

# Rare Earth Elements: Conventional and Non-Conventional Deposits

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## Summary

The renovated interest for the REE elements compels to strengthen and promote the study of their classical outcrops and the discovery of new elements of the same group along the same lines China followed over the last years. In magmatic outcrops, REE tend to concentrate in the most alkaline typologies (undersaturated and oversaturated) and in carbonatites, especially in their latest stages, being these pegmatitic or associated to hydrothermal fluids, frequently saline and rich in F or B. In addition, other mechanisms of transport of REE can occur. However, to obtain an economic deposit, sometimes these pre-concentrations need improve their cut-off grades by means of supergene enrichment. Deposits of hydrothermal origin are associated with hypersaline fluids with the resulting hydrothermal alterations (albitizations, scapolitizations...) or fluids very rich in F or B. Consequently, some skarns, IOCG or U deposits associated to unconformities constitute the hydrothermal deposits more given to contain REE. In addition, fluids associated with shear zones, rich in CO<sub>2</sub>, also transport REE. In the exogenous medium REE can efficiently be concentrated in saline environments, as caliches, evaporites, primary or diagenetic phosphorites, submarine muds and Fe-Mn submarine crusts, while more stable minerals, as monazite or xenotime concentrate in placers. The combustion of carbons can result in differentiated residue rich in REE. Moreover, laterites, bauxites and clays, product of the weathering of other rocks, can become enriched in REE. The potential in REE is explored in geothermal fluids and manganese deposits, as well as in ancient sedimentary series including hard grounds or diagenetic zeolite deposits, or even some deposits associated with reductive geochemical traps, like red beds or series including black shales.

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**Key-words:** Rare Earth elements, magmatism, alkaline, undersaturated, saturated, pegmatites, NYF, LCT, topaz rhyolites, skarn, hydrothermal, IOCG, discordance, metamorphism, evaporite, laterite, bauxite, caliche, phosphorite, placer, ionic exchange clays, coal, oceanic mud, nodules, ferruginous crusts, manganese crusts, manganese deposits, zeolites, geothermal, red bed, black shales.

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## 1. Introduction

Under the denomination of the Rare Earth Elements (REEs), a group of elements of the periodic table sharing very similar properties has been included: the lanthanides (elements from La to Lu) and the yttrium. Currently, though not from a geochemical but from an industrially applied point of view, Sc is prone to be included (*Service, 2010*). Generally, Rare Earth Elements tend to be divided into light (LREEs) and heavy (HREEs). However, there is no unanimity regarding the limits of this definition, but in this work, we will accept the criteria in which LREEs comprise from La to Eu and HREEs go from Gd to Lu, plus Y (*Chakhmouradian and Wall, 2012*). In some cases, the term of medium rare earth elements (MREE) is used for the elements Sm, Eu and Gd (*Hatch, 2012*). Although this term has a metallurgical origin, it can have several implications from a geochemical and mineralogical point of view, as it will be seen. Since their discovery, the rare earth elements have had very limited uses in industry. However, during the last decades a demand of these elements increased due to a strong expansion of

their applications in strategic sectors (*Long et al., 2010*). Nonetheless, this expansion does not correspond to a higher consumption of the ensemble formed by the industrialized countries, whereas their production is found under an almost monopolized situation (in the order of a 95%) controlled by China that, on the other hand, has a very low exportation rate (*Service, 2010*). Not all REE share the same demand, price or applications: HREE are more important regarding the emerging technologies as renewable energy sources, defence or electronic industries (*Hatch, 2012*).

During the last decades, the study of mineral deposits has rapidly advanced. Partly, this advance is due to the necessity to localize new deposits of these elements as its demand increases whilst the classical deposits become exhausted or prove to be insufficient. Regarding this aspect, it is precisely in China where major advances have been carried out (*Kynicky et al., 2012*). On the other hand, less effort has been dedicated in Occident. Thus, with respect to REE, it urges to discover new deposits due to geostrategic motives (*Chakhmouradian et al., 2015a*). However, little is known still about the behaviour of these elements in some mediums, or about their concentration mechanisms in some systems. In some of these cases, little is known about the minerals that contain them. Therefore, the main aim of this contribution is to thoroughly revise the state of knowledge of the classical REE deposits, as well as to aim towards some unconventional but potential deposits. For this revision, we will use bibliographical data in addition of some information offered by the mineral associations observed in museums. However, this work does not pretend to be a revision of the complete distribution of all REE minerals since some extremely rare minerals have only been described in paragenesis that are unable to generate deposits.

## 2. Conventional vs. Non-conventional Deposits

We have to recall that in order to generate a deposit it is required to increase the element concentration in the rock with respect to its initial

concentration in the crust or in the mantle. Regarding the REE, their name could suggest them to be elements found in very low concentrations, fact which is not entirely true. In any case, heavy REE are found in the crust in much lower concentrations than light REE (*Linnen et al., 2014*). If we analyse any traditional manual related to mineral deposits, it will be observed that they normally make mention to REE in carbonatites, maybe in undersaturated alkaline rocks or in alkaline granites and their NYF-type pegmatites, in addition to the placers where, in any case, they are extracted as a by-product related to the mining of other minerals. Little more is mentioned other than in some manuals which point to possible REE skarns. Nonetheless, in the last few years, deposits in previously unsuspected mediums have been localized. The major achievements regarding this field have taken place in China, where large deposits in laterites, clays and other unconventional deposits have been discovered.

However, a general bibliographical revision, not only on the main targets set by mining companies, but on the discoveries carried out by base mineralogists, even by amateurs, helps to take a glimpse that there are lots more mechanisms than suspected which can concentrate REE in different minerals and which follow very different processes. In this work some of these possibilities will be brought up. Therefore, in this report, we will consider the following types of deposits; conventional or non-conventional, proven or possible: a) deposits in alkaline undersaturated rocks; b) carbonatites; c) deposits in granitoids; d) deposits in rhyolites with topaz; e) NYF pegmatites; f) LCT pegmatites; g) nelsonites; h) skarns; i) metamorphic rocks; j) uranium in unconformities; k) IOCG; l) shear zones; m) MVT; n) phosphorites; o) evaporites; p) residual rocks; q) calcretes and soils; r) carbon; s) cationic exchange clays; t) gossans; u) placers v) ocean muds; w) Fe-Mn submarine deposits.

In fact, the number of mineral species, which can be considered as REE ores, has also increased. There are even some mineral species poorly characterised. In *Table 1* a list of the most common REE minerals is detailed, including all of those mentioned in this revision.

**Table 1.** List of the most common REE minerals, with their corresponding structural formulas, in alphabetical order. In boldface, REE minerals or containing REE, which are or have been extracted as ores for these elements or that have the potential to be at short-term. Clays are not included in this list.

MINERAL	FORMULA	MINERAL	FORMULA
Adamite	$(Zn,REE)_2(AsO_4)(OH)$	Aeschynite-(Ce)	$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)$
Aeschnynite-(Y)	$(Y,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$	Agardite-(Ce)	$CeCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$
Agardite-(Y)	$YCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$	Allanite-(Ce)	$\{CaCe\} \{Al_2Fe^{2+}\} (Si_2O_7)(SiO_4)O(OH)$
<b>Allanite-(Y)</b>	$\{CaY\} \{Al_2Fe^{2+}\} (Si_2O_7)(SiO_4)O(OH)$	Anatase	$(Ti,REE)_2O_2$
<b>Ancylite-(Ce)</b>	$SrCe(CO_3)_2 \cdot OH \cdot H_2O$	Andradite	$(Ca,REE)_3Fe^{3+}_2(SiO_4)_3$
Astrocyanite-(Ce)	$Cu_2(Ce,Nd,La)_2(UO_2)(CO_3)_3(OH)_2 \cdot 1.5H_2O$	Atelosite-(Y)	$Y_3Si_3O_8(OH)_8$
<b>Bastnäsite-(Ce)</b>	$(Ce,La)(CO_3)F$	Bijvoetite-(Y)	$(Y,Dy)_2(UO_2)_4(CO_3)_4(OH)_6 \cdot 11H_2O$
<b>Brannerite</b>	$(U,Ca,Y,Ce)(Ti,Fe)_2O_6$	<b>Britholite-(Ce)</b>	$(Ce,Ca)_3(SiO_4,PO_4)_3(OH,F)$
Brockite	$(Ca,Th,Ce)(PO_4) \cdot H_2O$	<b>Burbankite</b>	$(Na,Ca)_3(Sr,Ba,Ca,REE)_3(CO_3)_3$
Bussite-(Ce)	$(Ce,REE)_3(Na,H_2O)_6MnSi_9Be_5(O,OH)_{30}F_4$	<b>Calcio-ancylite-(Ce)</b>	$(Ca,Sr)Ce_3(CO_3)_4(OH)_3 \cdot H_2O$
<b>Calkinsite-(Ce)</b>	$(Ce,La)_2(CO_3)_3 \cdot 4H_2O$	<b>Carbocernaite-(Ce)</b>	$(Ca,Na)(Sr,REE)(CO_3)_2$
Carliseckeite-(Nd)	$NaNdCa_3(PO_4)_3F$	Caysichite-(Y)	$Y_4(Ca,REE)_4Si_8O_{36}(CO_3)_6(OH) \cdot 7H_2O$
<b>Cebaite-(Ce)</b>	$Ba_3Ce_2(CO_3)_3F_2$	<b>Cerianite-(Ce)</b>	$(Ce^{4+},Th)_2O_2$
<i>Ceropyrochlore</i>	$Ce(Nb,Ti)_2O_6$	<b>Cerite-(Ce)</b>	$Ce_9Fe^{3+}(SiO_2)_6[(SiO_3)(OH)](OH)_3$
Cerottungstite-(Ce)	$(Ce,Nd,Y)W_2O_6(OH)_3$	Cheralite-(Ce)	$(Ca,Ce,Th)(P,Si)_4O_4$
Chevkinite-(Ce)	$(Ca,Ce,Th)_4(Fe^{2+},Mg)_2(Ti,Fe^{3+})_3Si_4O_{22}$	Chukrovite	$Ca_3(Ce,Y)[F]SO_4(AlF_6)_2 \cdot 10H_2O$
<b>Churchite-(Y)</b>	$YPO_4 \cdot H_2O$	Coffinite	$(U^{4+},Th,REE)(SiO_4)_{1-3}(OH)_{4x}$
<b>Cordylite-(Ce)</b>	$NaBaCe_2(CO_3)_4F$	Coskrenite-(Ce)	$(Ce,Nd,La)_2(C_2O_4)(SO_4)_2 \cdot 12H_2O$ $(Ce)(Sr,Ca,Ba)_3(Ce,La)(PO_4)(CO_3)_3 \cdot x(OH,F)_x$
<b>Crandallite</b>	$CaAl_3(PO_4)_2(OH)_3 \cdot H_2O$	Daqingshanite	
<b>Davidite-(Ce)</b>	$(Ce,La)(Y,U,Fe^{2+})(Ti,Fe^{3+})_{20}(O,OH)_{38}$	Decrespignyite-(Y)	$Cu(Y,REE)_4(CO_3)_4(OH)_5Cl \cdot 2H_2O$
<b>Diaspore</b>	$(Al,REE)OOH$	Dissakisite-(Ce)	$\{CaCe\} \{Al_2Mg\} (Si_2O_7)(SiO_4)O(OH)$
<b>Dollaseite-(Ce)</b>	$\{CaCe\} \{MgAlMg\} (Si_2O_7)(SiO_4)(OH)F$	Donnayite-(Y)	$NaCaSr_3Y(CO_3)_6 \cdot 3H_2O$ $Na_4(Ca,Ce)_2(Fe^{2+},Mn^{2+},Y)ZrSi_8O_{22}(OH \cdot Cl)_2$
Doverite	$YCaF(CO_3)_2$	<b>Eudyalite</b>	
<b>Euxenite-(Y)</b>	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$	Ewaldite	$Ba(Na,Ca,Y,Ce,K)(CO_3)_2 \cdot 2.6H_2O$
Fergusonite-Ce	$(Ce,La,Y)NbO_4$	<b>Fergusonite-(Y)</b>	$YNbO_4$
Fersmite	$(Ca,Ce,Na)(Nb,Ta,Ti)_2(O,OH,F)_6$	<b>Florenite-(Ce)</b>	$CeAl_3(PO_4)_2(OH)_6$
<b>Florenite-(La)</b>	$(La,Ce)Al_3(PO_4)_2(OH)_6$	<b>Fluocerite-(Ce)</b>	$(Ce,La)F_3$
<b>Fluocerite-(La)</b>	$(La,Ce)F_3$	Fluorapatite	$(Ca,Ce)_5(PO_4)_3F$
<b>Fluorbritholite-(Ce)</b>	$Ca_2(Ce,Ca)_3(SiO_4,PO_4)_3(F,OH)$	Fluorite	$(Ca,REE)F_2$
Formanite-(Y)	$YTaO_4$	Françoisite-(Nd)	$(Nd,Ce,Sm)(UO_2)_2(PO_4)_2O(OH) \cdot 6H_2O$
<b>Gadolinite-(Y)</b>	$Y_2Fe^{2+}Be_2Si_2O_{10}$	<b>Gagarinite-(Y)</b>	$NaCaY(F,Cl)_6$
Gerenite-(Y)	$(Ca,Na)_2(Y,REE)Si_6O_{18} \cdot 2H_2O$	<b>Gorceixite</b>	$(Ba,REE)Al_3[(PO_4)_2(OH)_5] \cdot H_2O$
Gittinsite	$CaZrSi_2O_7$	<b>Goyazite</b>	$SrAl_3(PO_4)_2(OH)_3 \cdot H_2O$
Grossular	$(Ca,REE)_3Al_2(SiO_4)_3$	Gysinite-(Nd)	$Pb(Nd,La)(CO_3)_2(OH) \cdot H_2O$
Häleniusite-(La)	$(La,Ce)OF$	Hellandite-(Y)	$(Y,Ca)_6(Al,Fe^{3+})Si_4B_4O_{20}(OH)_4$
Hingganite-(Y)	$(Y,Yb,Er)_2Be_2Si_2O_8(OH)_2$	Horváthite-(Y)	$NaY(CO_3)F_2$
<b>Huanghoite-(Ce)</b>	$Ba(Ce,La,Nd)(CO_3)_2F$	Huttonite	$(Th,REE)(Si,P)O_4$
Imoriite-(Y)	$Y_2(SiO_4)(CO_3)$	Joquinite-(Ce)	$Ba_2NaCe_2Fe^{2+}Ti_5Si_2O_{26}(OH) \cdot H_2O$
Kainosite-(Y)	$Ca_2(Y,Ce)_2Si_4O_{12}(CO_3) \cdot H_2O$	Kamotoite-(Y)	$Y_2(UO_2)_4(CO_3)_3O_4 \cdot 14H_2O$ $(Ce,La,Th)(Ti,Nb)(Al,Fe)(Si,P)_2O_7(OH)_4 \cdot 3H_2O$
Kamphaugite-(Y)	$Ca(Y,REE)(CO_3)_2(OH) \cdot H_2O$	Karnasurtite-(Ce)	
Keiviite-(Y)	$(Y,Yb)_2Si_2O_7$	Khanneshite	$(Na,Ca)_3(Ba,Sr,Ce,Ca)_3(CO_3)_3$
Kobeite-(Y)	$(Y,U)(Ti,Nb)_2(O,OH)_6$	<b>Lanthanite-(Nd)</b>	$(Nd,La)_2(CO_3)_3 \cdot 8H_2O$ $Ca(Gd,Dy)_2(UO_2)_2(SiO_4)(CO_3)_8(OH)_2 \cdot 4 \cdot 48H_2O$
Lávenite	$(Na,Ca)_4(Mn,Fe)_2(Zr,Ti,Nb)_2(Si_2O_7)_2(O,F)_4$	Lepersonnite-(Gd)	
Levinsonite-(Y)	$(Y,Nd,La)Al(C_2O_4)(SO_4)_2 \cdot 12H_2O$	Lokkaite-(Y)	$Ca(Y,Gd,Nd,Dy)_4(CO_3)_7 \cdot 9H_2O$

