fosfati

I depositi di ossidi di ferro e fosfati ($\pm$ Ti) sono associati a diverse rocce ignee (sia acide che basiche) e di conseguenza hanno diversi tipi di origine. Il minerale principale per l'estrazione di REE è l'apatite e in alcuni casi xenotimo e monazite. A parte la miniera di Mineville (USA) questi depositi non sono economici per uno sfruttamento esclusivo delle terre rare. In questo caso lo sfruttamento è legato principalmente all'apatite (quindi ai fosfati) e le REE sono considerate un by-product.

Depositi secondari delle Terre Rare - Bauxite

La bauxite è una roccia sedimentaria, costituita essenzialmente da ossidi di alluminio idrati, di colore giallo o rosso mattone, usata come materia prima per l'estrazione dell'alluminio. Questi depositi si formano principalmente per alterazione di rocce contenenti minerali di alluminio, in cui gli altri elementi inizialmente presenti vengono allontanati per alterazione fisica e chimica seguendo questi steps.

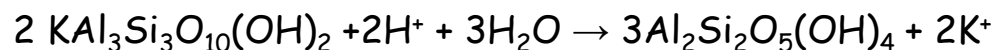
Step 1: acidificazione dell'acqua meteorica



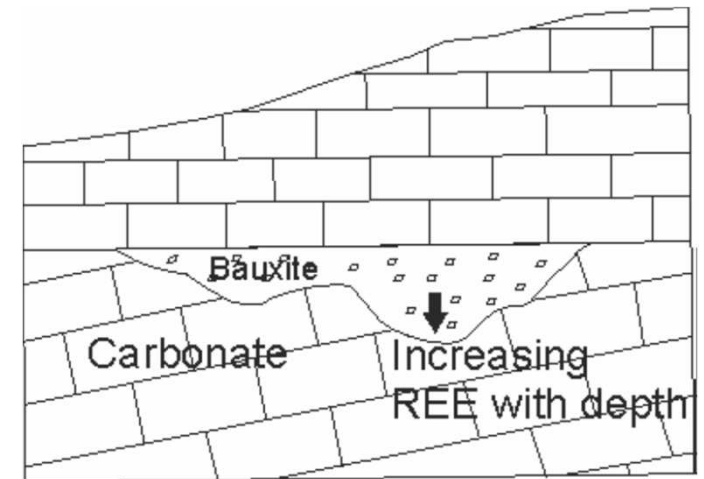
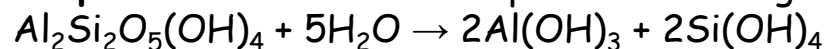
Step 2: Acidi carbonici e humus (dal suolo) reagiscono con il feldspato, rimuovono potassio e silice, e idratano la struttura allumosilicatica formando un'argilla tipo illite:



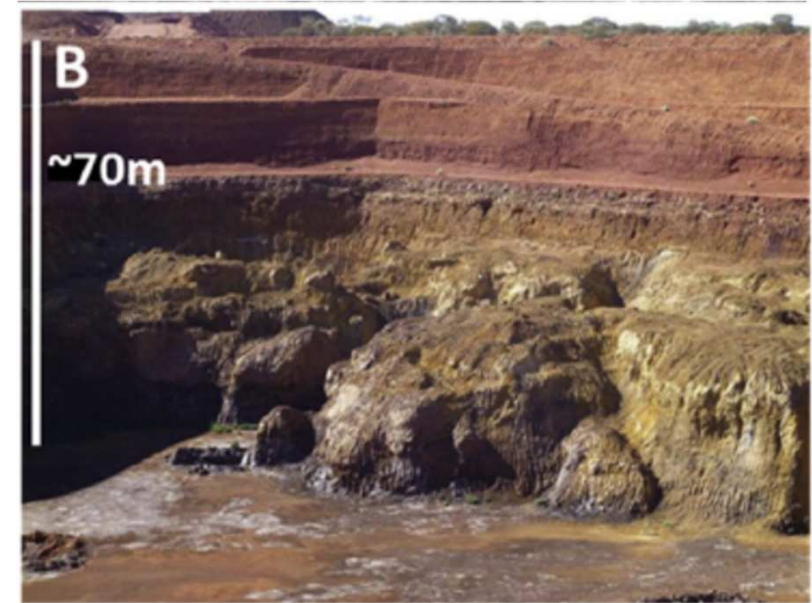
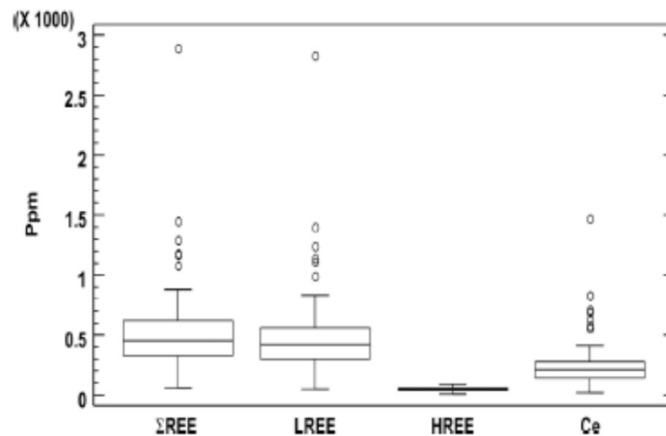
Step 3: ulteriore lisciviazione rimuove il potassio rimanente e trasforma l'illite in caolinite:



Step 4: la caolinite si decompone formando gibbsite e silice idrata:



Depositi secondari delle Terre Rare - Bauxite & Laterite

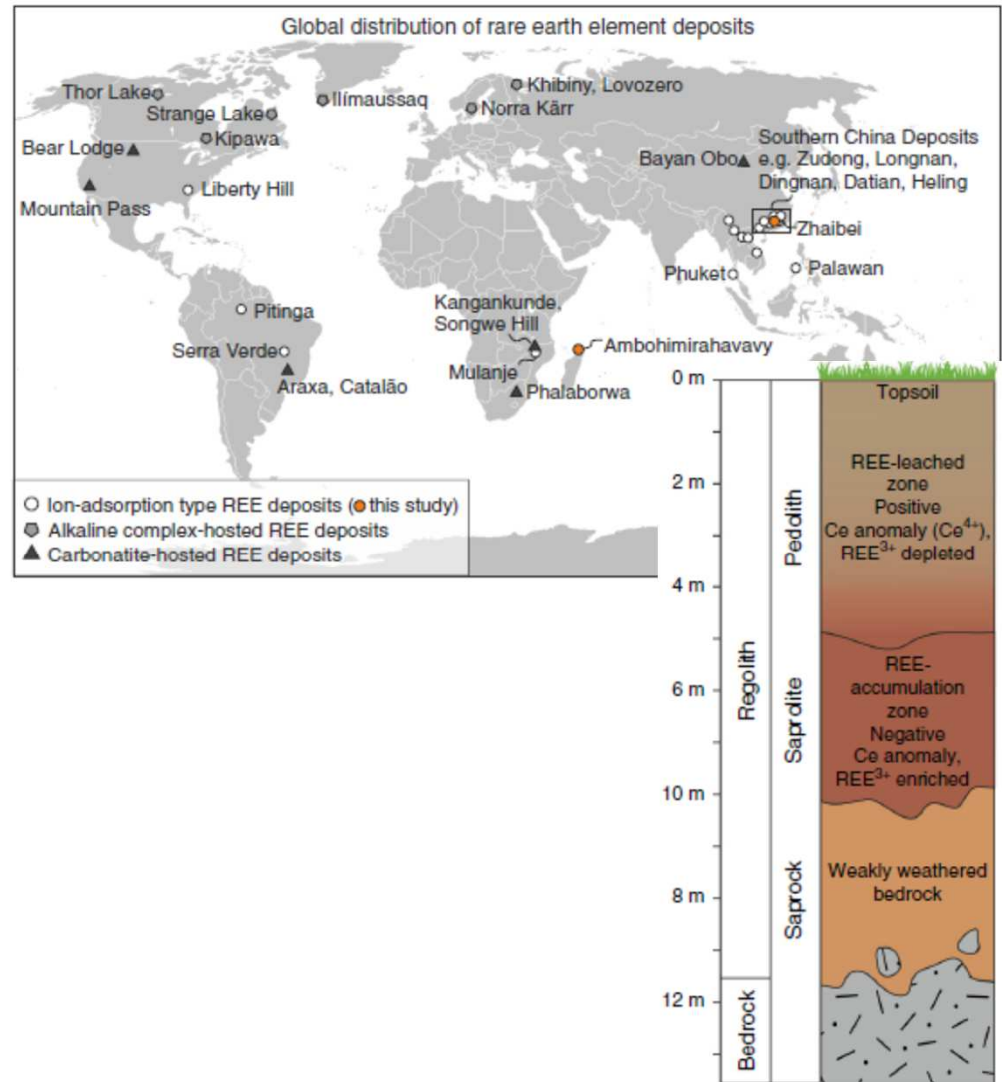


Sampling site	Major oxides			Critical raw materials (CRMs)														ΣREE	LREE	HREE											
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	V	Cr	Co	Nb	Ni	Y	Sc	Ga	La	Ce	Pr	Nd	Sm				Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	(wt.%)			(ppm)														(ppm)													
	12.00	64.68	3.79	3.92	449	583	5	76	60	60	42	76	15.5	34.0	nd	12.0	3.4	1.2	nd	nd	nd	nd	nd	1.2	7.1	1.1	75.5	64.9	10.6		
Median	4.8	52.5	20.2	2.8	405.0	544.9	36.9	71.0	200.0	55.5	54.5	59.6	96.5	212.5	20.7	74.2	14.8	3.4	12.8	2.05	11.7	2.3	6.8	1.1	7.1	1.1	446.0	407.6	45.7		
Min.	0.4	15.5	1.4	0.7	140.9	123.6	5.3	14.5	59.7	25.0	16.0	14.7	10.6	24.0	7.7	9.0	2.7	1.1	4.5	0.9	5.6	1.2	3.7	0.5	3.4	0.5	55.9	46.3	6.6		
Max.	43.6	75.7	40.8	5.4	876.8	1130.0	348.9	129.0	1072.0	143.0	110.0	94.0	644.0	1470.0	55.3	604.0	117.0	25.5	30.3	4.0	20.6	3.8	10.9	9.2	15.8	2.3	2887.8	2835.0	85.9		
Std.	9.2	9.8	7.6	0.9	156.9	269.1	40.7	26.3	165.5	18.4	14.4	11.9	74.6	199.7	9.1	64.4	12.3	2.7	4.7	0.6	3.0	0.5	1.4	0.9	1.9	0.3	343.2	335.6	16.6		

1 = data from [Mongelli et al., 2014](#); 2 = data from [Mongelli et al., 2016](#); 3 = unpublished data; 4 = data from [Mondillo et al., 2011](#); 5 = data from [Boni et al., 2013](#); 6 = data from [Mameli et al., 2007](#); nd = not detected; Min. = minimum value; Max. = maximum value; std. = standard deviation. Bold numbers indicate the outlier values.

Depositi secondari delle Terre Rare - Ion-adsorption clays

All'interno del protolite si possono trovare vari minerali contenenti REE. In alcuni casi questi minerali possono resistere all'alterazione, ma molto più spesso si formano delle fasi secondarie a REE che possono essere assorbiti sulle superfici dei minerali argillosi durante i processi di alterazione.



Depositi secondari delle Terre Rare: Ion-adsorption clays

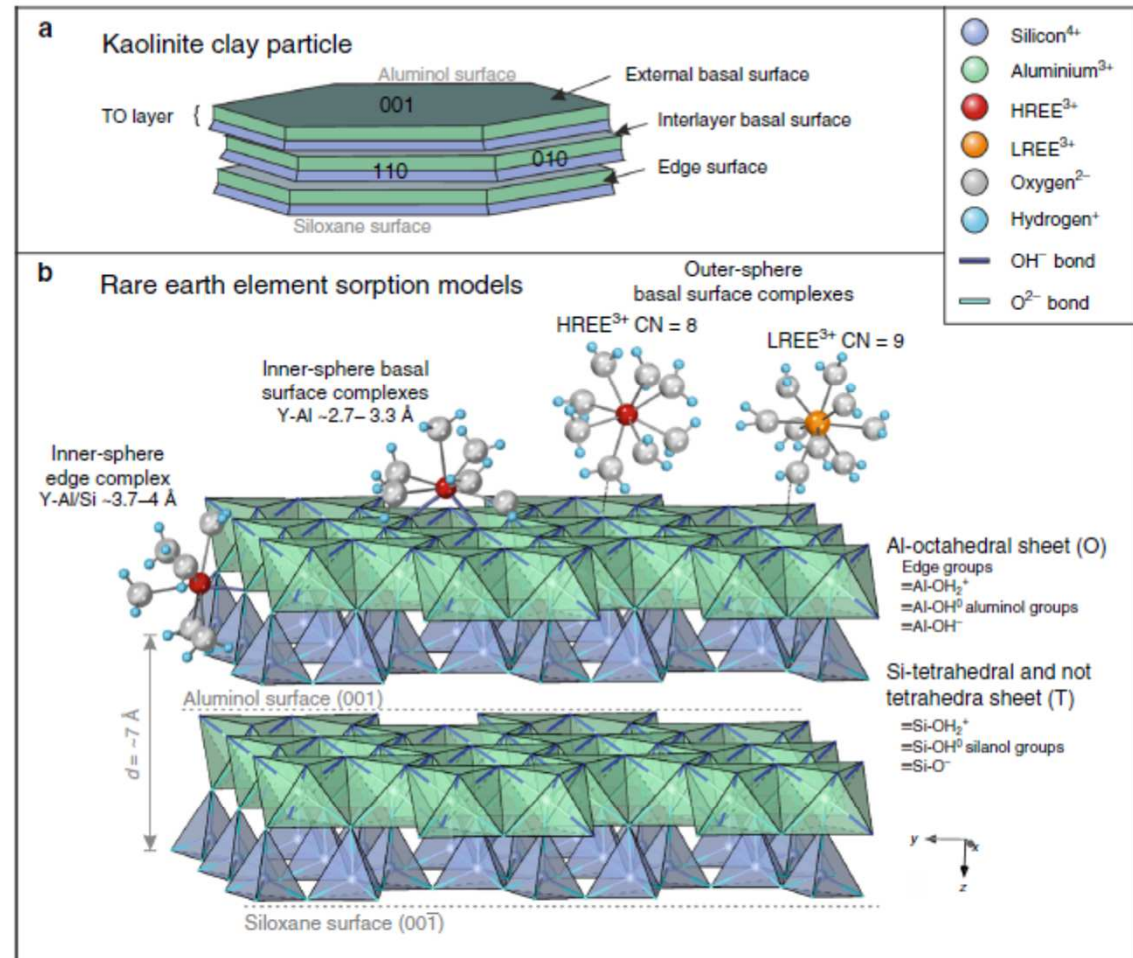


Fig. 8 Schematic adsorption model of rare earth elements onto kaolinite. **a** Schematic kaolinite structure showing the 1:1 stacking of Al-octahedral (O) and Si-tetrahedral (T) sheets, forming TO layers with aluminol and siloxane external basal surfaces, edge and interlayer surfaces. **b** Rare earth sorption model associated with Al-octahedral (O) sheets of kaolinite. Light and heavy rare earth element (LREE³⁺ and HREE³⁺) complexes may occur as eight- to nine-coordinated inner-sphere (basal surface or edge) complexes via mono- or bidentate bridging oxygens, or loosely adsorbed as 8- or 9-fold hydrated outer-sphere complexes. Our data demonstrate that Y in the studied ion-adsorption ores are dominantly present as 8-fold hydrated outer-sphere basal surface complexes. The data show no evidence for Al or Si scattering within a distance of 4 Å, thereby excluding the inner-sphere adsorption model. A similar sorption model can be made for halloysite (7 and 10 Å), which typically displays a tubular morphology with the aluminol basal surface on the inside of the tubes⁶⁵. CN coordination number.

Depositi secondari delle Terre Rare: Ion-adsorption clays

REO% in Bayan Obo, Mountain Pass and ion adsorption clay deposits (Sources: [Gupta and Krishnamurthy, 2005](#); [Schüler et al., 2011](#); [Shi, 2009](#)).

Ore	Bayan Obo		Mountain Pass	Ion adsorption clays					
REOs	Bastnaesite	Monazite	Basnasite	*Site A	*Site B	*Site C	*Site D	*Site E	*Site F
La ₂ O ₃	27	23.4	33.2	2.1	20	8.5	29.8	27.4	13.1
CeO ₃	50	45.7	49.1	12.8	1.3	1.1	7.2	3.1	1.3
Pr ₆ O ₁₁	5	4.2	4.3	1.1	5.5	1.9	7.4	5.8	4.9
Nd ₂ O ₃	15	15.7	12	5.1	26	7.4	30.2	18.7	13.4
Sm ₂ O ₃	1.1	3.1	0.8	3.2	4.5	2.6	6.3	4.3	4
Eu ₂ O ₃	0.2	0.1	0.1	< 0.3	1.1	0.2	0.5	< 0.3	0.2
Y ₂ O ₃	0.3	3.1	0.1	62.9	25.9	49.9	10.1	26.4	41.7
Gd ₂ O ₃	0.4	2	0.2	5.7	4.5	6.8	4.2	4.4	5.1
Tb ₂ O ₃	Trace	0.1	0.02	1.1	0.6	1.4	0.5	0.7	1.2
Dy ₂ O ₃	Trace	1	0.03	7.5	4.1	8.6	1.8	4	7.1
Ho ₂ O ₃	Trace	0.1	< 0.01	1.6	< 0.3	1.4	0.3	0.5	1.1
Er ₂ O ₃	1	0.5	< 0.01	4.3	2.2	4.2	0.9	2.3	3.1
Tm ₂ O ₃	Trace	0.5	< 0.01	0.6	< 0.3	1.2	0.1	0.3	1.5
Yb ₂ O ₃	Trace	0.5	< 0.01	3.3	1.4	4.1	0.6	2	2
Lu ₂ O ₃	Trace	0.1	< 0.01	0.5	< 0.3	0.7	0.1	< 0.3	0.5

*Sites A to F represent six provinces in southern China.

Depositi secondari delle Terre Rare - Placers

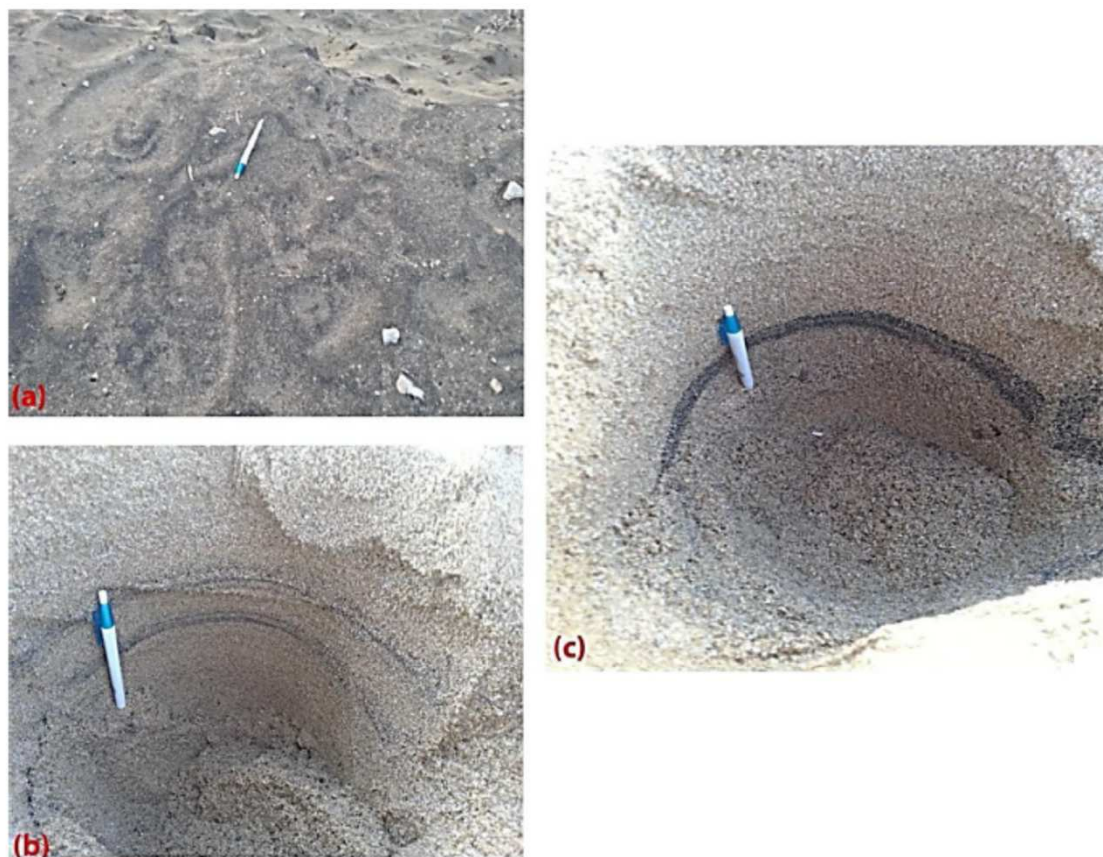
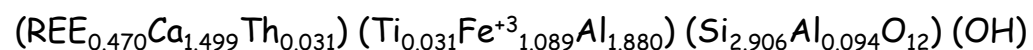


Fig. 2. Sampling locations showing the presence of coastal black sands.