<b>Loparite-(Ce)</b>	(Ce,Na,Ca)(Ti,Nb)O <sub>3</sub>	<b>Lueshite</b>	NaNbO <sub>3</sub>
<b>Microlite</b>	(Ca,Y <sup>3+</sup> ,U,Na) <sub>2-4</sub> (Ta,Nb,Ti,Fe <sup>3+</sup> ) <sub>2</sub> O <sub>7</sub>	<b>Miserite</b>	K(Ca,Ce) <sub>6</sub> Si <sub>2</sub> O <sub>22</sub> (OH,F) <sub>2</sub>
<b>Mckelveyite-(Y)</b>	NaCaBa <sub>3</sub> Y(CO <sub>3</sub> ) <sub>6</sub> ·3H <sub>2</sub> O (H <sub>3</sub> O <sup>+</sup> ,Na,Ca) <sub>2</sub> Ca <sub>3</sub> REE(Ti,Zr)(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (O,O H,F) <sub>4</sub>	<b>Monazite-(Ce)</b>	(Ce,La,Nd,Th)PO <sub>4</sub>
<b>Mosandrite</b>		<b>Nacareniobite</b>	Na <sub>3</sub> Ca <sub>3</sub> (Ce,La)Nb(Si <sub>2</sub> O <sub>7</sub> )OF <sub>3</sub>
<b>Nenadkevichite</b>	(Na,□) <sub>8</sub> Nb <sub>4</sub> (Si <sub>4</sub> O <sub>12</sub> ) <sub>2</sub> (O,OH) <sub>4</sub> ·8H <sub>2</sub> O	<b>Paratoite-(La)</b>	(REE,Ca,Na,Sr) <sub>12</sub> Cu <sub>2</sub> (CO <sub>3</sub> ) <sub>16</sub>
<b>Parisite-(Ce)</b>	Ca(Ce,La) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> F <sub>2</sub>	<b>Perovskite</b>	(Ca,REE)TiO <sub>3</sub>
<b>Perrierite-(Ce)</b>	Ce <sub>4</sub> MgFe <sub>2</sub> <sup>2+</sup> Ti <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> O <sub>8</sub>	<b>Polycrase-(Y)</b>	(Y,Ca,Ce,U,Th)(Ti,Nb,Ta) <sub>2</sub> O <sub>6</sub>
<b>Pyrochlore</b>	(Ca,Na,REE) <sub>2</sub> Nb <sub>2</sub> O <sub>6</sub> (OH,F)	<b>Rhabdophane-(Ce)</b>	(Ce,La)PO <sub>4</sub> ·H <sub>2</sub> O
<b>Rhabdophane-(La)</b>	(La,Ce)PO <sub>4</sub> ·H <sub>2</sub> O	<b>Rinkite-(rinkolite)</b>	(Ca,Ce) <sub>4</sub> Na(Na,Ca) <sub>2</sub> Ti(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> F <sub>2</sub> (O,F) <sub>2</sub>
<b>Rhabdophane-(Nd)</b>	(Nd, Eu, Sm)PO <sub>4</sub> ·H <sub>2</sub> O	<b>Rosenbuschite</b>	(Ca,Na,Ce) <sub>3</sub> (Zr,Ti)(Si <sub>2</sub> O <sub>7</sub> )(F,O) <sub>2</sub>
<b>Sahamallite</b>	(Mg,Fe)(Ce,La,Nd,Pr) <sub>2</sub> (CO <sub>3</sub> ) <sub>4</sub>	<b>Samaraskite</b>	(REE,Fe <sup>2+</sup> ,Fe <sup>3+</sup> ,U,Th,Ca)(Nb,Ta,Ti)O <sub>4</sub>
<b>Shabaite-(Nd)</b>	Ca(Nd,Sm,Y) <sub>2</sub> (UO <sub>2</sub> )(CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·6H <sub>2</sub> O	<b>Shomiokite-(Y)</b>	Na <sub>3</sub> Y[CO <sub>3</sub> ] <sub>3</sub> ·3H <sub>2</sub> O PbCu(Nd,Gd,Sm,Y)(CO <sub>3</sub> ) <sub>3</sub> (OH)·1.5H <sub>2</sub> O
<b>Sazykinaite-(Y)</b>	Na <sub>3</sub> YZr[SiO <sub>3</sub> ] <sub>6</sub> ·6H <sub>2</sub> O	<b>Schuiligite-(Nd)</b>	
<b>Spessartine-(Y)</b>	(Mn,Y)Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	<b>Steenstrupine-(Ce)</b>	Na <sub>14</sub> Ce <sub>6</sub> Mn <sub>2</sub> Fe <sub>2</sub> (Zr,Th)(Si <sub>6</sub> O <sub>18</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>7</sub> ·3H <sub>2</sub> O (Sr,La,Ce,Ca) <sub>4</sub> Fe <sup>2+</sup> (Ti,Zr) <sub>2</sub> Ti <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> O <sub>8</sub>
<b>Stillwellite-(Ce)</b>	(Ce,La,Ca)BSiO <sub>5</sub>	<b>Strontiochevkinite</b>	
<b>Synchysite-(Ce)</b>	Ca(Ce,La)(CO <sub>3</sub> ) <sub>2</sub> F	<b>Synchysite-(Y)</b>	Ca(Y,Ce)(CO <sub>3</sub> ) <sub>2</sub> F
<b>Tanteuxenite</b>	(Y,Ce,Ca)(Ta,Nb,Ti) <sub>2</sub> (O,OH) <sub>6</sub>	<b>Tengerite-(Y)</b>	Y <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·2-3H <sub>2</sub> O
<b>Thalenite-(Y)</b>	Y <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (F,OH)	<b>Thombarite-(Y)</b>	Y <sub>4</sub> (Si,Ha) <sub>4</sub> O <sub>12-x</sub> (OH) <sub>4+2x</sub>
<b>Thorite</b>	(Th,U,REE)SiO <sub>4</sub>	<b>Thorogummite-(Y)</b>	(Th,U)(SiO <sub>4</sub> ) <sub>1-x</sub> (OH) <sub>4x</sub>
<b>Thorutite</b>	(Th,U,Ca)Ti <sub>2</sub> (O,OH) <sub>6</sub>	<b>Thortveitite</b>	(Sc,Y) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
<b>Titanite-(Y)</b>	(Ca,Y)TiOSiO <sub>4</sub>	<b>Tömebohmitte-(Ce)</b>	(Ce,La) <sub>2</sub> Al(SiO <sub>4</sub> ) <sub>2</sub> (OH)
<b>Uraninite</b>	(U,Th,Ce)O <sub>2</sub>	<b>Uranopolycrase</b>	(U <sup>4+</sup> ,Y)(Ti,Nb) <sub>2</sub> O <sub>6</sub>
<b>Variscite</b>	AlPO <sub>4</sub> ·2H <sub>2</sub> O	<b>Västmanlandite-(Ce)</b>	Ca(Ce,La) <sub>3</sub> Al <sub>2</sub> Mg <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> ) <sub>3</sub> (OH) <sub>2</sub> F
<b>Vitussite-(Ce)</b>	Na <sub>3</sub> (Ce,La,Nd)(PO <sub>4</sub> ) <sub>2</sub>	<b>Waimirite</b>	YF <sub>3</sub>
<b>Wakefieldite-(Y)</b>	Y(VO <sub>4</sub> )	<b>Woodhouseite</b>	CaAl <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>
<b>Yttrocraite-(Y)</b>	(Y,Th,Ca,U)(Ti,Fe) <sub>2</sub> (O,OH) <sub>6</sub>	<b>Yttritungstite</b>	YW <sub>2</sub> O <sub>6</sub> (OH) <sub>3</sub>
<b>Zugshunsite-(Ce)</b>	(Ce,Nd,La)Al(C <sub>2</sub> O <sub>4</sub> )(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O		

### 3. Deposits Associated to Undersaturated Alkaline Rocks

Undersaturated alkaline rocks can be found within a wide range of geological contexts (Sørensen, 1974), including oceanic isles (Ignacio et al., 2008). Yet, those having a heightened metallogenic interest are related to continental rifting (i.e., Kampunzu and Mohr, 1991). Both plutonic and volcanic alkaline rocks can contain a wide variety of accessory minerals rich in REE. However, plutonic rocks belonging to this typology are much more interesting than their volcanic equivalents due to volumetric reasons; in addition, hydrothermal reworking phenomena, which help to concentrate the mineralization, rarely occur in volcanic deposits.

Intrusive alkaline complexes can contain both ultrabasic rocks and undersaturated

alkaline rocks, saturated alkaline rocks and even carbonatites. In addition, they can have associated a broad fenitization of the host rock and a group of dikes of equivalent composition, as, for example, in the Tchivira complex in Angola (Bambi, 2015).

In these complexes, neither ultrabasic plutonic rocks nor basic rocks tend to present interesting mineralization. The accessory minerals, which can contain REE in these rocks, are perovskite, apatite and (rarely) titanite. Sometimes, cumulates rich in perovskite can occur. However, this mineral is not especially rich in REE (Arzamastsev et al., 2002).

In particular, from a metallogenic point of view, we consider of interest rocks with peralkaline associations, especially, the agpaite (see for nomenclature Mitchell,

1996; Dudkin, 1997), which contain economically interesting mineralization (Kogarko, 1990; Sørensen, 1992). Agpaitic rocks, in virtue of their alkalinity, contain accessory minerals such as alkaline pyroxenes and alkaline amphiboles, in contrast with the miaskitic rocks, which do not contain these minerals. In addition, the agpaitic rocks contain hundreds of mineral species, of different and complex compositions.

Komiakov (1995) established a parameter (the alkalinity module, Kalc), based on the

theoretical structural formula of a given mineral, which is used to determine the tendency of this mineral to occur in certain contexts. Thereby, the Kalc of a mineral is the percentage of the number of atoms of alkalis per formula in relation to the total number of cations. Therefore, by taking the general formula  $A_xM_ySipO_z$ , the Kalc of a mineral can be defined as  $Kalc = (x/(x+y+p)) * 100$ . On that basis, Komiakov (1995) defines a series of intervals, in which minerals with similar Kalc will tend to co-crystallize. As a result, new rock catego-