Element	Magnetic fraction (mg/kg)	Non-magnetic fraction (mg/kg)
La	557.8	3522.4
Ce	938.8	6140.6
Pr	93.7	616.9
Nd	287.3	1958.8
Sm	30.4	231.0
Eu	5.2	37.3
Gd	20.5	152.4
Tb	2.2	17.0
Dy	11.0	83.2
Ho	2.0	14.1
Er	6.1	40.3
Tm	1.0	6.0
Yb	7.5	38.3
Lu	1.5	5.8
ΣLREE	1908.0	12469.6
ΣHREE	56.9	394.5
ΣREE	1964.9	12864.1
Y	60.2	421.2
ΣREE + Y	2025.1	13285.3
ΣREE + Y	0.2 wt. %	1.3 wt. %

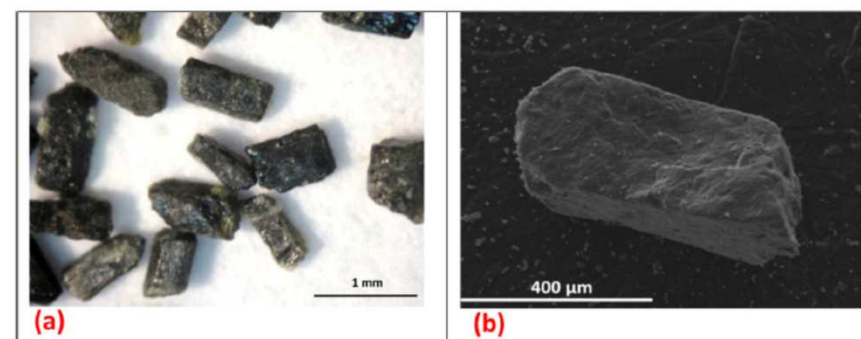
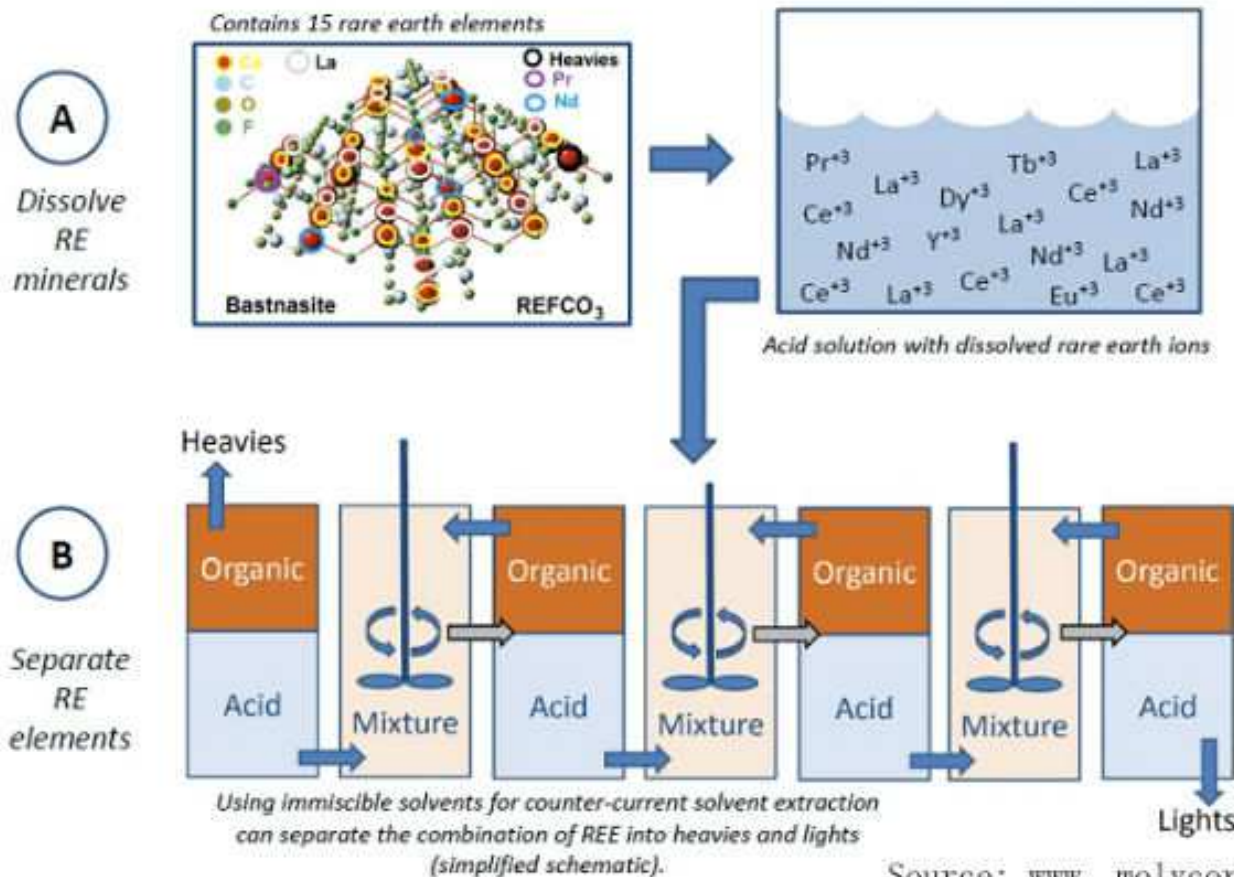


Fig. 5. (a) Allanite crystals observed by binocular microscope (b) backscattered image (BSE) of a single allanite crystal.