	Metales raros y accesorios		K <sub>alc</sub>	Félsicos y formadores de rocas		K <sub>alk</sub>
hiperagpaíticos K <sub>alc</sub> >40%	olympita	Na <sub>2</sub> Li(PO <sub>4</sub> ) <sub>2</sub>	75	villiaumita	NaF	100
	phosinaíta	Na <sub>13</sub> Ca <sub>3</sub> (Ce,La,Th,Nd,Pr)(Si <sub>4</sub> O <sub>12</sub> )(PO <sub>4</sub> ) <sub>4</sub>	53	analcima	Na <sub>2</sub> (Al <sub>2</sub> Si <sub>2</sub> O <sub>12</sub> ) · 2H <sub>2</sub> O	25
	vuonnemita	Na <sub>11</sub> Ti <sup>4+</sup> Nb <sub>3</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> O <sub>3</sub> (F,OH)	55	egirina	NaAlSi <sub>2</sub> O <sub>6</sub>	25
	vitusaíta-(Ce)	Na <sub>3</sub> (Ce,La,Nd)(PO <sub>4</sub> ) <sub>2</sub>	50			
	lomonosovita	Na <sub>2</sub> Ti <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> )(PO <sub>4</sub> ) <sub>2</sub>	50	sodalita	Na <sub>8</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )Cl <sub>2</sub>	40
	zirsinalita	Na <sub>6</sub> (Ca,Mn <sup>2+</sup> ,Fe <sup>2+</sup> )Zr(Si <sub>6</sub> O <sub>18</sub> )	43	Li-arfvedsonita	[Na][Na] <sub>2</sub> [Li,Fe <sup>2+</sup> ,Fe <sup>3+</sup> ] <sub>2</sub> Si <sub>6</sub> O <sub>22</sub> (OH) <sub>2</sub>	24
	chkalovita	Na <sub>2</sub> BeSi <sub>2</sub> O <sub>6</sub>	40			
	kazakovita	Na <sub>6</sub> Mn <sub>2</sub> +Ti(Si <sub>6</sub> O <sub>18</sub> )	40	riebeckita	[Na <sub>2</sub> ][Fe <sup>2+</sup> Fe <sup>3+</sup> ] <sub>2</sub> Si <sub>6</sub> O <sub>22</sub> (OH) <sub>2</sub>	13
	epistolita	Na <sub>2</sub> (Nb,Ti) <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · nH <sub>2</sub> O	33	natrita	Na <sub>2</sub> CO <sub>3</sub>	100
	murmanita	Na <sub>2</sub> (Ti,Nb,Mn) <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	33			
	rasvumita	KFe <sub>2</sub> Si <sub>3</sub>	33	ussingita	Na <sub>2</sub> AlSi <sub>3</sub> O <sub>8</sub> OH	33
	steenstrupina-(Ce)	Na <sub>14</sub> Mn <sub>2</sub> <sup>2+</sup> (Fe <sup>3+</sup> ) <sub>2</sub> Ce <sub>2</sub> (Zr,Th)(Si <sub>6</sub> O <sub>18</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (HPO <sub>4</sub> )(OH) <sub>2</sub> · 2H <sub>2</sub> O	32			
	tisinalita	Na <sub>3</sub> H <sub>3</sub> (Mn,Ca,Fe)TiSi <sub>4</sub> (O,OH) <sub>8</sub> · 2H <sub>2</sub> O	27	natrosilita	Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	50
	lovozerita	Na <sub>2</sub> Ca(Zr,Ti)(Si <sub>6</sub> O <sub>18</sub> )[(OH) <sub>4</sub> O <sub>2</sub> ] · H <sub>2</sub> O	20			
altamente agpaíticos 35<Kalc<40%	baritolamprofillita	(Ba,Na) <sub>2</sub> (Na,Ti,Fe <sup>3+</sup> ) <sub>4</sub> Ti <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> O(OH,F)	33	villiaumita	NaF	100
	parakeldyshita	Na <sub>2</sub> ZrSi <sub>2</sub> O <sub>7</sub>	40	egirina	NaAlSi <sub>2</sub> O <sub>6</sub>	25
	keldishita	(Na,H) <sub>2</sub> ZrSi <sub>2</sub> O <sub>7</sub>	40	enigmatita	Na <sub>2</sub> Fe <sup>2+</sup> Ti(Si <sub>6</sub> O <sub>18</sub> ) <sub>2</sub>	14
	eudialita	Na <sub>13</sub> Ca <sub>6</sub> (Fe <sup>2+</sup> ,Mn <sup>2+</sup> ) <sub>7</sub> Zr <sub>3</sub> [Si <sub>25</sub> O <sub>73</sub> ](O,OH,H <sub>2</sub> O) <sub>3</sub> (OH,Cl) <sub>2</sub>	29	sodalita	Na <sub>8</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )Cl <sub>2</sub>	40
	lamprofillita	(Sr,K,Ba) <sub>2</sub> (Na,Ti,Mn <sup>2+</sup> ,Fe <sup>3+</sup> ) <sub>2</sub> Ti <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> O(O,OH,F)	33	nefelina	(Na,K)AlSi <sub>3</sub> O <sub>4</sub>	33
	leifita	(Na,H <sub>2</sub> O)Na <sub>4</sub> [Be <sub>2</sub> Al <sub>2</sub> (Al,Si) <sub>13</sub> O <sub>30</sub> ]F <sub>2</sub>	26	analcima	Na <sub>2</sub> (Al <sub>2</sub> Si <sub>2</sub> O <sub>12</sub> ) · 2H <sub>2</sub> O	25
	loparita	(Na,Ce,Ca,Sr,Th)(Ti,Nb,Fe)O <sub>3</sub>	50	cancrinita	(Na,Ca,□) <sub>6</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )(CO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	36
	lorenzita	Na <sub>2</sub> Ti <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> O <sub>3</sub>	33	feldespatato-K	KAlSi <sub>3</sub> O <sub>8</sub>	20
	seidozerita	Na <sub>8</sub> Mn <sub>2</sub> <sup>2+</sup> Zr <sub>3</sub> Ti <sub>3</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>4</sub> O <sub>4</sub> F <sub>4</sub>	33			
	astrofillita	(K,Na) <sub>2</sub> (Fe,Mn) <sub>2</sub> Ti <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (O,OH) <sub>7</sub>	15	Li-arfvedsonita	[Na][Na] <sub>2</sub> [Li,Fe <sup>2+</sup> ,Fe <sup>3+</sup> ] <sub>2</sub> Si <sub>6</sub> O <sub>22</sub> (OH) <sub>2</sub>	24
agpaíticos intermedios 25<Kalc<35%	gaidonnayita	Na <sub>2</sub> Zr(Si <sub>3</sub> O <sub>9</sub> ) · 2H <sub>2</sub> O	33	arfvedsonita	[Na][Na] <sub>2</sub> [Fe <sup>2+</sup> ,Fe <sup>3+</sup> ] <sub>2</sub> Si <sub>6</sub> O <sub>22</sub> (OH) <sub>2</sub>	19
	hilairita	Na <sub>2</sub> Zr(SiO <sub>3</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	33	egirina	NaAlSi <sub>2</sub> O <sub>6</sub>	25
	epididimita	Na <sub>2</sub> Be <sub>2</sub> Si <sub>2</sub> O <sub>15</sub> · H <sub>2</sub> O	20	biotita	KMg <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	13
	apatito	Ca <sub>2</sub> Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> F	0	nefelina	(Na,K)AlSi <sub>3</sub> O <sub>4</sub>	33
	titanita	CaTi(SiO <sub>4</sub> )O	0	noseana	Na <sub>6</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )(SO <sub>4</sub> ) · H <sub>2</sub> O	38
	eudialita	Na <sub>13</sub> Ca <sub>6</sub> (Fe <sup>2+</sup> ,Mn <sup>2+</sup> ) <sub>7</sub> Zr <sub>3</sub> [Si <sub>25</sub> O <sub>73</sub> ](O,OH,H <sub>2</sub> O) <sub>3</sub> (OH,Cl) <sub>2</sub>	29	feldespatato-K	KAlSi <sub>3</sub> O <sub>8</sub>	20
poco agpaíticos 15<Kalc<25%	eudialita	Na <sub>13</sub> Ca <sub>6</sub> (Fe <sup>2+</sup> ,Mn <sup>2+</sup> ) <sub>7</sub> Zr <sub>3</sub> [Si <sub>25</sub> O <sub>73</sub> ](O,OH,H <sub>2</sub> O) <sub>3</sub> (OH,Cl) <sub>2</sub>	29	katoforita	(Na/CaNa)(Mg <sub>4</sub> Al)(AlSi <sub>3</sub> ) <sub>2</sub> O <sub>23</sub> (OH) <sub>2</sub>	10
	lavenita	(Na,Ca) <sub>2</sub> (Mn <sup>2+</sup> ,Fe <sup>2+</sup> )Zr <sub>2</sub> (Si <sub>2</sub> O <sub>7</sub> )(O,OH,F) <sub>2</sub>	17	augita	(Ca,Na)(Mg,Fe <sup>2+</sup> ,Al,Ti)[(Si,Al) <sub>2</sub> O <sub>6</sub> ]	14
	britholita	Ca <sub>3</sub> (Ce,Ca) <sub>2</sub> (SiO <sub>3</sub> ,PO <sub>4</sub> )(OH,F)	25	biotita	KMg <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	13
	leucofanita	NaCaBeSi <sub>2</sub> O <sub>6</sub> F	20	cancrinita	(Na,Ca,□) <sub>6</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )(CO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	36
	apatito	Ca <sub>2</sub> Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> F	0			
	titanita	CaTi(SiO <sub>4</sub> )O	0			
	procloro	(Na,REE,Ca) <sub>2</sub> Nb <sub>3</sub> (O,OH) <sub>3</sub> F	0			
zircon	ZrSiO <sub>4</sub>	0				
miaskíticos Kalc<15%	allanita	{CaCe}{Al <sub>2</sub> Fe <sup>2+</sup> }(Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> )(OH)	0	hastingsita	(Na)(Ca <sub>2</sub> )(Fe <sup>2+</sup> ,Fe <sup>3+</sup> )(Al <sub>2</sub> Si <sub>2</sub> O <sub>22</sub> )(OH) <sub>2</sub>	6
	aeschyrita	(Ce,Ca,Fe,Th)(Ti,Nb) <sub>2</sub> (O,OH) <sub>6</sub>	0	augita	(Ca,Na)(Mg,Fe <sup>2+</sup> ,Al,Ti)[(Si,Al) <sub>2</sub> O <sub>6</sub> ]	14
	corindón	Al <sub>2</sub> O <sub>3</sub>	0	biotita	KMg <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	13
	schorlomitita	Ca <sub>3</sub> (Ti,Fe <sup>3+</sup> ) <sub>2</sub> (Si,Fe <sup>3+</sup> ) <sub>2</sub> O <sub>4</sub>	0	nefelina	(Na,K)AlSi <sub>3</sub> O <sub>4</sub>	33
	ilmenita	Fe <sup>2+</sup> TiO <sub>3</sub>	0	feldespatato-K	KAlSi <sub>3</sub> O <sub>8</sub>	20
	fluorita	CaF <sub>2</sub>	0	Albita	NaAlSi <sub>3</sub> O <sub>8</sub>	20
calcita	CaCO <sub>3</sub>	0	Cancrinita	(Na,Ca,□) <sub>6</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )(CO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	36	

Table 2. Typomorphic minerals in undersaturated alkaline rocks, with their chemical composition and their corresponding agpaitic module (modified from Mitchell, 1996).

ries can be established according to these intervals:

- a) Hiperagpaitic rocks with  $Kalc > 40$ ;
- b) Highly agpaitic rocks with  $Kalc$  between 35-40
- c) Medium agpaitic rocks with  $Kalc$  between 25-35
- d) Low agpaitic rocks with  $Kalc$  between 15-25
- e) Miaskitic rocks with  $Kalc$  lower 15.

The presence of one of these typomorphic minerals can easily provide an orientation on the agpaiticity degree of a rock and on its potential to contain rare elements mineralization. The main minerals used by Komiakov to

1997). These massifs are usually found in ancient shields, forming series of ultrabasic alkaline, alkaline ultrabasic, alkaline basic and sienitic massifs, close to each other.

The most important deposits worldwide of undersaturated alkaline rocks are located in the alkaline massifs of Khibiny and Lovozero, both of them situated in Kola Peninsula, Russia (Vlasov et al., 1966; Kogarko et al., 1995; Petrov, 2004), and in the complex of Illimaussaq in Greenland (Sørensen, 1970; Kogarko et al., 1995; Sørensen, 2001; Sørensen and Larsen, 2001; Sørensen et al., 2006). The mineral associations found in

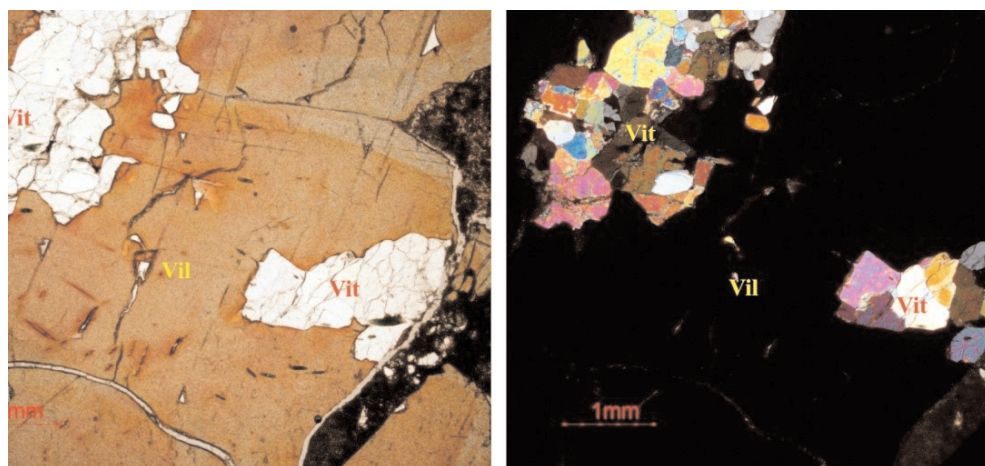


Fig. 1. Detail of an ultraagpaitic pegmatite in thin section, with villiaumite (Vil) intergrown with vitusite-(Ce) (Vit). Left, in PPL; right, with crossed nicols.

define these fields are found in table 2. It should be noted that several minerals could be found in different fields.

For example, the presence of villiaumite, halite, carbonates or alkaline phosphates can be useful exploration criteria. It is not rare for these minerals to be abundant in lujavrites or in other evolved alkaline rocks, or even in alkaline pegmatites. It is also common for them to be found with REE minerals in enough quantities to constitute metallogenicanomalies, even deposits. The types of potential REE ores can be extremely diverse and are far from being completely catalogued (Fig. 1). So far, 17 different alkaline massifs with agpaitic mineralization have been described (Dudkin,

these massifs are extremely complex regarding a mineralogical point of view. They comprise more than 450 mineral species discovered so far (Dudkin, 1997), lots of which are exclusive from one or several of these deposits.

The Khibiny massif is the largest agpaitic massif of the world, with 1327 km<sup>2</sup>. In this massif, the foidolites with agpaitic mineralization make up a large arched body of ijolite-urtite of approximately 70 km long and 2 km thick. Ijolites, urtites and juvites, plus a large number of pegmatites and late endogenous veins with diverse minerals belonging to the agpaitic series, have been described too in this complex. It consists of an assemblage of

multiphasic intrusions concentrically zoned (Arzamastsev *et al.*, 2013). From oldest to youngest, it is made up of the following intrusions (Arzamastsev *et al.*, 2008): a) a complex composed by a alkaline subvolcanic dikes cut by, b) ultrabasic plutonic intrusions with peridotites, pyroxenites and melilitic rocks; c) khibinites, or nepheline sienites of the peripheral zone; 4) banded complex of melteigites-ijolites-urtites; 5) nepheline sienites rich in K (rischorrites), juvites, urtites and nepheline-apatite rocks; 6) nepheline sienites corresponding to the central part of the massif (foyaite) and pulaskites; 7) essexite dikes, alkaline picrites, nephelinites, phonolites, trachytes; 8) carbonatite dikes. A wide range of agpaite mineralizations have been assessed in Khibiny even though, currently, the most interesting resource are the enormous deposits of nepheline-apatite rocks. Apatite from these units is the main ore in this complex. However, this mineral does not appear to be especially rich in REE.

The most interesting resources of REE in the alkaline rocks of the Kola Peninsula are located in the Lovozero complex, which covers a total area of 650 km<sup>2</sup> and is found near the Khibiny complex. The Lovozero complex consists of an assemblage of multiphasic intrusions (Arzamastsev *et al.*, 2013). From oldest to youngest, it is made up of the following intrusions (Arzamastsev *et al.*, 2008): a) a caldera formed in an TTG type complex dating of the late Archean, beginning volcanic activity in the external rings of the structure; b) subalkaline ultrabasic melts and alkaline sienites which formed the

Kurga intrusion, at the NE of the crater; c) intrusion of ultrabasic alkaline melts (although olivinic pyroxenites, melilitolites and olivinic melteigites were formed at the other side of the caldera); d) formation of the sodalite-bearing syenitic complex; e) formation of the banded complex of lujavrite-foyaite-urtite with loparite; f) formation of the lujavrite complex with eudialyte., Urtites with agpaite accessories make up bands up to 14 m thick in the rhythmical series of the banded lujavrite-urtite massif of Lovozero. Finally, alkaline pegmatites associated to agpaite mineralization are found forming laminar bodies, dikes, veins and «schlieren». The last veins forming are especially rich in rare agpaite minerals and are typically found as irregular-shaped veins, with variable thickness ranging from few millimetres to various meters.

In the Lovozero complex, loparite-(Ce) has been mined since many years ago, in order to profit both Nb and REE (Kogarko *et al.*, 2002), although this mineral and others of the same group are commonly found in other massifs. In Khibiny and Lovozero, loparite-(Ce) occurs in the shape of twinned (Fig. 2) pseudocubic idiomorphic crystals, scattered between nepheline in nepheline syenites or surrounded by the layering defined by the aegirine in the lujavrites. Its composition varies according to the unit in which is found on and ranges from the most perovskitic terms to the most lueshtic, even rich in Th; this factor which controls its economic potential (Mitchell y Chakmouradian, 1996; 1998, 1999). It is estimated that in Lovozero, ore-resources of more than 1000 Mt with 0.8-1.5% REE2O3 can be found (Belolipetskii y Voloshin, 1996).

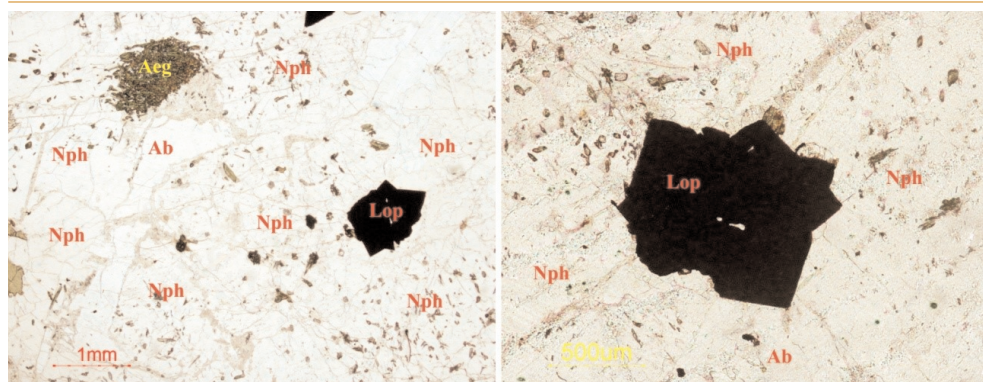
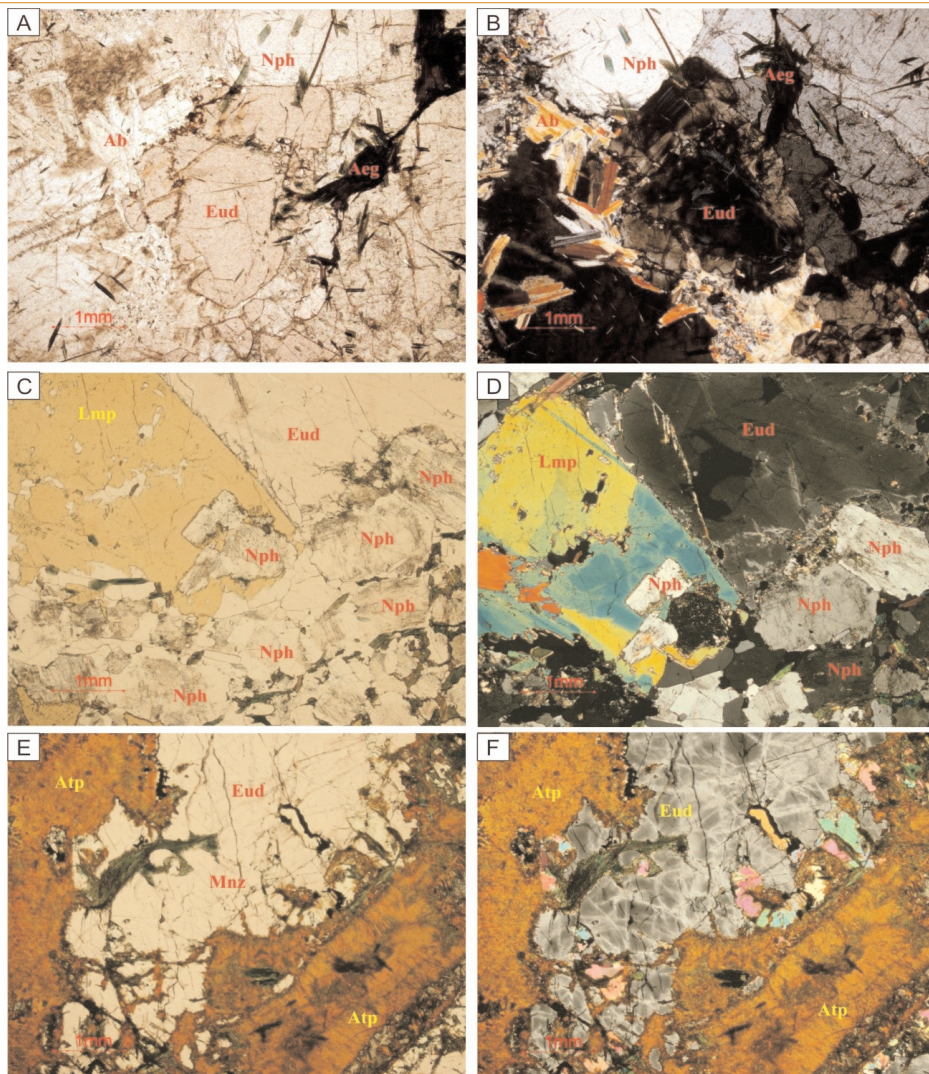


Fig. 2. Textural aspects of nephelinites with loparite-(Ce) in Mt. Karnasurt, Lovozero, Kola, Russia. Thin section, PPL. Left, loparite-(Ce) (lop) nearly opaqueidiomorphic crystals, with penetration twin, disperse between the nepheline (nph), albite (ab) and aegirine (aeg). Right, detail of a twinned loparite crystal, nearly opaque, included in the same association.

Eudialyte is a common accessory in lots of different types of alkaline rocks, especially in those found in the Kibiny and Lovozero massifs. Since years ago, mining of lujavrite rich in eudialyte has also been raised in Lovozero. In this massif, the thickness of the mineralized level reaches several dozens of metres and the modal proportion of eudialyte exceeds 50%. Moreover, this mineral can be ore of Nb, Y and

REE due to its complex chemical composition. However, in order to break its structure, complex metallurgical processes are required but their cost is still too high. Nonetheless, eudialyte is a mineral that tends to be easily replaced by late stage minerals. These can consist of different generations of eudialyte or other neoformed minerals (*Fig. 3*). Sometimes these minerals can be easily profitable.



*Fig. 3.* Textural aspects of khibinites with eudialyte in Khibiny, Kola, Russia. To the left, images in PPL; to the right, the corresponding images with crossed nicols. A) and B) idiomorphic crystals of eudialyte (Eud) in almost basal section, associated to nepheline (Nph), aegirine (Aeg) and albite (Ab). Note the zonation present in the eudialyte. C) and D) Zoned eudialyte (Eud) associated to lamprophyllite (Lmp) and nepheline (Nph), with some interstitial aegirine. E) and F) Eudialyte (Eud) replaced by needles of astrophyllite (Atp) and monazite (Mnz); some late aegirine can also be appreciated. Note the two generations of eudialyte and that the second one cuts through the first.



The Ilimaussaq massif, in Greenland, consists of a stratified complex of 136 km<sup>2</sup>, with a noticeable layering in diverse bodies, like the kakortokites. In these bodies, resources with more than 6,6 Mt of ore with 6% of ZrO<sub>2</sub>, 3% REE<sub>2</sub>O<sub>3</sub>, 0.2% Y<sub>2</sub>O<sub>3</sub> have been calculated (Jackson and Christiansen, 1993). The most valued ore in this case is the steenstrupine. It is a mineral of very complex composition and usually presents zonation accordingly (Khomyakov and Sørensen, 2001). However, it has as a penalty the fact to be a mineral

rich in thorium. Nevertheless, the steenstrupine is usually a common mineral in a great amount of alkaline complexes where hyperagpaitic facies can occur. This mineral can be found in the most evolved pegmatites together with other hyperagpaitic minerals (Fig. 4) and in the hydrothermal products. As the eudialyte, steenstrupine tends to be replaced by other minerals during the hydrothermal stages, especially by vitusite-(Ce) (Rønsbo et al., 1979), which, in its turn, is replaced by erikite (Pekov et al., 1997a).

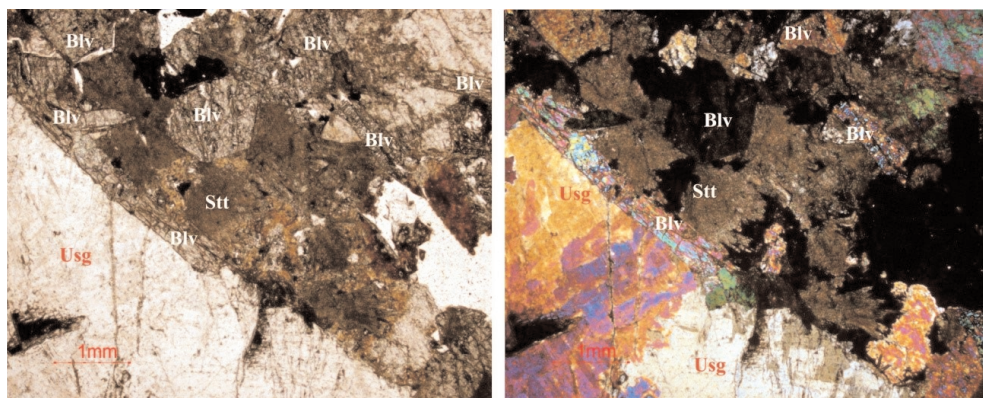


Fig. 4. Enrichment of REE minerals in a hyperagpaitic pegmatite pertaining to the Lovozero massif in Kola, Russia. Left image, in PPL, to the right, with crossed nicols. Stt, steenstrupine; Blv, belowite-(Ce), Usg, ussingite.

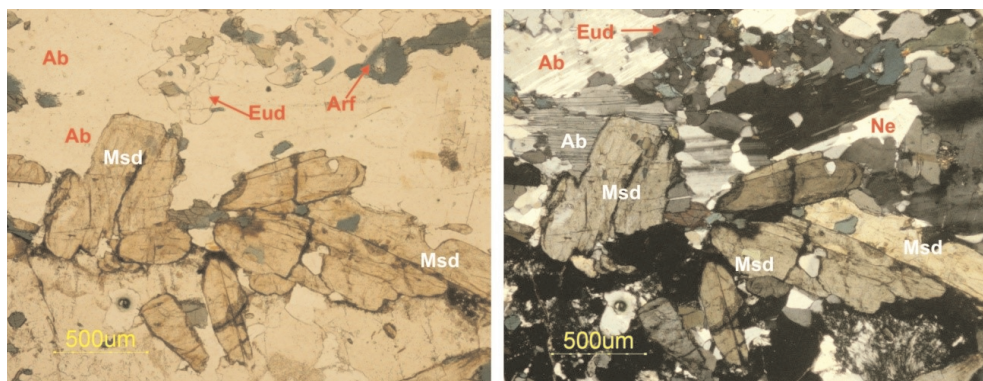


Fig. 5. Enriched layers in REE minerals in nepheline syenites (lakarites) of Norra Karr, Sweden. These rocks are composed of microcline, albite, nepheline, arfvedsonite, aegirine, fluorite, eudialyte and mosandrite. In the left image, mosandrite (Msd) and eudialyte (Eud) crystals can be observed between albite (Ab), nepheline (Ne) and arfvedsonite (Arf). Thin section, PPL. Right, the same association with crossed nicols.

In addition to the REE minerals aforementioned in these deposits, there are other minerals located in some alkaline massifs that can contribute to concentrate the REE. In Norra Karr, the REE ore consists of different varieties of nepheline syenites rich in mafic and REE mine-

rals, which can turn out to be abundant or even essential. Besides of eudialyte, these rocks are enriched in mosandrite-(Ce) (Fig. 5) and sometimes in britholite-(Ce) (Sjöqvist, 2013). The problem of these minerals is that zirconium silicates are refractory to metallurgical treatment.

The Pilanesberg massif (700km<sup>2</sup>), located in South Africa, is one of the largest massifs included between the undersaturated alkaline complexes. Small amount resources of REE in britholite veins have been evaluated in it (Lurie, 1973).

In the Tomtor massif (north of Siberia), agpaitic nepheline syenites constitute an external part of the massifs thickness. Its internal arc is made up of ijolites, whilst its nucleus is constituted by a great stock of carbonatites (Dudkin, 1997). In other cases, like in Saint Hilaire, Quebec, agpaitic nepheline syenites can be associated to gabbros, metagabbros and nepheline diorites (Horvart and Gault, 1990).

The pegmatitic facies belonging to the alkaline massifs, formed during late stage processes, constitute a source not only of rare minerals but, possibly, of REE minerals too. In these extreme and highly evolved compositional mediums, the enrichment in rare elements can be very important and produced by very different complexing agents. For instance, Pekov (1998) described a new mineral association of Y+HREE minerals found in the hyperalkaline pegmatites of mount Alluaiv, located in the Lovozero complex. This association can form bodies of important dimensions (meters), thus acquiring economic potential. This association comprises shomiokite-(Y), associated to natro-oxalate, sazykinaite-(Y) and mckelveyite in interstitial position to feldspars or forming massive replacements in the pegmatite. These minerals are produced by hydrothermal decomposition of the eudialyte at low temperatures, in alkaline conditions, in the presence of oxalates in closed systems. This author emphasizes the ability of the oxalate anion to be a complexing agent of REE. In any case, as it can be observed, the mineral associations belong to minerals in respect of which little information is found in literature. Little more than the parameters used to define them as mineral species is known.

The late hydrothermal stages can generate very complex associations due to the fact that late hydrothermal fluids can be very evolved and, consequently, able to concentrate a high concentration of rare elements. One of the complexes where most of these subsolidus processes have been studied is Mont Saint-Hilaire in Québec, Canada. This is due to the

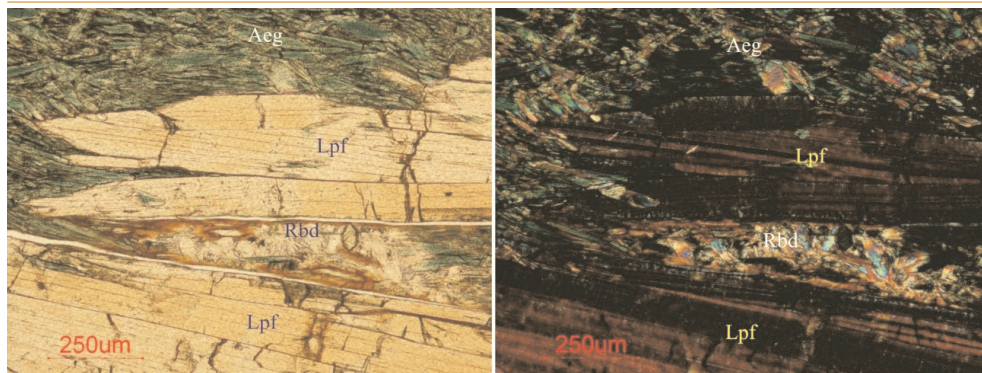
wide variety of mineral species it presents and its relative proximity with investigation centres and large nucleus of mineral collectors. Chao *et al.* (1978) describe late stage associations with donnayite-(Y), ewaldite, mckelveyite-(Y), synchysite, gaidonnayite, arfvedsonite, aegirine, calcite, sphalerite, catapleite, microcline, analcime, natrolite and chlorite. Grice and Chao (1997) mention the horvathite-(Y), Grice *et al.* (2009) describe the late stage associations with bussytite-(Ce), serandite, albite, analcime, ancylite-(Ce), calcite, catapleite, gonnardite, kupletskite, leucophanite, microcline, nenadkevichite, polilitionite and sphalerite. In particular, minerals corresponding to the ancylite-calcioancylite series are common in the latest stages of many other deposits (Pekov *et al.*, 1997b). In Ilimaussaq, some late stage veins can even be enriched in MREE or HREE rich-minerals, as the carlgieseckeite-(Nd) (Pekov *et al.*, 2012).

One of the largest mining operations, though still in preparation process, is the one taking place in Thor Lake, in the Northwest Territories, Canada. It consists of a complex mineralization where, unlike other places, the importance of the subsolidus remobilizations by hydrothermal fluids effects can be appreciated. In the same zone, an intrusion made up of peralkaline granite and syenite, both intruded by a stratified complex of nepheline syenites, ijolites and urtites, has been mapped (Pinckston and Smith, 1995). In this complex, initially, a mineralization consisting of cumulates of eudialyte was formed. However, successive hydrothermal alterations produced the replacement of the initial minerals and generated irregular bodies of metasomatic mineralization including; from cerianite-(Ce), britholite-(Ce), thorite and interstitial calcic catapleite to nepheline and aegirine, as well as great quantities of zircon, ferrocolumbite, pyrochlore, aeschynite, fergusonite-(Y), allanite-(Ce), monazite-(Ce), bastnäsite, phenakite and albite rich in Ga (Taylor and Pollard, 1996; Sheard *et al.*, 2012).