Dal giacimento al consumatore - Concentrazione degli REE

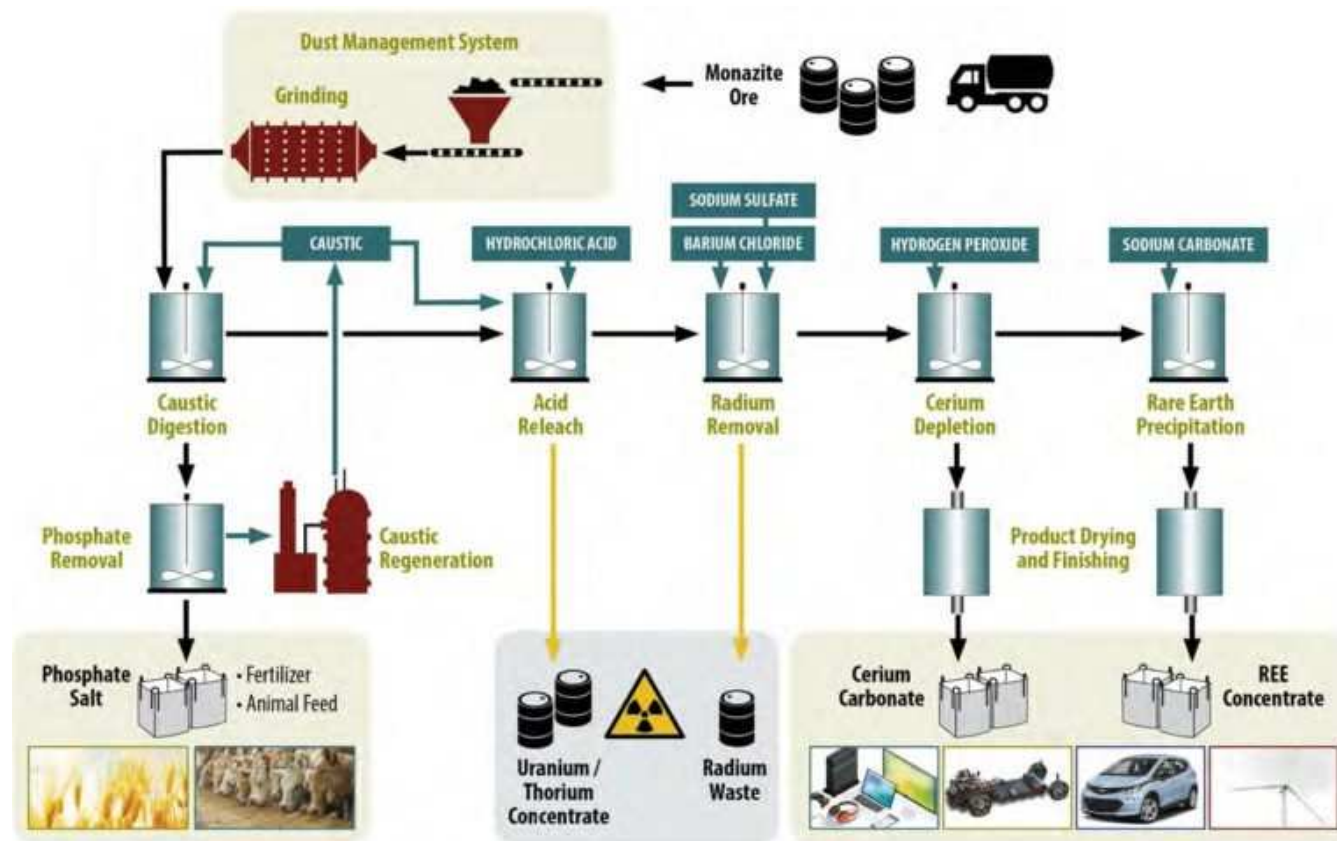
SEPARATING RARE EARTHS at MOUNTAIN PASS



Source: www.molycorp.com

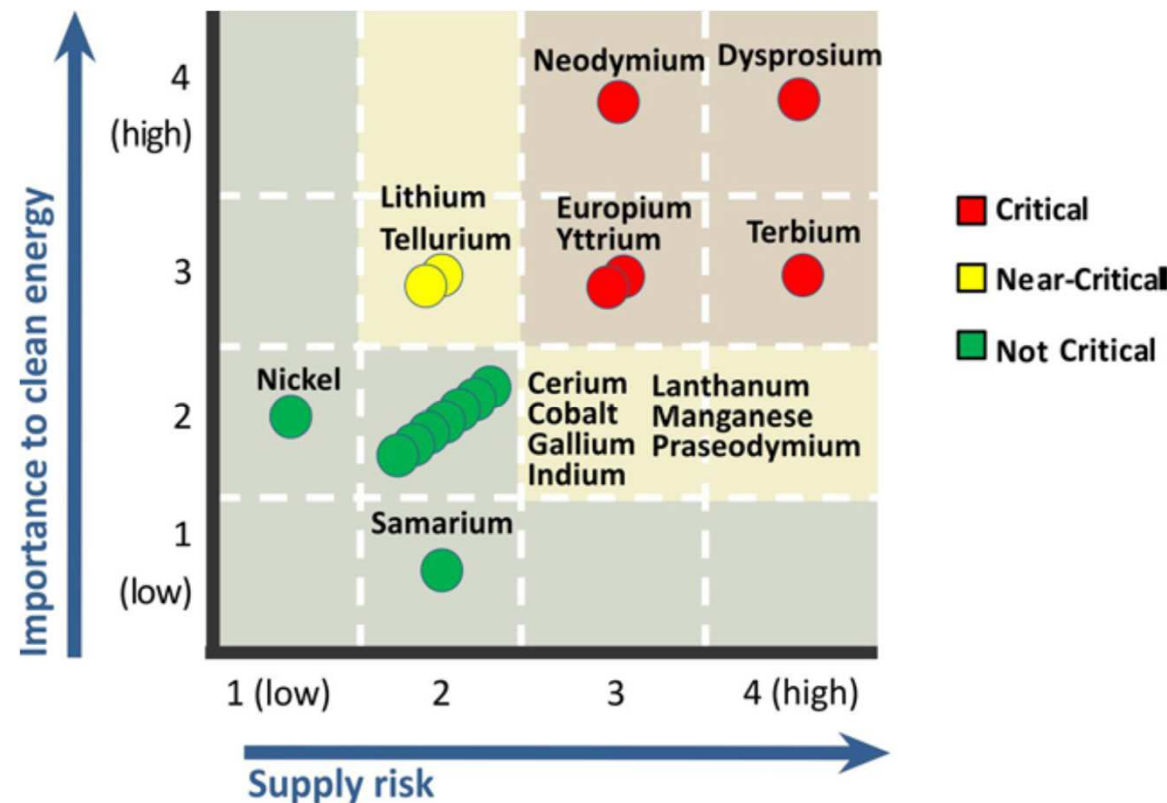


Dal giacimento al consumatore - Concentrazione degli REE

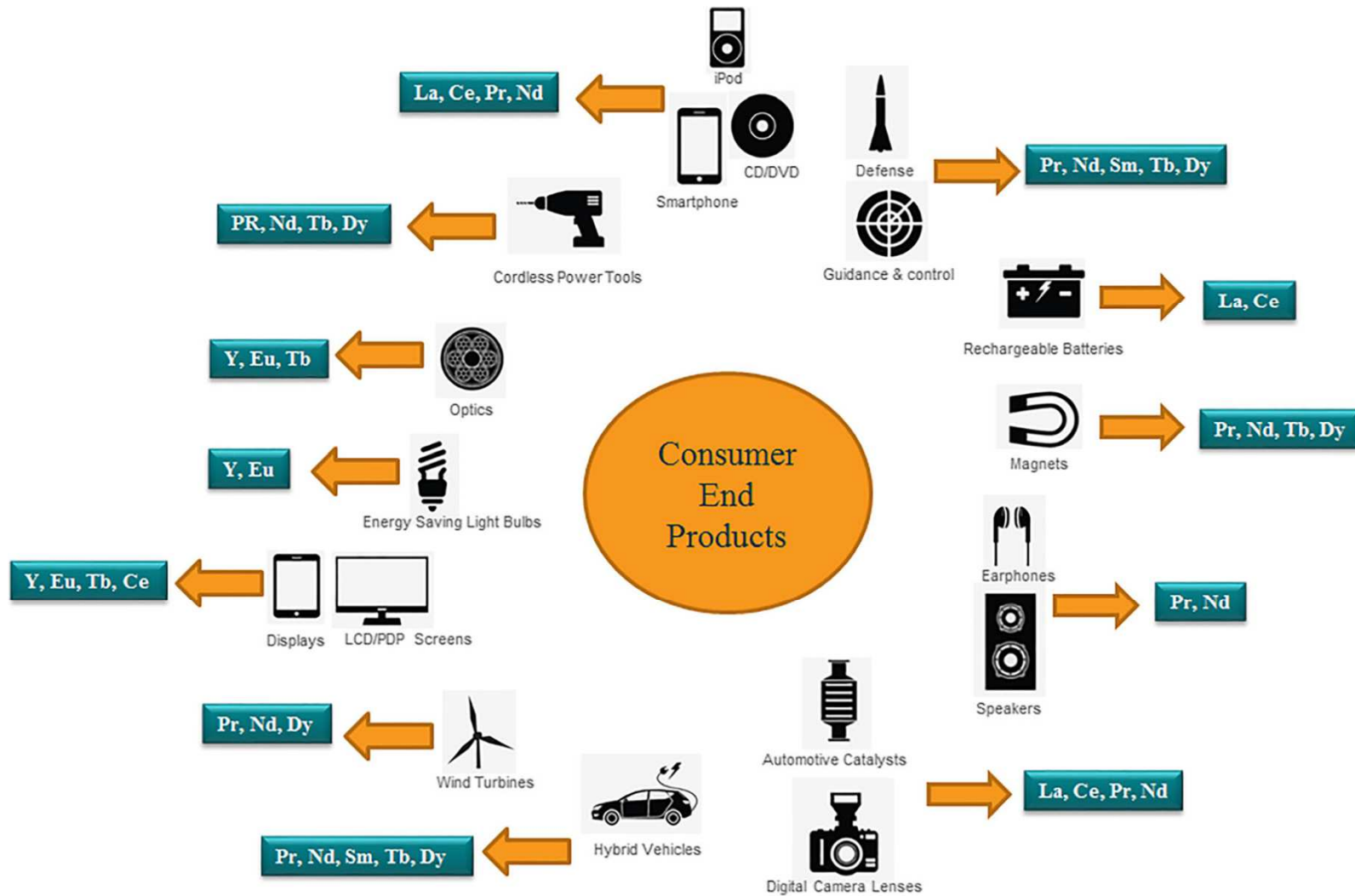


Utilizzo delle REE

Le terre rare per le quali c'è domanda crescente, più difficoltà di approvvigionamento e che sono di grande importanza per un'economia tecnologicamente avanzata e per l'economia pulita sono chiamate "Critical Rare Earth Oxides" ("CREOs") - Neodimio, Europio, Terbio, Disprosio e Ittrio.



Utilizzo delle REE



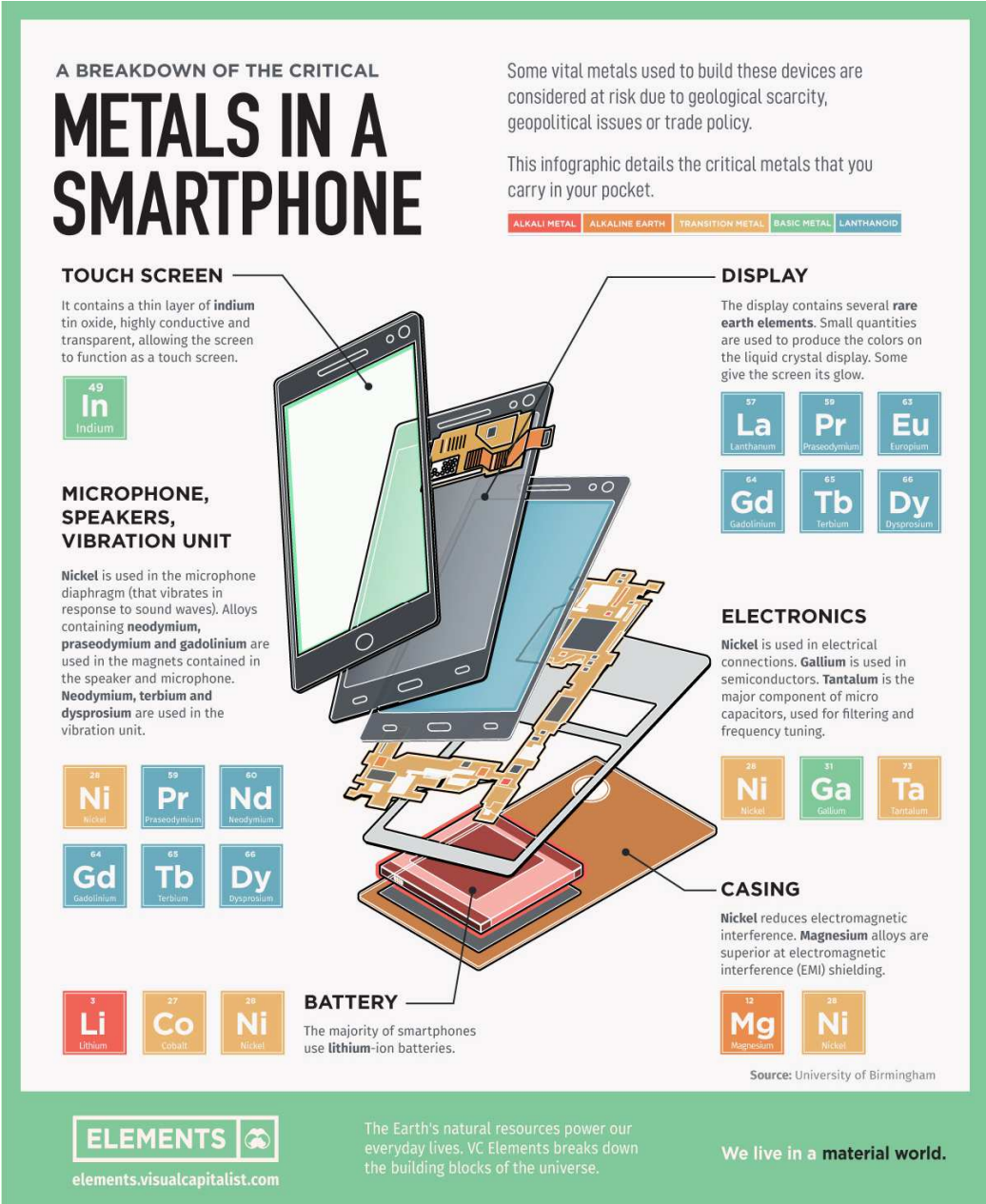
Utilizzo delle REE

9-11 Kg

Hybrid and electric cars can contain 20–25 pounds¹ of rare earths
(Twice the amount found in standard gasoline cars)