Finally, the weathering of these rocks can also produce the remobilization and concentration of REE elements, which can lead to the formation of deposits rich in these elements. Separation of Ce<sup>4+</sup> from the rest of the REE, often takes places in this stage, generating

cerianite ( $\text{CeO}_2$ ; *Frondel and Marvin, 1959*) or other minerals containing exclusively Ce. Evidently, the presence of minerals with complex compositions in the non-altered protoliths, also favours the existence of a wide

range of supergene minerals. Many of these consist of hydrated species commonly found in lots of different types of deposits and include minerals of the rhabdophane, crandallite, synchysite group etc. (*Fig. 6*).



*Fig. 6.* Detail in thin section of a supergene enrichment of REE minerals in pegmatite of alkaline rocks. Radial crystals of rhabdophane (Rbd) in interstitial position between crystals of lamprophyllite (Lpf) and aegirine (Aeg). Left, in PPL; right, with crossed nicols.

range of supergene minerals. Many of these consist of hydrated species commonly found in lots of different types of deposits and include minerals of the rhabdophane, crandallite, synchysite group etc. (*Fig. 6*).

#### 4. Deposits Associated to Carbonatites

Carbonatites are igneous rocks made up by more than a 50% modal by primary magmatic carbonates (*Woolley and Kempe, 1989*). They can crystallize forming intrusive, hypoabyssal, and volcanic bodies (*Barker, 1989, 1996*), including lavas and pyroclastic deposits of different types (e.g. *Woolley and Church, 2005; Campeny et al., 2014*). This definition would be simple, but some authors believe necessary to introduce genetic-type hints because there are carbonatites formed by very different processes. For *Mitchell (2005)* or *Woolley and Kjarsgaard (2008)*, there are magmatic carbonatites derived from mantle processes and associated to mellitic, nephelinitic, aillikitic and kimberlitic clans, in addition to the natrocarbonatites (carbonatites constituted by alkaline carbonates, *Gittins and McKie, 1979; Campeny et al., 2015*). However, some carbonated rocks associated to potassic peralkaline or both saturated and undersaturated sodic rocks would have been formed due to carbohydrothermal processes. Finally, these

placement point of view, between the igneous carbonatites, still another subdivision should be done in order to differentiate between continental carbonatites and oceanic ones, although the oceanic are a rare type (*Allègre et al., 1971; Hoernle et al., 2002*).

Carbonatites constitute a classic metallogenic element of first order as they contain Fe, Cu, Au, REE, Nb, U, fluorite, barite, apatite and even diamond ores. As it can be seen, lots of the minerals and critical elements for the UE are found in this type of medium. Moreover, in those countries located within geological settings with predominance of crystalline rocks and poor in sedimentary sequences, carbonatites constitute a main source of basic industrial mineral supplies, such as calcite or dolomite. Generally, most of the carbonatites contain some of these mineralizations in more or less grade. Due to this fact, during the last few years there has been an increase in their study, providing a continuous synthesis about the evolution of the knowledge regarding their resources (for example, *Berger et al., 2009*).

##### 4.1. Carbonatites associated to continental rift

Carbonatites s.s. typically occur in cratonic continental rift settings and are produced due to partial fusion processes in the mantle (*i.e.*

Barker, 1996). These carbonatites constitute a first order metallogenic objective as they include some of the largest ore deposits of rare elements worldwide (in particular, REE, Nb, Th, Zr). They also include extremely important deposits of Fe, Ti, V, Cu and other metals (with ores such as vanadinite magnetite, ilmenite, chalcopyrite and secondary sulphurs, etc.), in addition to apatite and lots of other industrial minerals (fluorite, barite, vermiculite, without forgetting the carbonates themselves;

Mariano, 1989; Verplanck et al., 2014). Carbonatitic massifs are usually associated to other types of rocks, which can present concentrations of REE, such as undersaturated alkaline rocks, melilitic rocks, phosphorites or nelsonites (Zaitsev et al., 2014). This occurs, for example, in the plutonic carbonatites of the Tchivira massif, in Angola. On the other hand, the hypoabyssal carbonatites belonging to the plug near Bongo are apparently isolated, suggesting a hypoabyssal emplacement (Fig. 7).

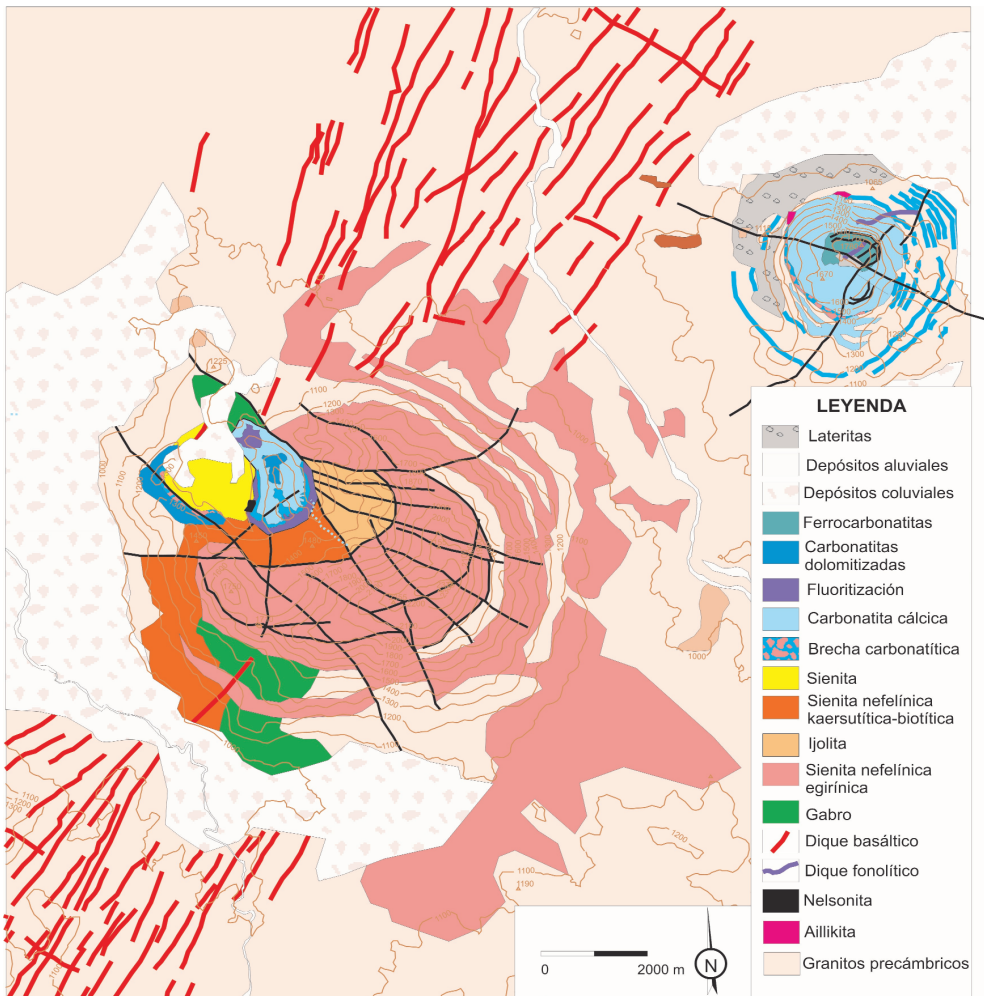


Fig. 7. Diverse types of carbonatite emplacements and associated REE mineralizations in the Lucapa rift, in Angola. On the left part of the map, the complex of Tchivira can be observed, with ring carbonatite bodies associated to basic plutonic rocks and undersaturated alkaline rocks, as well as basic dikes. Some bodies replacing the carbonatites have been represented, such as fluoridised, dolomitized or ankeritized bodies (all of them enriched in REE). On the right side, above, the Bonga complex is essentially carbonatitic, with important lateral breccias and with a plug morphology surrounded by ring dikes.

Nevertheless, not all carbonatites are mineralized or have the same potential, nor this one is the same for all of these elements. Moreover, in this type of deposits, it shall be taken into account that the mineralization can be concentrated in diverse stages that can take place either in the magmatic or in the subsolidus episodes, being these hydrothermal or supergene. Therefore, even though *Orris and Grauch (2002)* list a total of 120 showings of carbonatites mineralized in REE throughout the world, including some of the most classic ore deposits containing these elements, the volume of deposits is larger, because some deposits, which have been classically included in other categories (laterites, hydrothermal), in fact are genetically linked to carbonatites. On the other hand, in these deposits, REE have been historically exploited only as a subproduct of the profit derived from other rare elements, such as Nb, Zr or from phosphates.

4.1.a Primary Processes of REE Enrichment in Carbonatites

Carbonatitic intrusions usually are part of complex intrusions, in which successive intrusions of very diverse composition take place too. The early intrusions consist of basic or ultrabasic rocks (normally sterile in REE), followed by undersaturated alkaline rocks and finally a succession of calcic carbonatites (“sovites”), dolomitic (“beforsites”) and ankeritic or sideritic carbonatites (*Downes et al., 2005; Zaitsev et al., 2014*).

Each one of these magmatic stages can be accompanied by REE mineralization, especially the latest ones: the dolomitic carbonatites usually contain mineralization in the form of burbankite or bastnäsité; whilst the ferroan carbonatites contain monazite or allanite (*Kirnarskii, 1997; table 3*).

Generally, primary minerals in the carbonatites have a poor range of variety. Apart from the carbonates (calcite, dolomite, ankerite or siderite, and even more rarely burbankite), variable proportions of spinels can occur (mainly magnetite, *Fig. 8*, possibly vanadian), ilmenite (typically rich in Mn), perovskite group minerals (like lueshite as in *Lesnaya Varaka, Chakhmouradian and Mitchell, 1998*), apatite group minerals (*Roeder et al., 1987*) and diverse silicates (olivine, humite group, phlogopite, Si-poor pyroxenes, calcic garnets, etc.). Some primary magmatic minerals in carbonatites can accumulate REE. In the first place, the magmatic carbonates themselves (calcite, dolomite, ankerite, siderite, alkaline carbonates) can generally accept some hundreds of ppm of ΣREE (up to 6000 ppm, as well as up to 8000 ppm of Sr and 7000 of Ba; *Hornig-Kjarsgaard, 1998*). In second place, the fluorapatite (*Fig. 8*), which can have up to more than 3% concentrations in REEO weight (*Hornig-Kjarsgaard, 1998*), frequently from britholitic-type substitutions. The fluorapatite, on the other hand, can be concentrated in some parts of the carbona-

Estado de formación del mineral Grupo de roca de minerales	1. ULTRABÁSICO			2. ALCALINO		3. CARBONATÍTICO							
	Ultrabásico	Foidolitas y/o sienitas nefelíticas	Rocas melíticas	Skarns	Rocas con Flogopita-olivino-dióxido	Foscoritas	Carbonatitas						
							Calcita	Dolomita calcita	Dolomita	Ankerita-siderita	Cuarzo-calcita		
Silicatos de Mg	Forsterita	(Forsterita)	(Forsterita)	-	Forsterita	Forsterita	Forsterita	Forsterita	Cinohumita	Serpentina	Serpentina	-	
Piroxenos	Augita-dióxido Egirina-dióxido	Egirina-dióxido	Egirina-dióxido Augita-dióxido	Dióxido	Dióxido	Dióxido	Dióxido	-	-	-	-		
Ambloes	-	-	Hastingsita	Hastingsita	Actinolita-tremolita-hastingsita	Katoforita	Katoforita	Actinolita-tremolita	Actinolita-tremolita	-	-		
Filosilicatos	-	Biotita Fe-flogopita	Fe-flogopita Flogopita	Fe-flogopita Flogopita	Flogopita	Flogopita Tetraferri-flogopita	Flogopita Tetraferri-flogopita	Flogopita-tetraferri-flogopita	Flogopita-tetraferri-flogopita	Ciorita	Ciorita	-	
Carbonatos y sulfuros	-	-	-	-	(Calcita)	Calcita	Calcita Kumehorita Mn-calcita	Calcita (Dolomita)	Dolomita	Ankerita Siderita	Calcita Fluorita		
Oxidos de Fe	Titanomagnetita	Titanomagnetita	Titanomagnetita	Titanomagnetita	Titanomagnetita	Magnetita	Magnetita	Magnetita	Magnetita	Hematites	Hematites Limonita		
Minerales de titanio	Perovskita Titanomagnetita Ilmenita	Perovskita Titanomagnetita Ilmenita	Perovskita Titanomagnetita Ilmenita	Titanomagnetita	Titanomagnetita	-	Perovskita con Nb y Ta ("Dysanrita")	Ilmenita	Lueshita Ilmenita	Silicatos de titanio	Silicatos de titanio		
Minerales de zirconio	-	-	-	-	Calzitrita	Baddeleyita Calzitrita Zirkelita	Baddeleyita Calzitrita Zirkelita	Baddeleyita Zirkelita	Zircón	Silicatos de zirconio	Silicatos de zirconio		
Minerales de tántalo y de niobio	-	-	-	-	-	Uranoproclore ("Nacheetolita")	Pirocloro	Pirocloro	Pirocloro con Ba-Sr	Ferrocolumbita	Silicatos de zirconio y titanio		
Minerales de TFR	-	-	-	-	-	-	-	-	Burbankita Bastnäsita	Monazita Allanita	-		
Sulfuros	(Piroclita)	(Piroclita)	-	-	-	Piroclita Calcopirita	Piroclita Calcopirita	Piroclita Calcopirita	Galena Estalerita Pirita	Galena Estalerita Pirita	-		

Table 3. Mineral composition of the carbonatitic stages (*Kirnarskii, 1997*).

titic intrusions, like in the margins of the intrusion and, specially, in the peripheral ring dikes of the central intrusions, as in Mount Bonga in Angola (Bambi, 2015). It should be noted that it is in the dikes rich in fluorapatite where the highest proportions of primary pyrochlore occur.

On the other hand, other liquidus minerals, like primary pyrochlore (Fig. 7), monazite or others are generally accessory minerals in intrusive carbonatites (less than 5% modal). Therefore, they rarely contribute significantly in concentrating the REE in the bulk rock. Moreover, the Ce proportion is usually low in primary pyrochlores included in plutonic and hypabyssal carbonatites

(Bambi, 2013; Fig. 8a,b). However, primary pyrochlore of the matrix of volcanic carbonatites and aillikites, as those of Catanda (Angola) may be strongly enriched in Ce-Ta-U-Zr (Bambi, 2015; Fig. 8c,d). In this case, the primary pyrochlore presents an outstanding zonation, which evolves from sodic fluorocalciopyrochlore to kenocalciopyrochlore rich in HFSE, especially Ta, Zr, U, Th and LREE. It should also be noted that the matrix belonging to some volcanic carbonatites of Catanda is also strongly enriched in zoned fluorapatite, with a britholitic external edge rich in LREE. Consequently, the original REE proportion can be higher in those rocks with a high concentration of primary fluorapatite or other fluorine-bearing minerals (Bambi et al., 2013).

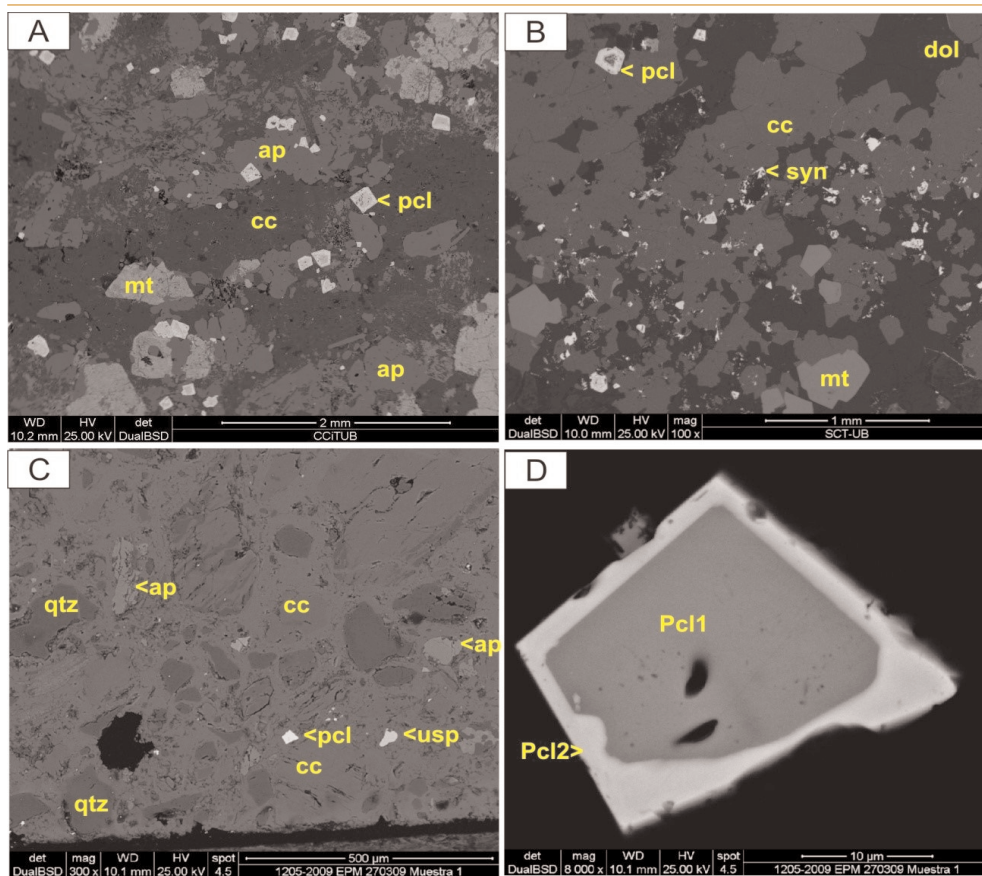


Fig. 8. Primary textures in the Lucaapa carbonatites, in SEM images, BSE mode. A, Aspect of a ring dike of a calcic carbonatite belonging to the hypabyssal intrusive of Bonga, predominantly constituted of calcite (cc), but strongly enriched in primary apatite (ap), idiomorphic pyrochlore (pcl) and magnetite (mt). B, aspect of the plutonic intrusion of Tchivira, with pyrochlore (pcl), very scarce magnetite (mt) and apatite, and with calcite partially replaced by hydrothermal dolomite (dol) in association with synchysite-(Ce) (syn). C, general overview of a pyroclastic carbonatite of Catanda, with quartz xenocrysts (qtz) and pyroclastic carbonate fragments cemented by a calcite matrix. Some crystals stand out, such as apatite crystals (ap), pyrochlore (pcl) and ulvöspinel (usp). D, detail of the pyrochlore crystal of the previous image, exhibiting zonation. Fluorocalciopyrochlore core (Pcl1) and calciopyrochlore rim (Pcl2) enriched in HFSE (Ta, Zr, U, Th) and LREE.

Enrichment in REE may occur mainly in the latest carbonatitic intrusions between the different carbonatitic bodies that can constitute a massif, such as the ferrocarnatites (*i.e.*, Nadeau *et al.*, 2015). However, it can be complicated to differentiate if these are primary or produced as a result to hydrothermal alterations.

Kravchenko *et al.* (2003) suggest that another factor that can exponentially favour the primary enrichment of REE is fractional crystallization, with enrichment of REE in the last meltings. This can be decisive in a body of large dimensions, such as Tomtor in Russia, where accumulations up to 8-31% REEO and 3-8% Nb<sub>2</sub>O<sub>5</sub> are produced. Yang *et al.* (2011) invoke this possibility to justify the enormous pre-concentrations that occur in the Bayan Obo carbonatite. Nevertheless, the fractional sequence, which is described as a primary crystallization of beforites followed by more enriched sovites and another one involving carbonatites of mixed composition, does not agree with the general scheme since intrusions are produced in reverse order to the one aforementioned (for example, see Kirnarskii, 1997 synthesis). These authors do not offer petrological data; therefore, it is possible that strongly mineralized late calcic carbonatites (and mixed ones) really consist of secondary carbonates produced by hydrothermal stages.

Some carbonatites occur in nelsonitic bodies that can have big dimensions and economic interest for the Fe-Ti-V oxides, the apatite or the abundant proportion of pyrochlore. This happens in Bailundo, Angola, where massive bodies up to 100 m in diameter of nelsonites, strongly mineralized in apatite and pyrochlore, plus with small amounts of LREE (Castellano *et al.*, 2011) occur. The alteration of apatite can lead in these cases to secondary enrichments in REE.

Sometimes late carbonatitic bodies can cut the carbonatitic massifs very rich in REE (with REEs at levels of % in weight), which can sometimes constitute most of the massif itself as in Mountain Pass (Castor, 2008) or Kangankunde (Wall and Mariano, 1996). They are nearly always enriched in Sr and Ba, and their main minerals are monazite-(Ce), fluocarbonates like bastnäsite-(Ce), synchysite-(Ce), parisite-(Ce) and hydrated carbonates like ancylite-(Ce); sometimes, there are also some other carbonates such as burbankite, car-

bocernaite, huanghoite-(Ce), calkinsite-(Ce) and fluocerite-(Ce) (Zaitsev *et al.*, 1998).

As a general rule, in the vast majority of non-altered analyzed carbonatites the light rare earth elements are enriched in relation to the heavy ones, though there are exceptions, like the carbonatitic dikes rich in xenotime-Y of Lofdal, Namibia (Wall *et al.*, 2008).

#### 4.1.b. Enrichment processes of REE in fenites and other metasomatized rocks

During the emplacement of the carbonatitic massifs, the interaction between the hydrothermal fluids exsolved from the carbonatitic magma with the host rocks takes place. This produces the fenitization of these last ones up to distances that can be of the order of hundreds of metres. The fenitization process implies strong carbonatization phenomena and the alkalization of the host rocks (generally, a strong potassic alteration, with the development of secondary potassic feldspar of high temperature (Fig. 9), albite, secondary biotite, pyroxenes and alkaline amphiboles, etc.), accompanied by dolomitization or ankeritization processes, together with a high loss of silica. The mineralization that can be formed in these rocks includes some types of pyrochlore, fluorite, and secondary apatite (Fig. 9); in the carbonatites of Angola the calcioancylite can be quite common (Fig. 9). In some cases, loparite or strontiochevkinite have been described (Haggerty and Mariano, 1983). Nevertheless, as a whole, it seems that the fenites tend to be relatively impoverished in REE in relation to the rocks of the complexes associated, like in the Oka carbonatite in Quebec (Eby, 1975).

Aspect of the mineralization in the fenitized zones. Top, left: aspect of the carbonatitic intrusion belonging to the eastern ring of Tchivira, seen from the north. In close-up view, a carbonatitic breccia with fragments of pink fenitized granite. Top, right: aspect of a fenitized breccia with carbonatitic matrix. Bottom, left: fenitized granite, totally replaced by secondary potassic feldspar (KFs). Note secondary pyrochlore rich in Sr (Pcl-Sr) and calcioancylite veinlets (Cacl). SEM image, BSE mode. Bottom, right: a similar image, in which fluorite (Fl) associated with calcioancylite can be appreciated. The rest of shiny points consist of hematite. SEM image, BSE mode.

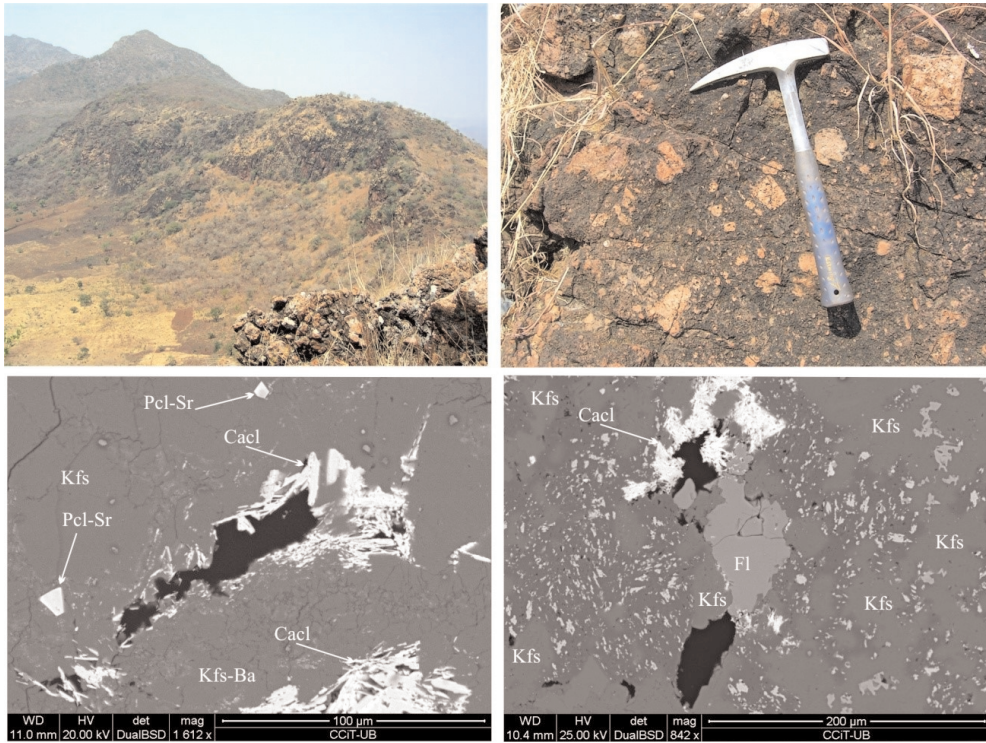


Fig. 9. Aspect of the mineralization in the fenitized zones. Top, left: aspect of the carbonatitic intrusion belonging to the eastern ring of Tchivira, seen from the north. In close-up view, a carbonatitic breccia with fragments of pink fenitized granite. Top, right: aspect of a fenitized breccia with carbonatitic matrix. Bottom, left: fenitized granite, totally replaced by secondary potassic feldspar (Kfs). Note secondary pyrochlore rich in Sr (Pcl-Sr) and calcioancylite veinlets (Cacl). SEM image, BSE mode. Bottom, right: a similar image, in which fluorite (Fl) associated with calcioancylite can be appreciated. The rest of shiny points consist of hematite. SEM image, BSE mode.

The mineralization replaces carbonated bodies, clearly sedimentary, and is made up of very complex mineral associations, which involves up to 120 mineral species (Chao *et al.*, 1992, 1997). Replacement takes place mainly along the stratification surfaces (Fig. 10), producing a very fine grained banded rock, mostly composed of fluorite (Fig. 11), phlogopite (Fig. 11), aegirine (Fig. 11), ferroan dolomite, calcite rich in Sr and Mn, quartz (Fig. 11), albite, barite, magnetite (which can be massive), hematite, norsethite, benstonite, baryto-calcite and strontianite. The most common minerals of the REE ores are monazite-(Ce) and bastnäsite-(Ce) (Fig. 11). In addition, late fluocarbonates such as cebaitite-(Ce), cordylite-(Ce), parisite-(Ce) and huanghoite-(Ce) (Fig. 11) are generally present as veins or replacements of other minerals in the deposit. Usually these form syntactic intergrowths (Yang Xueming *et al.*, 1999). The most com-

mon ore bearing minerals of Nb are columbite, fersmite, pyrochlore, aeschynite, fergusonite and ilmenorutile. The reserves are huge, of the order of 800 Mt of ore with 6% REE2O3 (Berger *et al.*, 2009).

The genesis of this deposit has been explained in very diverse ways, including exhalative deposits, skarns and lately IOCG, based in its strong hydrothermal character and its paragenesis (see discussion in Wu, 2008). However, the problem is that probably the deposit is the result of various superimposed phenomenons: between them the intrusion of carbonatites in a carbonated series (defined by the presence of some clearly carbonatitic dikes and radiogenic isotope data; Yang *et al.*, 2003, 2011; Zhang *et al.*, 2001), the replacement of the host rock (clearly defined by the textures and part of the minerals, including quartz and calcite), and the defor-



mation and metamorphism in various episodes, also defined by the textures and the dating of several minerals (Wang *et al.*, 1994; Chao *et al.*, 1997). In fact, the style of the Nb mineralization is typical of carbonatitic rocks affected by metamorphism, as it will be explained later.

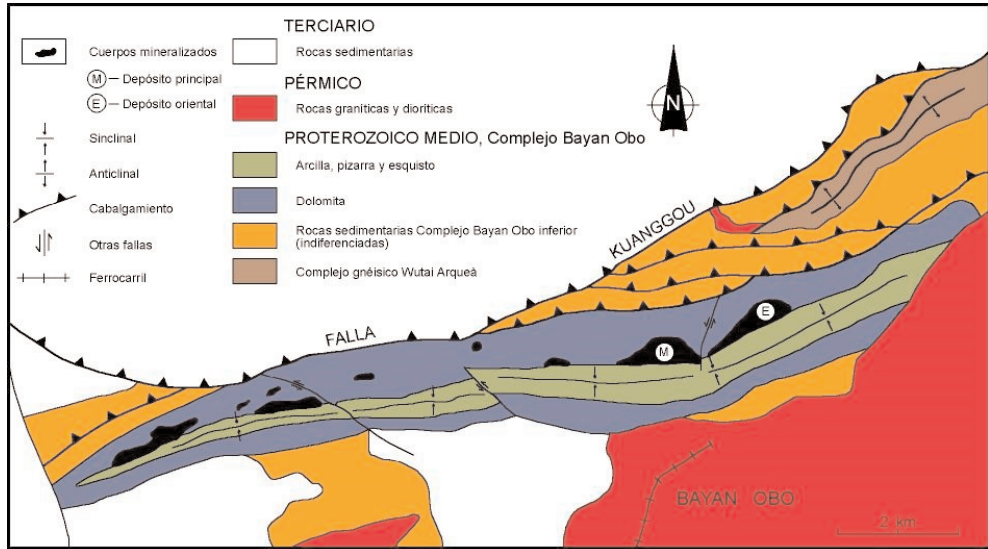


Fig. 10. Top, geologic map of the Bayan Obo mine. Modified from Chao *et al.* (1992). Bottom, image from Google Earth of the Bayan Obo mine. Its association with a strongly deformed zone by faults WSW-ENE can be distinguished.