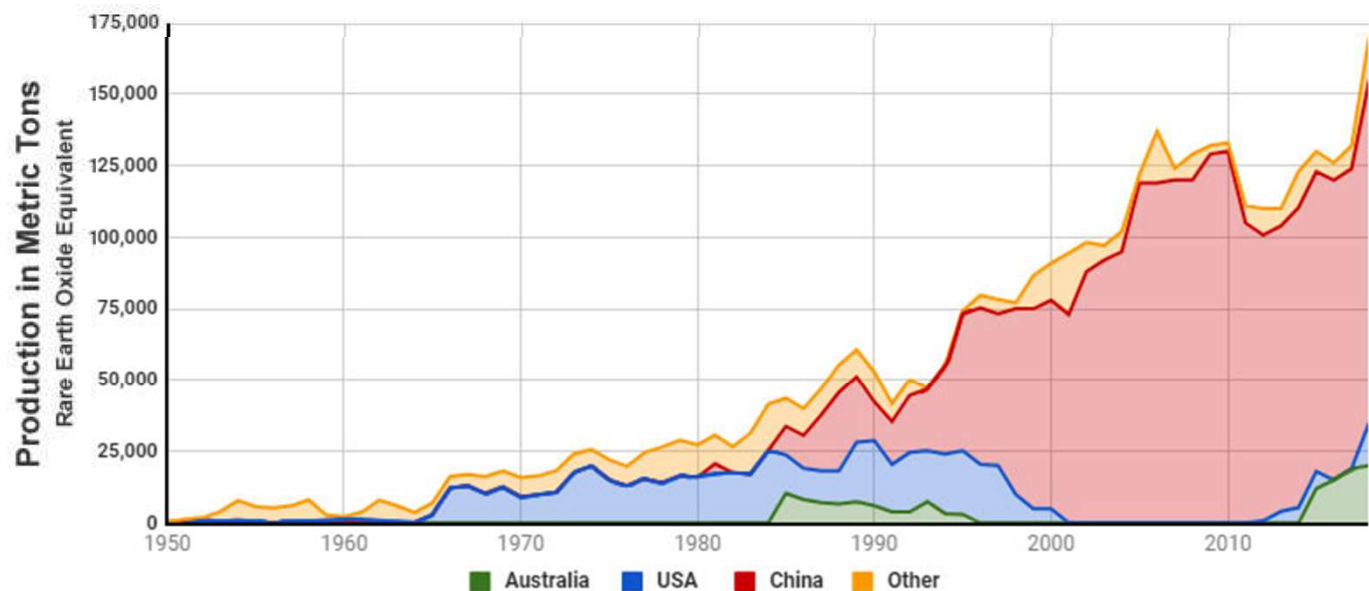


Utilizzo
delle REE



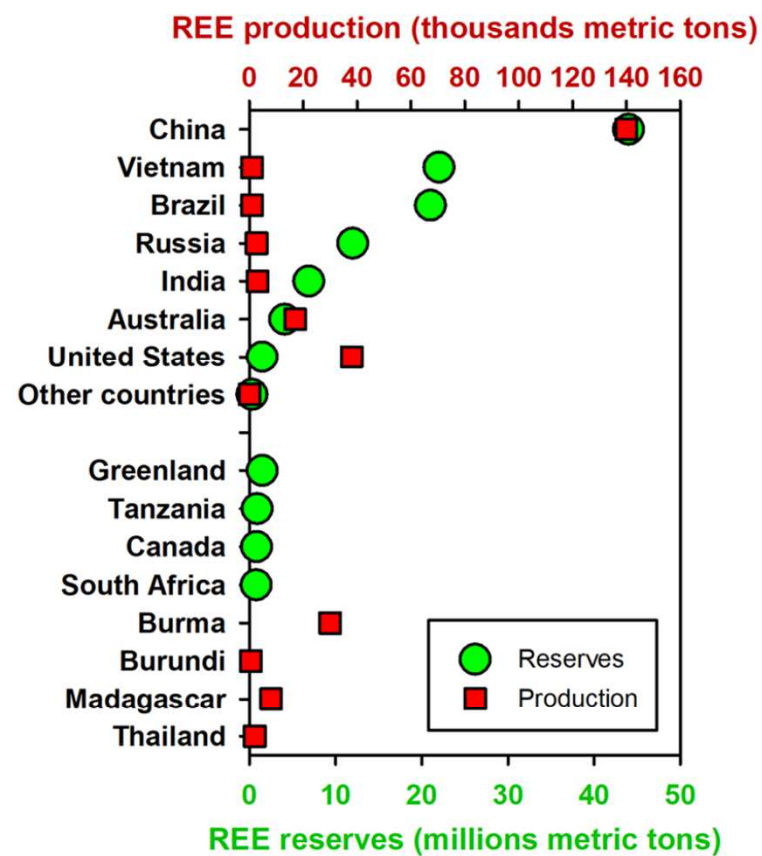
Smartphone Part	Critical Metal
Touch Screen	indium
Display	lanthanum; gadolinium; praseodymium; europium; terbium; dysprosium
Electronics	nickel, gallium, tantalum
Casing	nickel, magnesium
Battery	lithium, nickel, cobalt
Microphone, speakers, vibration unit	nickel, praseodymium, neodymium, gadolinium, terbium, dysprosium

Economia delle REE

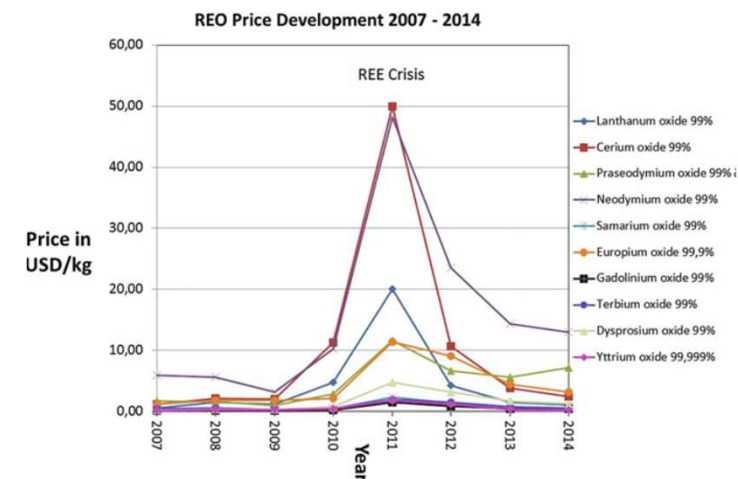
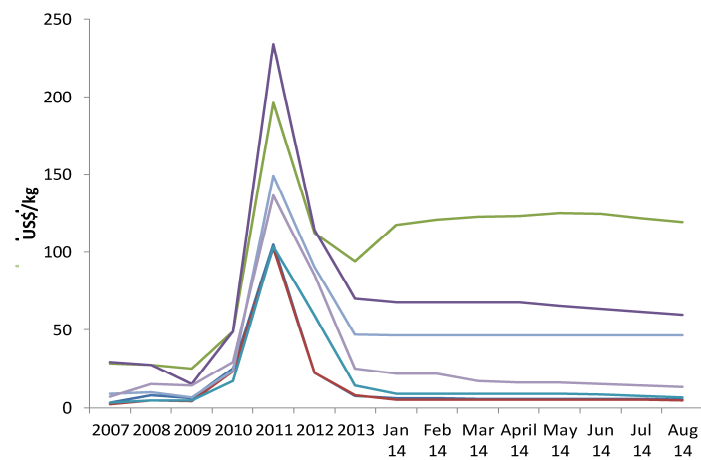
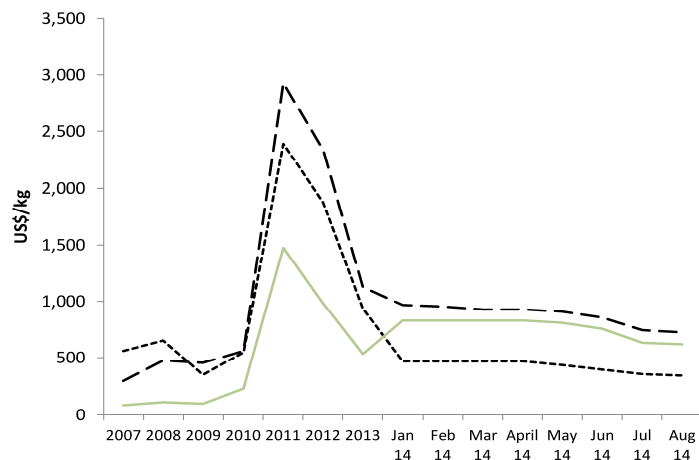


REO	Demand REOs	Supply REOs
CeO_2	60-70 kt	75-85 kt
Nd_2O_3	25-30 kt	30-35 kt
Eu_2O_3	625-725 t	450-550 t
Tb_4O_7	450-550 t	300-400 t
Dy_2O_3	1.5-1.8 kt	1.3-1.6 kt
Y_2O_3	12-14 kt	9-11 kt

Tabella 2.2: Domanda e Offerta globali previste annualmente per una di selezione REOs nel 2016. La domanda complessiva di tutti i REOs è stimata in ~150-170 kt/anno, mentre l'offerta è ~180-210 kt/anno. (Fonte: [34])



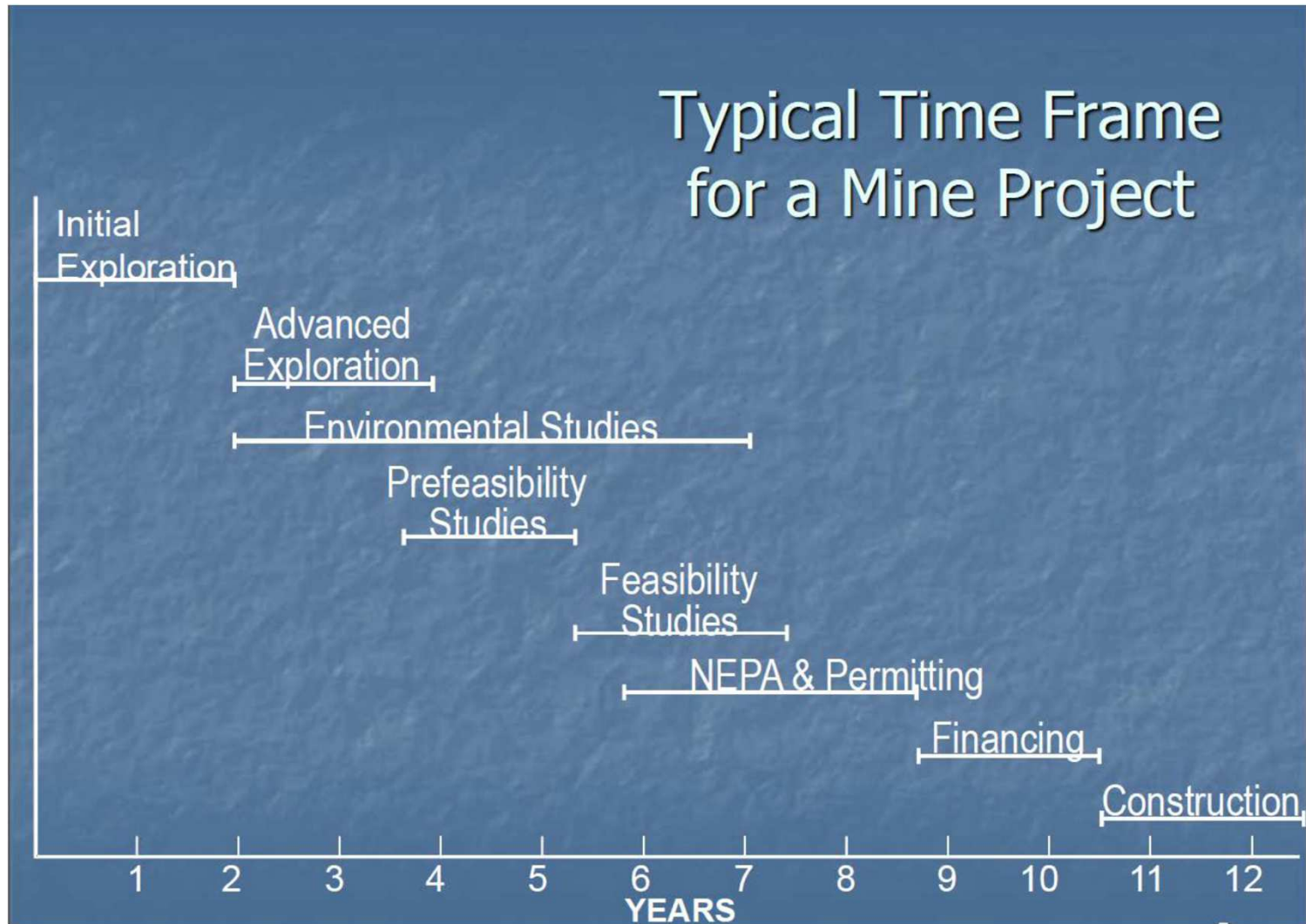
Economia delle REE



Rare earth oxide	2015	2016	2017	2018	2019	2020	2021	2022*
Terbium oxide, 99.99% minimum	564	415	501	455	507	670	1300	2000
Dysprosium oxide, 99.5% minimum purity	279	198	187	179	239	261	400	390
Neodymium oxide, 99.5% minimum	48	40	50	50	45	49	49	130
Europium oxide, 99.9% minimum purity	344	74	77	53	35	31	31	30
Lanthanum oxide, 99.5% minimum purity	3	2	2	2	2	2	2	1
Cerium oxide, 99.5% minimum purity	3	2	2	2	2	2	2	1

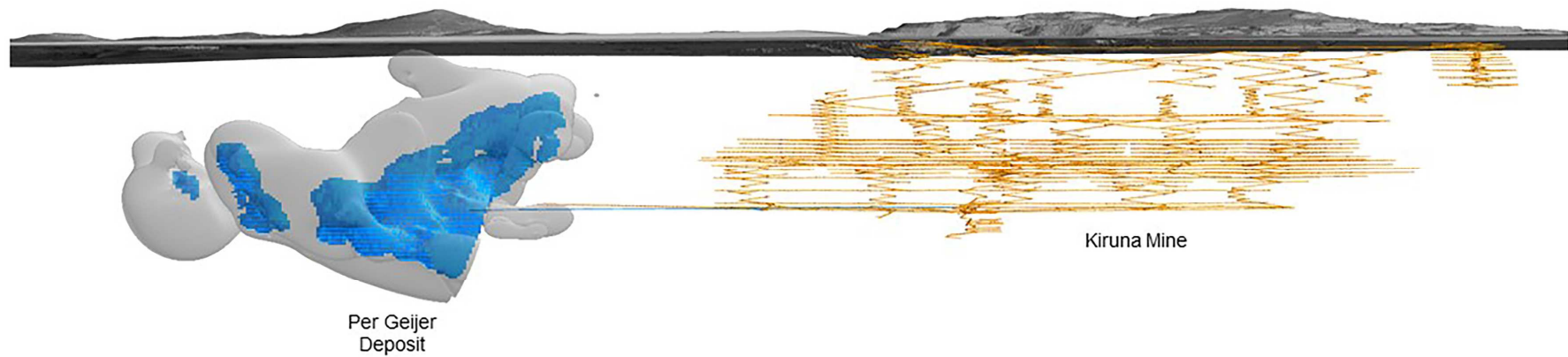
Rare Earth Oxide	Prezzo attuale (2/10/2023) (\$/Kg)	Aumento dal gennaio 2020
Dysprosium	533.10	+54.41%
Neodymium	126.00	+93.85%
Praseodymium	125.80	+72.87%
Terbium	2062.60	+208.77%