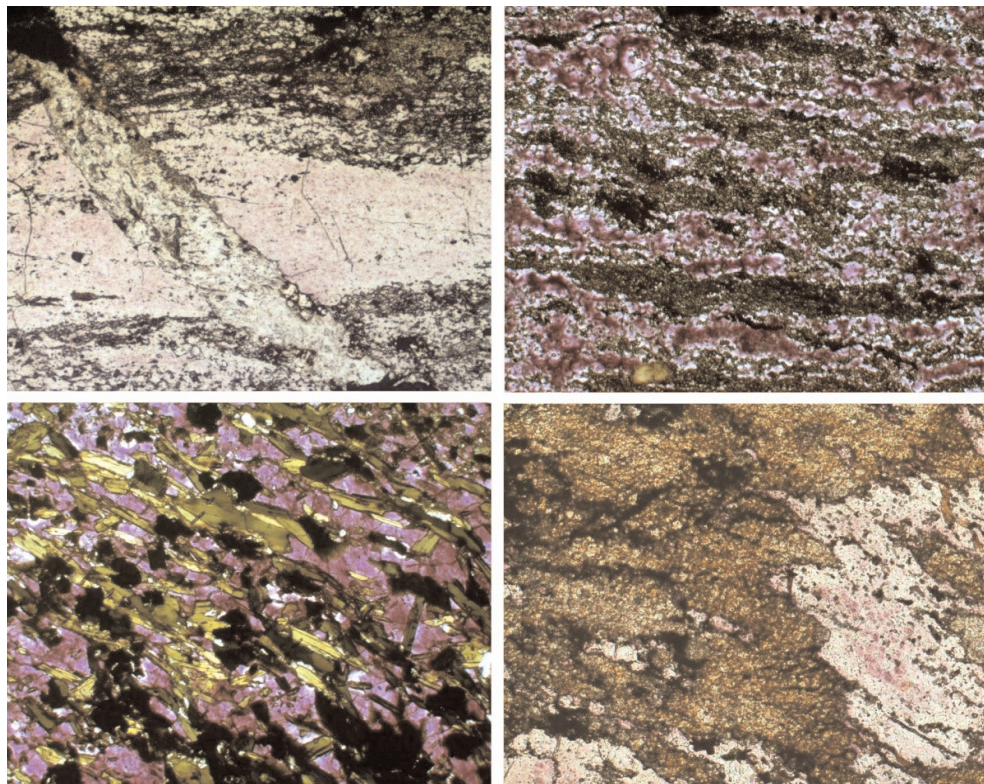


Fig. 11. Textural aspects of the Bayan Obo mineralization in thin section, PPL. Top, left: fluorite bands, slightly purple due to radioactivity with bastnäsite-(Ce), cut by quartz veins with monazite-(Ce). Top, right: banded ore with purple fluorite intergrown with bastnäsite-(Ce) and monazite-(Ce) bands. Bottom, left: phlogopite associated with fluorite. Bottom, right: huanghoite-(Ce) yellowish crystals associated to slightly purple fluorite.

#### 4.1.c. Enrichment of REE by late Hydrothermal Processes

The key problem to interpret the subsolidus associations is to be able to discriminate between the associations formed by hydrothermal or meteoric processes. Thus, those studies in which comparison between the paragenesis of fresh carbonatites in depth with the mineral associations in meteorized carbonatites were made from mining labours and drillings are very valuable. In such a way, Moore *et al.* (2015) describe, in non-affected zones by supergene processes, replacements of the primary carbonatite by hydrothermal associations in interstitial position between the primary carbonate grains, as fillings of veins or like pseudomorphic products.

In these associations, many minerals are

common, great part of which have economic interest and can provide essential enrichments for the exploitability of the carbonatite (Melgarejo *et al.*, 2012). In first place, fluorite, which occurs as crystals with a wide size range and in diverse multicolour generations that can replace completely the carbonatite (Fig. 12). This process generated large compact masses of economic interest, like in Okuruso, Namibia, Amba Dongar in India or Mato Preto in Brazil.

Quartz also precipitates and is usually fine grained in size. It occurs interstitially between carbonate grains; moreover, it also is observed in veinlets and even in metric-sized veins. Silicic host rocks are the source of this silica, which is released during the fenitization processes of the host rock (Melgarejo *et al.*, 2012; Fig. 12).

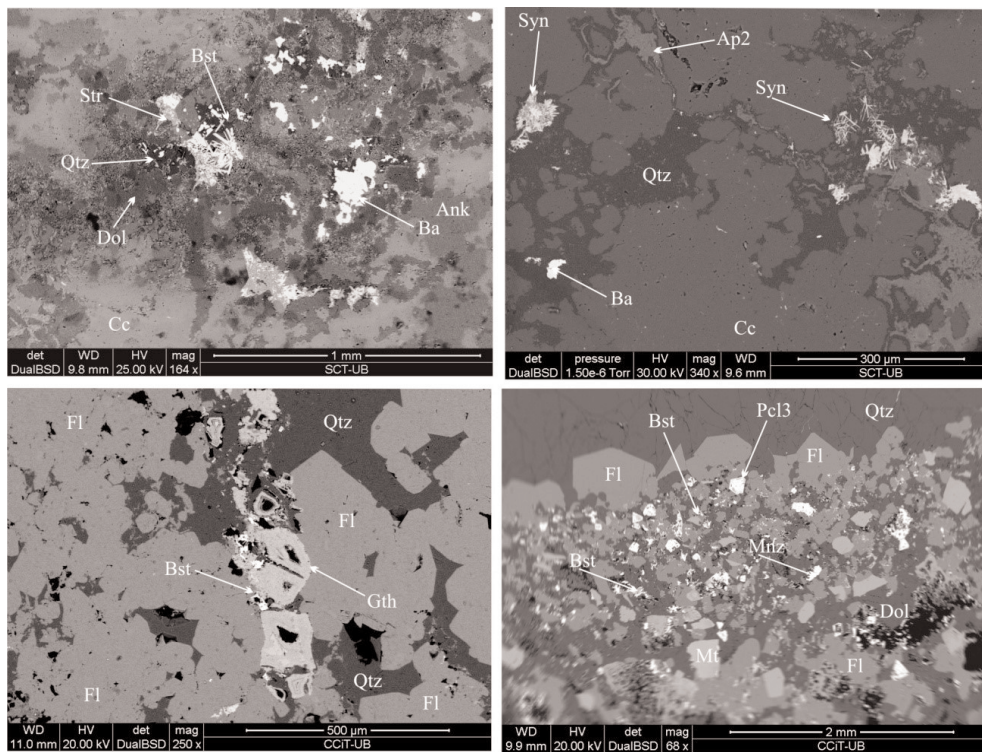


Fig. 12. Textural aspects of the Bayan Obo mineralization in thin section, PPL. Top, left: fluorite bands, slightly purple due to radioactivity with bastnaesite-(Ce), cut by quartz veins. Aspects of the mineral associations produced by the subsolidus hydrothermal processes in the Tchivira carbonatite, Angola, in SEM images in BSE mode. Top, left: the primary calcite (Cc) is replaced by ankerite (Ank) and dolomite (Dol), with strontianite (Str), barite (Ba) and bastnaesite-(Ce) (Bst). Top, right: primary calcite (Cc) replaced from the grain edges by quartz (Qtz) with barite (Ba), secondary apatite (Ap2) and synchysite-(Ce) (Syn). Bottom, left: aspect of a fluoritized zone with fluorite (Fl) masses replaced by quartz (Qtz), pyrite (replaced by goethite, Gth) and bastnaesite-(Ce) (Bst). Bottom, right: dolomite (Dol), fluorite (Fl), magnetite (Mt), monazite-(Ce)(Mnz), bastnaesite-(Ce) (Bst) and Sr-rich pyrochlore (Pcl3) replacing the original carbonate; the filling of the veins begins with drusite fluorite (Fl) followed by quartz (Qtz) with monazite-(Ce). Top, right: banded ore with purple fluorite intergrown with bastnaesite-(Ce) and monazite-(Ce) bands. Bottom, left: phlogopite associated with fluorite. Bottom, right: huanghoite-(Ce) yellowish crystals associated to slightly purple fluorite.

Diverse generations of hydrothermal carbonates (like calcite, dolomite, ankerite, kutnohorite, burbankite, witherite, strontianite; Fig. 12) replace the previous primary carbonates, either pseudomorphically or in fractures.

In most of the cases, one or more generations of fine-grained secondary apatite, generally carbonate-apatite or hydroxyapatite occur. This secondary apatite is produced by alteration of the primary apatite; in this process non-negligible quantities of F are liberated. In addition, during this stage, great quantities of barite, celestite, witherite and strontianite precipitate (Fig. 12). The source of Ba and Sr can be found in the large amounts of Ba and the Sr liberated during the hydrothermal replacement of the primary carbonates, albeit part of the Ba and Sr can derive from the lixiviation of the feldspars contained in the host rock. These

elements cannot enter in the structure of the lowest temperature hydrothermal carbonates. In some points, great quantities of these minerals accumulated

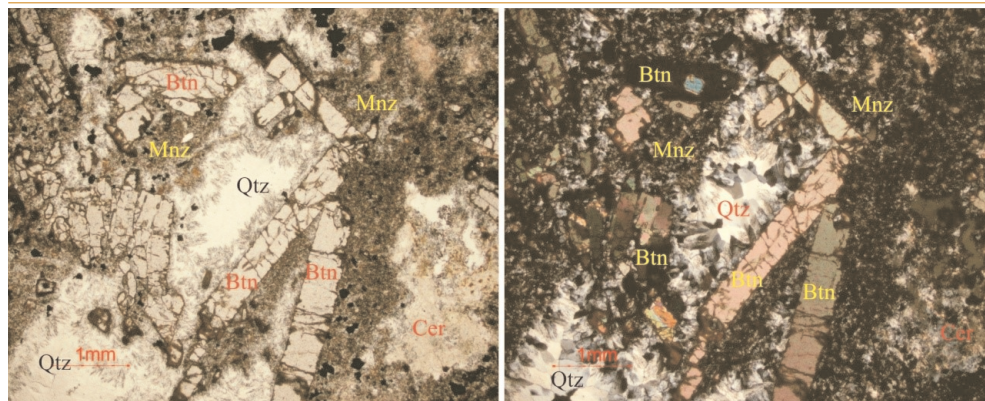
It is likewise frequently that these minerals are accompanied by several late generations of pyrochlore, either as replacement products of primary pyrochlore or as in independent crystals, even in crystals of geodic growth associated with quartz (Melgarejo et al., 2012; Fig. 12).

Regarding the REE, their major enrichments in carbonatites (typically, in LREE) take place during this episode. They generally occur as carbonates, like the ancylite from Sevlyavr (Kola, Russia; Bulakh et al., 1998), Tundulu in Malawi (Ngwenya, 1994) or Lueshe, Congo (Maravic and Morteani, 1980). Minerals of the

synchysite-(Ce) group are very common too, as in Bailundo, Angola (*Castellano et al., 2011*), Tchivira, Angola (*Melgarejo et al., 2012; Fig. 12*) or Virulundo, Angola (*Torró et al., 2012*). Moreover, phosphates can appear in the same association, as florencite-(Ce) (like in Kangankunde in Nyasaland; *Mckay, 1962*), goyazite with REE (like in Wigu in Tanganika; *Mackay, 1962*), or carbonates such as bastnäsite-(Ce) (like in Barra do Itapirapuã in Brasil; *Ruberti et al., 2008*) and parisite-(Ce) (like in Fazenda Varela, Brasil; *Manfredi et al., 2013*), in addition to REE silicates (*Doroshkevich et al., 2009*). Sometimes, REE can be incorporated in the structure of late perovskites (*Martins et al., 2014*).

Hydrothermal paragenesis do not only include these minerals, but usually very complex associations appear too. These associations can be made up of sulphides, arsenides, tellurides, selenides, native elements and sulphosalts (*Pilipiuk et al., 2001; Bambi, 2015*), which can produce mineralizations of economic interest.

One problem aside is constituted by diverse vein mineralizations, common in diverse points around the world, apparently disassociated with typical carbonatitic bodies hosted in very diverse rocks. The veins are constituted by quartz, fluorite, barite and REE minerals (nearly always minerals belonging to the bastnäsite, synchysite, parisite or rhabdophane group). Generally, the paragenesis are identical to those observed in the intracarbonatitic veins, meaning that they could correspond to distal manifestations of the carbonatites formed by hydrothermal or carbohydrothermal processes. Some important examples are found in Mountain Pass (USA), Kangankunde in Malawi (*Wall and Mariano, 1996*) or in Karonge, Burundi (*van Wambeke, 1977; Fig. 13*). The Hoidas Lake deposit in Saskatchewan in Canada (still in exploration) was developed in connection to shear zones. It bears quartz, apatite, monazite and other minerals, thought the most significant is that this monazite is extremely rich in Nd and MREE (*Rogers, 2011*).



**Fig. 13.** Aspect of a thin section of mineral associations in veins associated with carbonatitic intrusions, though in a distal position from these. Left, in PPL. Large tabular crystals of bastnäsite-(Ce) (Btn) developed by free growth in a vein cavity, on top of which crystallizations of comb quartz (Qtz) are formed. Bastnäsite is replaced by fine grain aggregates of monazite-(Ce) (Mnz) and cerianite-(Ce) (Cer). Right, the same association with crossed nicols. It should be emphasized the straight extinction of some bastnäsite crystals. Karonge (Gakara) mine, rural province of Bujumbura, Burundi.

The distal disposition of these deposits in relation to the carbonatites can create confusion concerning its relationship with the carbonatitic source, which frequently does not outcrop. The source of many examples of mineralizations with uncertain genetic model, although spatially associated with other types of igneous rocks, could be likewise carbonatitic. This happens in many deposits of the

USA, like for example in Gallinas Mountains (Lincoln Co, New Mexico; *Perhac and Heinrich, 1964*). In this area abundant veins with fluorite-bastnäsite-barite-quartz exist (*Fig. 14*) with minor quantities of thorite, parisite and eventually Cu-Pb-Zn sulphides (*Schreiner, 1993; McLemore, 2010*), with even gold (*Woodward and Fulp, 1994*), as well as mineralizations contained in breccias. All

of these are hosted in alkaline subvolcanic rocks of anorogenic affinity (specially, latites or trachytes, but also rhyolites; *Perhac, 1970*). A first examination of the geology of the zone could suggest an association with these volcanic rocks, but in the same area some carbonatite outcrops have been localized. Thus, it can be possible that these REE mineralizations constitute distal mineralizations associated to carbonatites, in the same line as described in Karonge, but with much larger proportions of fluorite (*Staatz, 1992*). Similar deposits have been described in many points of the EEUU; defining a vein type mineralization bearing quartz gangue and Fe oxides with thorite and monazite, with minor quantities of brockite, allanite and bastnäsite (*Staatz, 1974*). Some typical examples include Lemhi Pass district, in Idaho and Montana, (*Staatz, 1972, 1979*), and Powderhorn and Wet Mountain in Colorado (*Olson et al., 1977, Armbrustmacher, 1988*). However, thorite is absent whereas bastnäsite, brockite and monazite are the main minerals in Bear Lodge Mountains in Wyoming (*Staatz, 1983*). Contrastingly, neither thorite nor monazite occur in Laughlin Peak in New Mexico, and brockite with xenotime or REE- and Th-rich crandallite are the main ores (*Staatz, 1985*). Analysis of fluid inclusions in quartz reveals high temperatures, in the order of 400°C and salinities in the order of 15% eq NaCl, though rich in sulphates.