Futuro



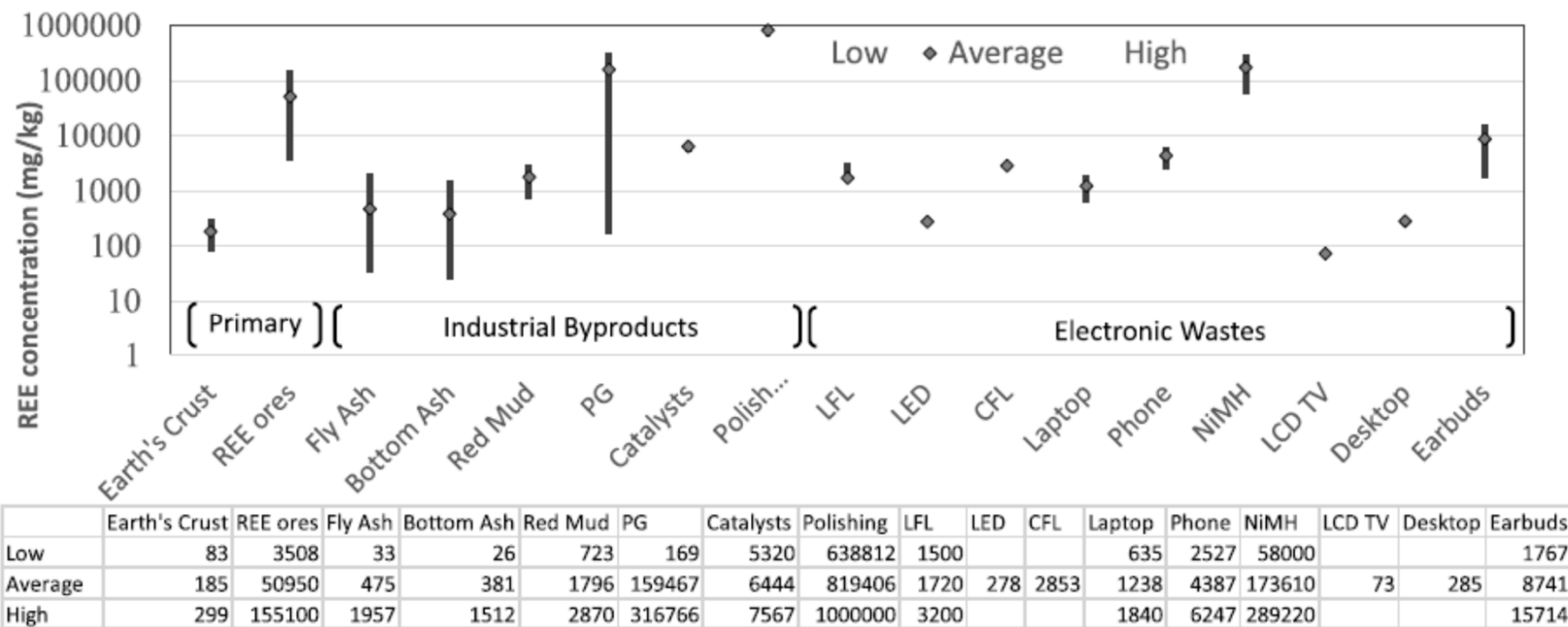
Futuro

Per Geijer Deposit



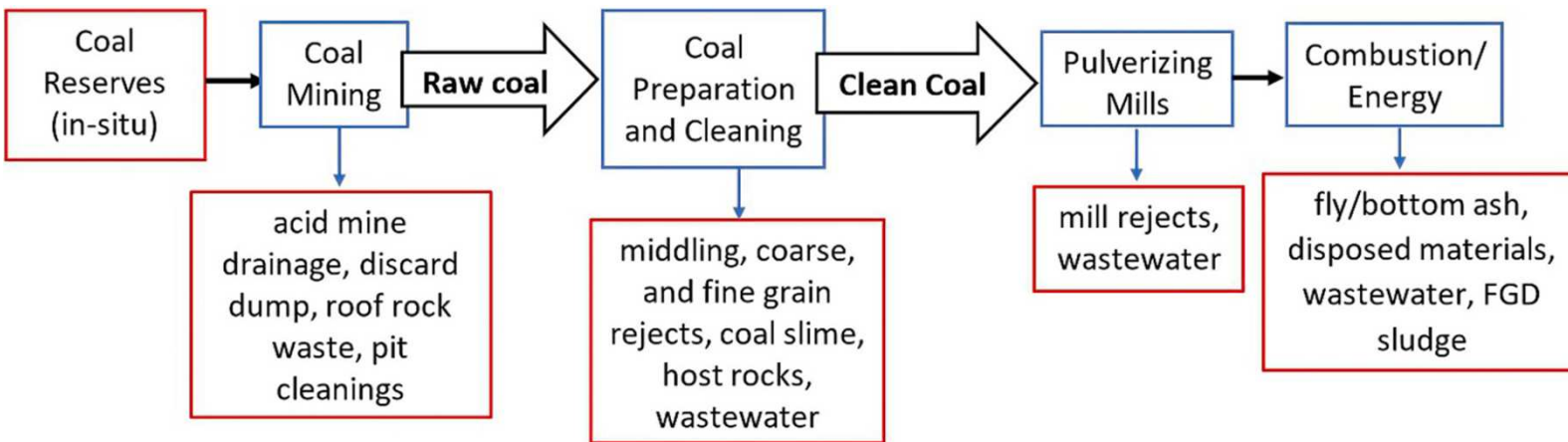
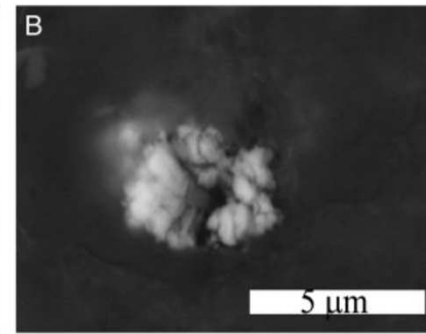
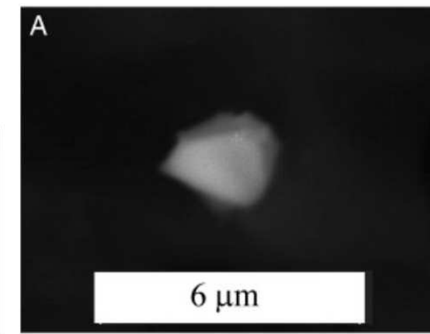
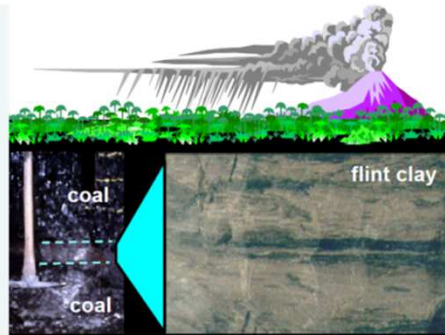
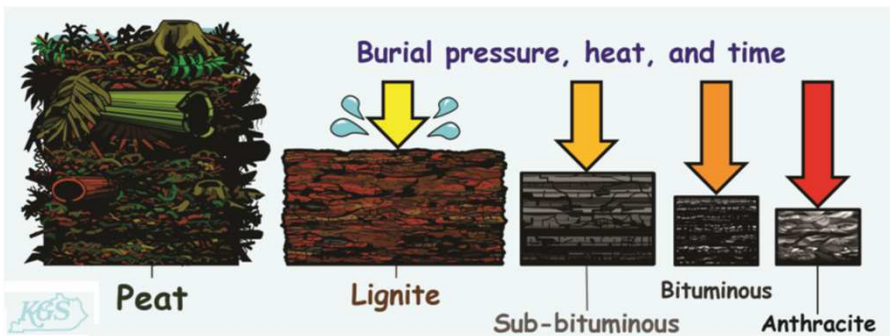
Eiffel Tower for scale at 330 m tall

Futuro - REE da scarti (Byproducts e REEcycling)

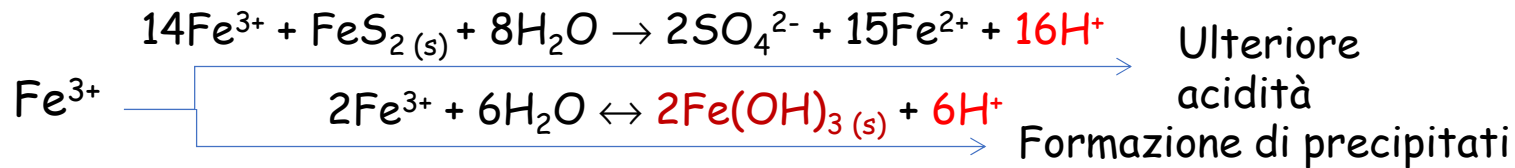
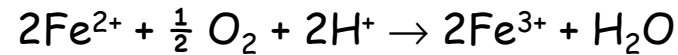
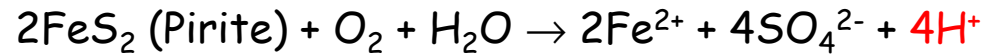


Total rare earth element (REE) content (in ppm or mg/kg) for ores and potential secondary sources (log scale): Earth's crust, REE ores, fly and bottom ash from coal combustion, red mud from bauxite mining, fuel cracking catalysts from petroleum refining, powders from polishing processes, phosphogypsum labelled as PG, electronic waste including Linear Fluorescent Lamps (LFL), Light Emitting Diodes (LED), Compact Fluorescent Lamps (CFLs), laptops, smart phones, nickel metal hydrid (NiMH) batteries, LCD TVs, desktop computers and earbuds.

Futuro - REE da scarti (carbone)

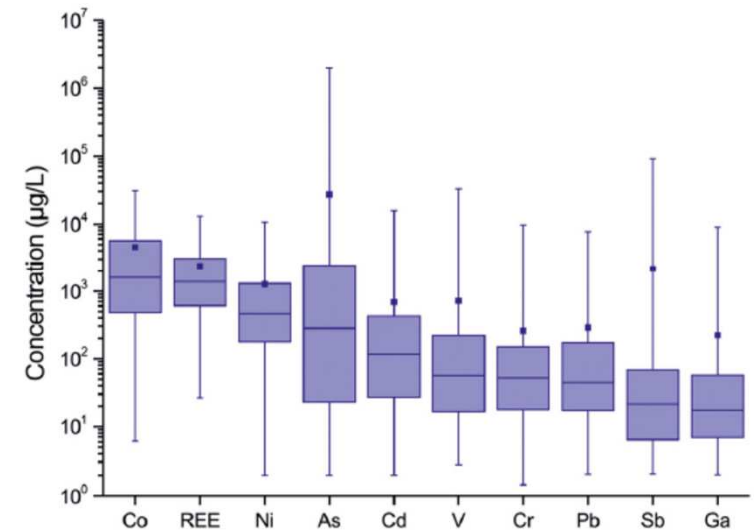


Futuro - REE da scarti (drenaggio acido di miniera)



REE concentration in some AMD.

Location	pH	$\Sigma[\text{REE}]$ ($\mu\text{g/L}$)	Mean $\Sigma[\text{REE}]$ ($\mu\text{g/L}$)
Jaintia Hills coalfield (India)	1.6–4.8		714.7
Iberian Pyrite Belt	1.8–3.4	638–5,167	2,739
Wisniowka mining area (Poland)	2.4–2.6	8,370–24,800	17,916
Discharge to the Odiel River (Iberian Peninsula)	2.4–2.7	2800–4,600	
Inactive Zn–Pb mine of Santa Lucia (Cuba)	2.5–2.6	370–860	
Almagrera mine tailing dam (Iberian Pyrite Belt)	2.6		3,500
Active and passive mines across Illinois (USA)	2.6–4.3	0.69–9,879	1,091
Monte Romero mine (Iberian Pyrite Belt)	2.7		7,900
Xingren coalfield (China)	2.7–4.6	118–926	435
Sitai coal mine and the Malan coal mine (China)	2.99–3.37	72–127	
Former uranium mining site (Germany)	2.9		4,017



Futuro - Agromining

Il concetto di phytomining è sostanzialmente relazionato alla prospezione botanica, quindi alla ricerca e allo studio della biochimica dei metalli e alla biogeografia delle piante iperaccumulatrici di metalli. In tal senso quindi si va incontro alla cosiddetta phytoremediation ovvero all'utilizzo di piante per l'estrazione di metalli da suoli inquinati. Le biomasse recuperate in questo modo hanno però un valore economico relativamente basso (Cd, As, ecc) e lo smaltimento ha comunque un certo costo.

Ci sono però alcuni elementi come Ni, Co, Tl e Au che hanno un valore di mercato più elevato per cui potrebbe essere possibile un loro sfruttamento economico.

L'agromining quindi implica la necessità di:

1. Selezionare delle piante iperaccumulatrici con una grande biomassa
2. Valutazione della diversità genetica e selezione della specie più adatta
3. Sviluppo di pratiche di agromining per massimizzare il ritorno economico
4. Sviluppo di metodi per estrarre l'elemento scelto dalla biomassa

Futuro - Agromining

La scoperta che le piante possono accumulare REE risale agli anni 30 grazie alla scoperta di contenuti apprezzabili di REE nelle foglie del noce *Carya cathayensis* con concentrazioni fino a $2300 \mu\text{g g}^{-1}$ su suoli costituiti da graniti e gneiss. Le ceneri di queste foglie arrivano a contenuti di 2.5% di REE.



Table 2 Information of sampling sites and concentration and characteristic parameters of REEs in samples of *Dicranopteris linearis*

Study area	Soil type	$\sum \text{REEs}$ in leaf	$\sum \text{REEs}$ in soil	BFs	LREE/HREE	δCe	δEu	Reference
Fujian, China	REE mine	3260	414	7.88				Li et al. (1992)
Guangxi, China	Non-mining area	1910	15	130				
Shikoku Island, Japan	Non-mining area	412						Ichihashi et al. (1992)
Guangdong, China	Gold deposit	1960	277	7	159	0.67	0.49	Miao et al. (2011)
Jiangxi, China	Background area	424	159	3	77.8	5.98	0.43	Wei et al. (2001)
	Background area	225	93.6	2	109	11	0.52	
	LREE-enriched mine	1660	1030	2	18.4	0.14	0.23	
	LREE-enriched mine	22,710	1220	2	9.47	0.54	0.23	
	REE Mine where both LREEs and HREEs were enriched	1410	342	4	5.01	0.57	0.32	
	HREE-enriched mine	977	195	5	2.20	0.13	0.13	
	Non-mining area	1120	15	75	40.8	4.20	0.25	
	LREEs mine	2650	331	8	6.78	0.26	0.40	
	HREEs mine	2090	207	10	6.90	0.24	0.05	Wang et al. (2005)
	Non-mining area	1500	–	–	24.3	0.51	0.40	
	Non-mining area	1500	–	–	24.3	0.51	0.40	
Fujian, China	REE mine tailings	2190	202	11	–	–	–	Li et al. (2013a)
	Non-mining area	351	499	0.7	–	–	–	
Jiangxi, China	REE mine tailings and Non-mining area	Young: 479	–	–	–	–	–	Liu et al. (2019b)
		Middle: 1560						
		Mature: 2750						

$\sum \text{REEs}$: the sum of 16 rare earth elements

BFs (bio-concentration factor): the ratio of the concentration in leaf of a plant to the concentration in the soil

LREE/HREE: the ratios of the sum concentrations of light rare earth elements (LREEs, La to Eu) to heavy rare earth elements (HREEs, Gd to Lu)

δCe : $\delta \text{Ce} = \text{Ce}/(0.5\text{Pr} + 0.5\text{La})$, the value of Ce, La and Pr are chondrite-normalized

δEu : $\delta \text{Eu} = \text{Eu}/(0.5\text{Sm} + 0.5\text{Gd})$, the value of Eu, Sm and Gd are chondrite-normalized

Depositi secondari delle Terre Rare: Agromining

La scoperta che le piante possono accumulare REE risale agli anni 30 grazie alla scoperta di contenuti apprezzabili di REE nelle foglie del noce *Carya cathayensis* con concentrazioni fino a 2300 $\mu\text{g g}^{-1}$ su suoli costituiti da graniti e gneiss. Se bruciate, le ceneri di queste foglie arrivano a contenuti di 2.5% di REE.

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	Background area	225	93.6	2	109	11	0.52	
	LREE-enriched mine	1660	1030	2	18.4	0.14	0.23	
	LREE-enriched mine	22,710	1220	2	9.47	0.54	0.23	
	REE Mine where both LREEs and HREEs were enriched	1410	342	4	5.01	0.57	0.32	
	HREE-enriched mine	977	195	5	2.20	0.13	0.13	Wang et al. (2005)
	Non-mining area	1120	15	75	40.8	4.20	0.25	
	LREEs mine	2650	331	8	6.78	0.26	0.40	
	HREEs mine	2090	207	10	6.90	0.24	0.05	
	Non-mining area	1500	–	–	24.3	0.51	0.40	
Fujian, China	REE mine tailings	2190	202	11	–	–	–	Li et al. (2013a)
	Non-mining area	351	499	0.7	–	–	–	
Jiangxi, China	REE mine tailings and Non-mining area	Young: 479	–	–	–	–	–	Liu et al. (2019b)
		Middle: 1560						
		Mature: 2750						

$\sum \text{REEs}$: the sum of 16 rare earth elements

BFs (bio-concentration factor): the ratio of the concentration in leaf of a plant to the concentration in the soil

LREE/HREE: the ratios of the sum concentrations of light rare earth elements (LREEs, La to Eu) to heavy rare earth elements (HREEs, Gd to Lu)

δCe : $\delta \text{Ce} = \text{Ce}/(0.5\text{Pr} + 0.5\text{La})$, the value of Ce, La and Pr are chondrite-normalized

δEu : $\delta \text{Eu} = \text{Eu}/(0.5\text{Sm} + 0.5\text{Gd})$, the value of Eu, Sm and Gd are chondrite-normalized

Depositi secondari delle Terre Rare: Agromining

Table 1

Concentrations of rare earth elements in the fern leaves, roots and soil ($n = 5$, $\mu\text{g g}^{-1}$, dry mass)

	La	Ce	Pr	Nd
Leaf	1503.4–2148.4	2829.7–3956.6	463.5–609.5	1023.1–1358.7
Rhizome	213.3–544.4	233.7–243.0	105.1–126.3	337.8–352.4
Adventitious root	118.8–141.5	108.4–157.7	36.9–201.5	146.3–1247.9
Soil	150.5–453.1	244.9–281.1	33.1–137.1	119.2–474.9

Table 2

Concentrations of rare earth elements in different components of fern leaves ($n = 5$, $\mu\text{g g}^{-1}$, dry mass)

	La		Ce		Pr		Nd	
	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%
Crude peptides	20.8 ± 1.3	1.0	102.4 ± 13.6	2.7	7.0 ± 0.6	1.2	17.9 ± 4.7	1.4
Free amino acids and pigments	11.3 ± 0.8	0.5	36.8 ± 3.8	1.0	2.6 ± 0.1	0.4	6.4 ± 0.2	0.5
Cell debris (membrane)	212.6 ± 15.1	10.4	577.9 ± 45.8	15.4	57.1 ± 10.3	9.6	125.9 ± 12.9	10.1
Cell wall	1802.6 ± 87.3	88.1	3031.6 ± 265.4	80.9	527.6 ± 23.1	88.8	1094.1 ± 53.7	87.9
Leaflet	2047.3 ± 165.3	100.0	3748.3 ± 312.5	100.0	594.5 ± 45.7	100.0	1244.9 ± 86.5	100.0

Depositi secondari delle Terre Rare: Agromining

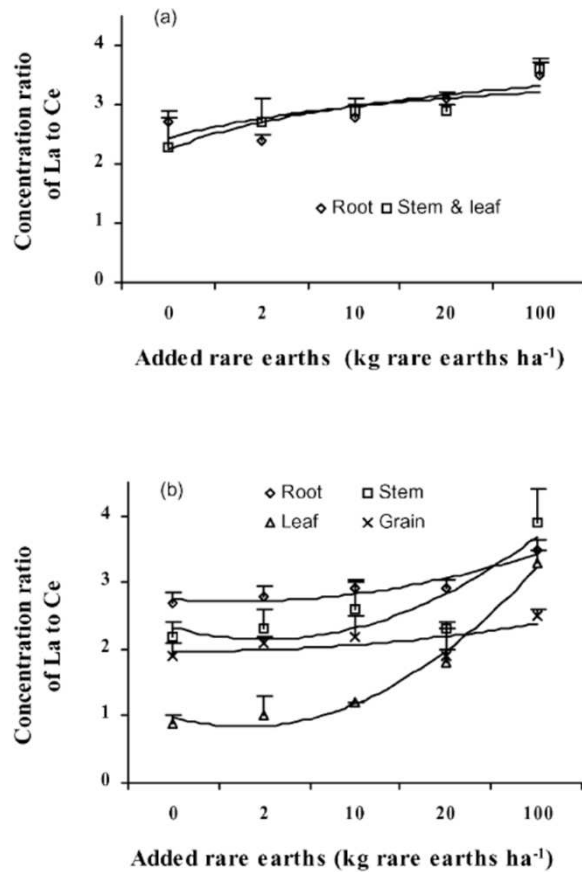


Fig. 4. Concentration ratio of La/Ce in maize (a) at 10 days and (b) at maturity stage after application of rare earths.

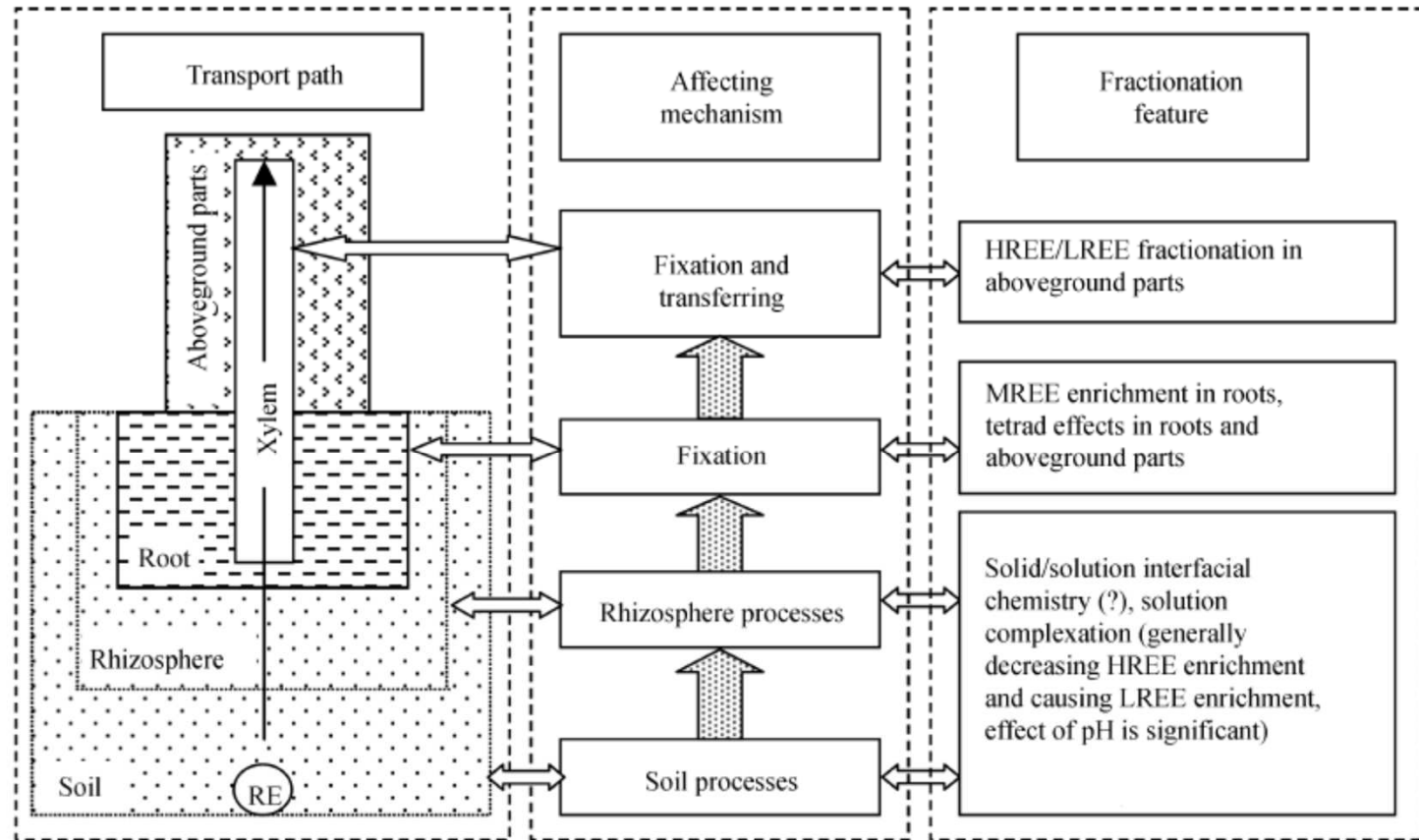


Figure 9 Conceive model of REE fractionations in plants.

Futuro - Agromining

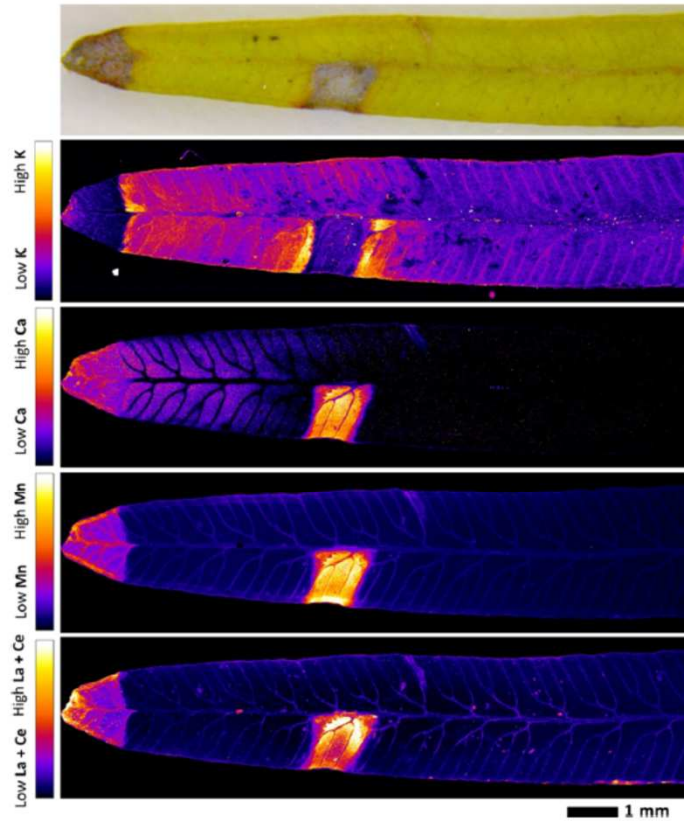


Figure 2. Synchrotron-based X-ray fluorescence microscopy elemental maps of a hydrated *D. linearis* pinnule. The maps measure 12.95×2.88 mm. The elemental image was acquired with a step size of $8 \mu\text{m}$ with a dwell of 15 ms per pixel using a 12.0 keV incident beam.

REE	REEs concentration in dry plant	REEs concentration in ash (500 °C, 2 h)
La	983	7575
Ce	180	1421
Pr	167	1310
Nd	504	4069
Sm	65.9	527
Eu	9.21	72.4
Gd	43.5	348
Tb	4.73	36.4
Dy	17.7	134
Ho	2.49	18.7
Er	4.98	40.7
Tm	0.50	4.80
Yb	3.23	23.5
Lu	0.50	4.05
Y	45.8	371
Sc	0	2.02
Σ REEs	2032	15,956

Futuro - REEciclyng

Battery Material Recycling Business Structure

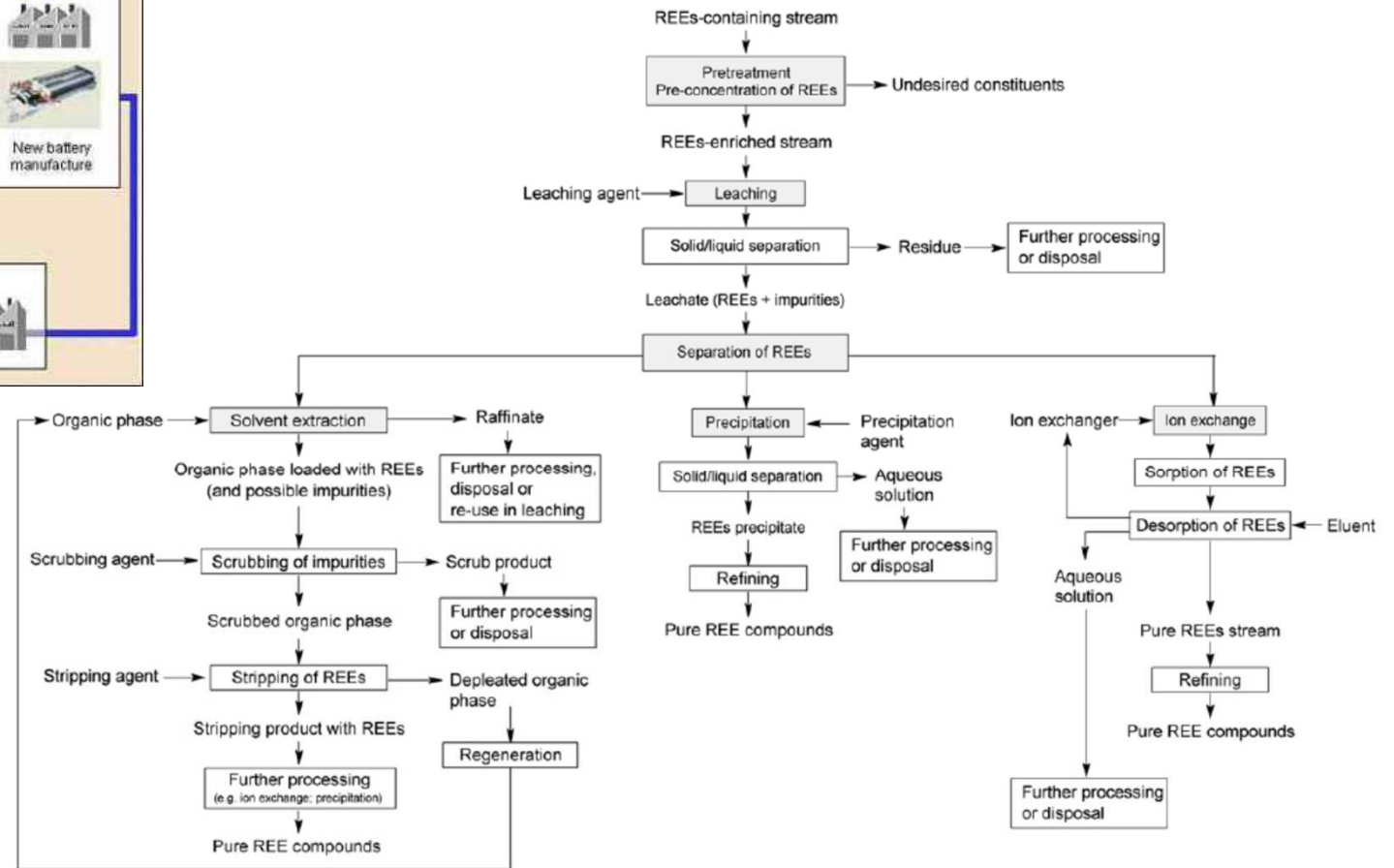
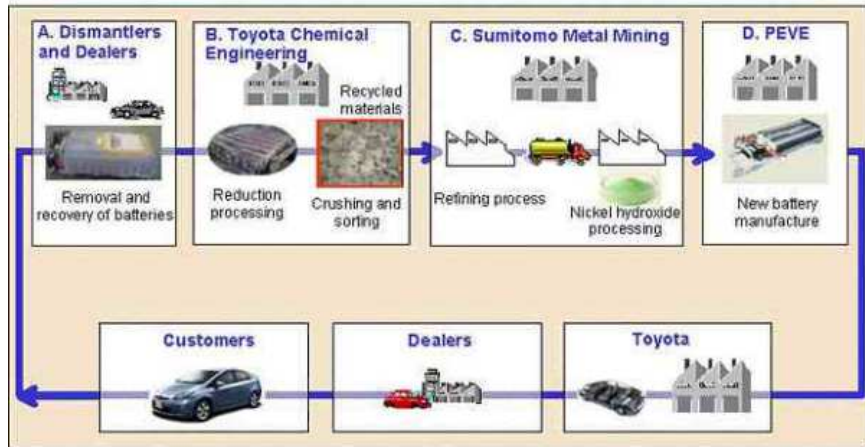


Fig. 1. A simplified flowsheet based on pre-treatment, leaching, solvent extraction, ion exchange and precipitation for the separation of REEs from solid streams.