These fluids are interpreted as magmatic fluids; though it is presumed that a second fluid rich in CO<sub>2</sub> and poorly saline of external origin intervened in both the fluocarbo-nates and the fluorite precipitation, at slightly lower temperature (*Williams-Jones et al., 2000*). Similar temperature conditions but of higher salinity (up to 50% NaCl eq) were found in the Snow Bird deposit (Montana, USA) where, once again, fluocarbo-nates with quartz and fluorite were formed and ankerite occurred in addition (*Metz et al., 1985; Samson et al., 2004*), or in Lemhi Pass between the limit of Idaho and Montana.

#### 4.1.d. Enrichment of Rare Earth Elements in Carbonatites Due to Metamorphism

Some carbonatites can have suffered metamorphic phenomenons in very diverse grades, and important modifications of the original mineralogy took place. Generally, pyrochlore seems not to be stable under these conditions, so it is replaced by a variety of oxides which, on the other hand, tend to re-concentrate Sc, Y and HREE, like columbite, ixiolite, fergusonite, fersmite or euxenite (for example, *Franchini et al., 2005, Chakhmouradian et al., 2014*). Columbites or, especially, ixiolites with high Sc contents are quite common mainly in LCT granitic pegmatites, as *Wise et al. (1998)* refer. Nevertheless, in pegmatites these minerals are not abundant enough to

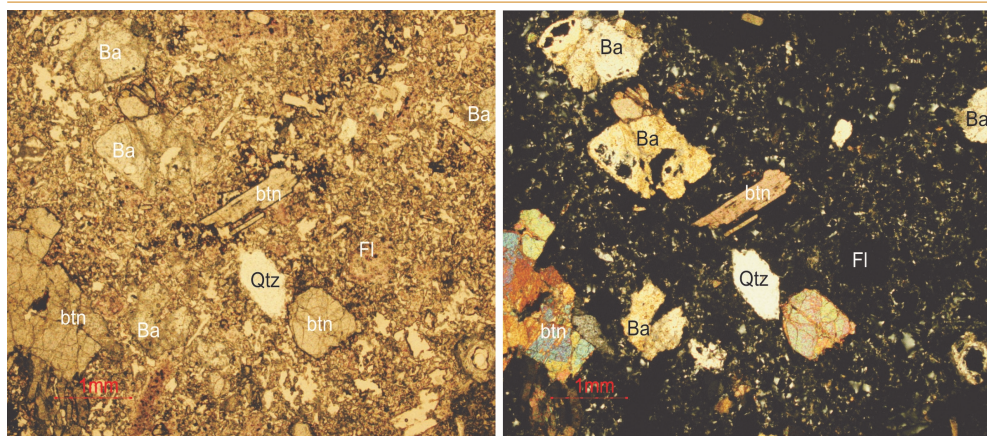
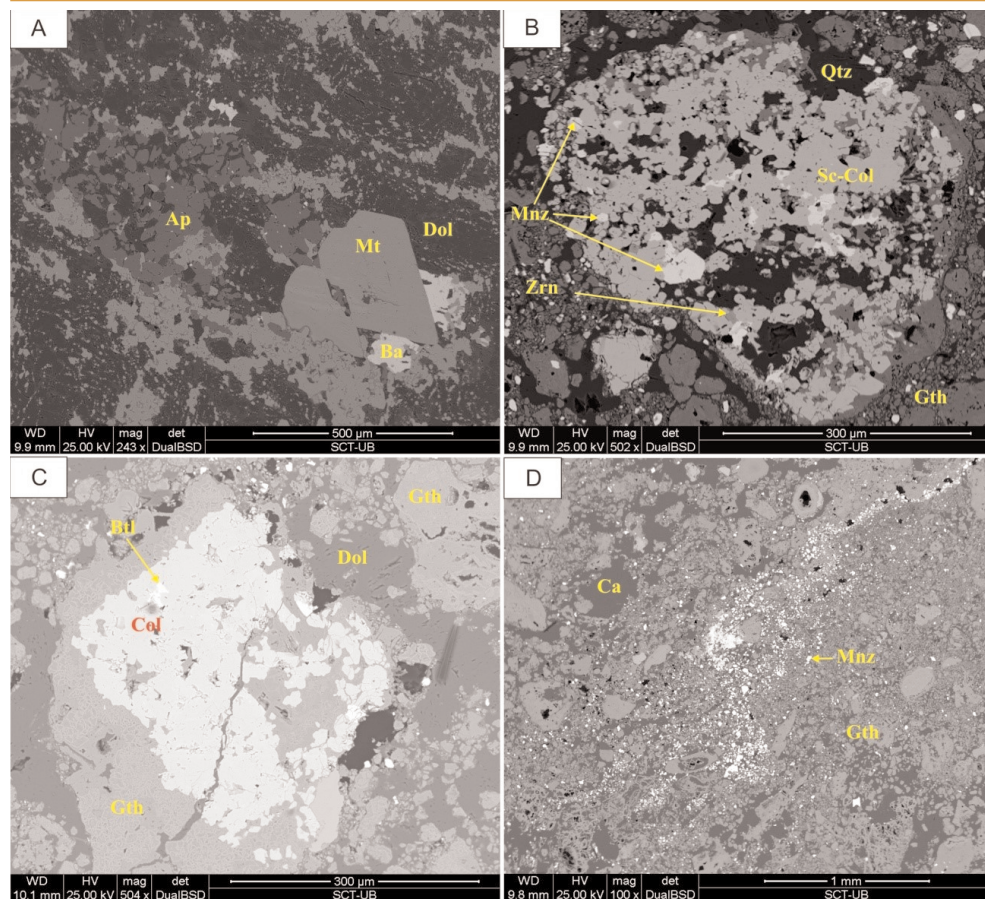


Fig. 14. Aspect in thin section of mineral associations in veins and breccias with fluorite-quartz-REE associated with carbonatitic intrusions, though in distal positions regarding them. Left, in PPL. Big tabular batnäsäsite(Ce) crystals (Btn) developed by free growth in a vein cavity, associated to corroded barite (Ba), fluorite (Fl) and quartz (Qtz) crystals, surrounded by fine grain matrix of quartz and fluorite. Right, the same association in crossed nicols. Gallinas Mts, Red Cloud District, Lincoln Co., New Mexico, USA.

constitute economic ores of these elements, whilst in carbonatites these can be the main ore. So, according to *Lehbib et al. (2011)* the deformed carbonatites from Gleibat Lefhuda in Western Sahara (RASD) contain pyrochlore pseudomorphed for *Sc-rich columbite* (Fig. 15); late minerals in this association include quartz and REE phosphates as britholite-(Ce) and monazite-(Ce) (Fig. 15).



**Fig. 15.** Different aspects of mineral associations produced by subsolidus hydrothermal and metamorphic processes in the carbonatite of Gleibat Lefhuda, Western Sahara (RASD), in SEM images in BSE mode. A, Aspect of the deformed rock, slightly altered, constituted by dolomite (Dol), magnetite (Mt) and apatite (Ap); the magnetite is partially replaced by hematite and the barite (Ba) is secondary. Note the foliation. B pyrochlore crystal pseudomorphed by Sc-rich columbite (Sc-col), quartz (Qtz) with zircon (Zrn) and monazite-(Ce) (Mnz). C, Pyrochlore crystal completely replaced by columbite (col) and britholite-(Ce) (Btl) between dolomite. The goethite (Gth) is possibly pseudomorphing hydrothermal ankerite. D, Monazite-(Ce) (Mnz) rich bands, with mylonitic aspect, between supergene goethite and calcite.

Diverse authors propose that the Bayan Obo deposit owes part of its high grade to enrichment processes during metamorphism. In fact, in this deposit columbite is also abundant.

#### 4.1.e. Enrichment of rare earth elements by supergene processes

Meteorization of carbonatites can produce a wide range of secondary minerals, many of which can re-concentrate REE, even though in lateritic profiles part of these elements can still remain fixed in some minerals of earlier stages which are refractory to meteorization (*Nasraoui et al., 2000*).

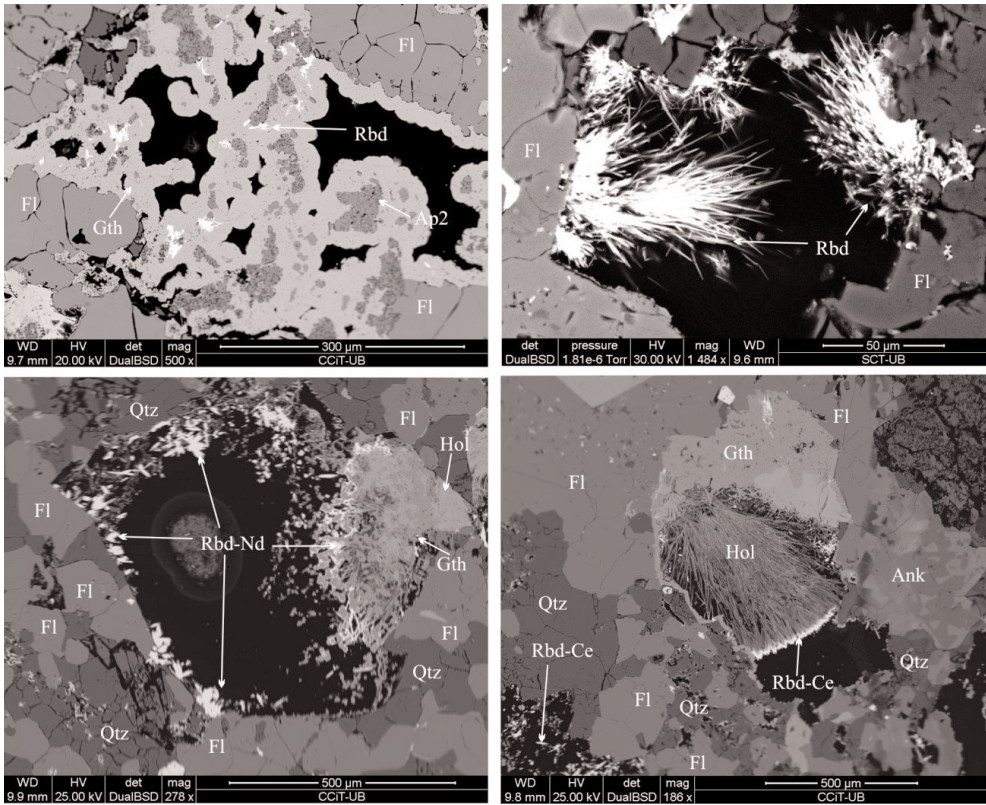


Fig. 16. Aspects of mineral associations produced by supergene subsolidus processes in the Tchivira carbonatite, Angola, in SEM images with BSE mode. Top, left: pyrite crystals inside fluorite (Fl) with a generation of late apatite (Ap2) replaced by goethite (Gth), and rhabdophane-(Ce) (Rbd). Top, right: radial crystallization of rhabdophane-(Ce) (Rbd) in a cavity left by the dissolution of a pyrite crystal. Synchysite-(Ce) (Syn). Bottom, left: in a cavity produced by the dissolution of a pyrite crystal, hosted between fluorite (Fl) and quartz (Qtz), a first generation of goethite (Gth) has crystallized, followed by hollandite (Hol) and finally rhabdophane-(Nd) (Rbd-Nd). Below, to the right, dissolved crystals in hydrothermal replacement zone containing quartz (Qtz), ankerite (Ank) and fluorite (Fl). The porosity is filled by hollandite (Hol) followed by rhabdophane-(Ce) (Rbd-Ce).

LREE and HREE are generally separated during the meteorization process; moreover, Ce even separates from the rest of REE forming minerals due to the differential behaviour of  $Ce^{4+}$  (for example, Braun *et al.*, 1990; Torró *et al.*, 2012). Therefore, the simultaneous alteration of the primary apatite, apart from favouring a new generation of late apatite, of carbonate-apatite or hydroxyapatite composition, can lead to the production of many secondary phosphates which concentrate different REE. This way, churchite can be formed. This mineral can sometimes concentrate HREE (Lottermoser, 1987; Jones *et al.* 1996), whereas rhabdophane or crandallite group minerals and secondary monazite preferably concentrate LREE (Braun *et al.*, 1990; Lottermoser, 1990; Melgarejo *et al.*, 2012). It is frequent to observe in the same association minerals of the rhabdophane group rich in  $Ce^{4+}$ ,

whilst the rest of the LREE (especially Nd) are enriched in another type of rhabdophane (rhabdophane-(Nd), Fig. 16).

These phosphates tend to concentrate themselves in the upper part of a lateritic profile, whilst both the secondary apatite and the churchite would do it in the lowest part. This apatite can sometimes fix HREE (Morteani and Preinfalk, 1996), albeit some authors suggest that these elements tend to be adsorbed in Fe and Mn oxides and hydroxides, clays and organic matter (Nasraoui *et al.*, 2000). This mechanism can be highly efficient for concentrating REE. In fact, it is nearly always required a lateritic enrichment to reach the precise concentrations of REE in order to have a deposit. This happens in the lateritized carbonatites of Brasil, like Araxá, in which 800,000 t of laterite with proportions of 13.5%

Minerales	Fórmula	Carbonatitas	Carbonatita dolomitizada	Carbonatita ankeritizada	Roca de cuarzo-fluorita	Fenita
Calcita I	CaCO <sub>3</sub>	■				
Apatito I	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	■				
Magnetita	Fe <sup>2+</sup> Fe <sup>3+</sup> O <sub>4</sub>	■				
Pirocloro I	(Ca,Nb) <sub>2</sub> (Nb <sub>2</sub> O <sub>7</sub> )F	■				
Pirocloro II	(Ca,Nb <sub>2</sub> ) <sub>2</sub> (Nb <sub>2</sub> O <sub>7</sub> )F <sub>2</sub>	■				
Pirita	FeS <sub>2</sub>	■				
Calcopirita	FeCuS <sub>2</sub>	■				
Dolomita I	CaMg(CO <sub>3</sub> ) <sub>2</sub>	■				
Feldespato potásico	KAlSi <sub>3</sub> O <sub>8</sub>					■
Ankerita	CaFe(CO <sub>3</sub> ) <sub>2</sub>		■			
Dolomita (ferrica)	Ca(Mg,Fe)(CO <sub>3</sub> ) <sub>2</sub>		■			
Dolomita II	CaMg(CO <sub>3</sub> ) <sub>2</sub>		■			
Fluorita	CaF <sub>2</sub>				■	
Bastnásita-(La)	(La,Ce)(CO <sub>3</sub> )F		■			
Apatito II	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH		■			
Cuarzo	SiO <sub>2</sub>			■	■	■
Hematites	Fe <sup>3+</sup> O <sub>2</sub>			■		
Calcita II	CaCO <sub>3</sub>			■		
Galena	PbS				■	
Zircón	ZrSiO <sub>4</sub>				■	
Rutilo (nióbbico)	(Ti, Nb, Fe <sup>3+</sup> )O <sub>2</sub>				■	
Rutilo	TiO <sub>2</sub>				■	
Pirocloro III (Sr)	(Ca,Sr) <sub>2</sub> (Nb <sub>2</sub> O <sub>7</sub> )				■	
Pirocloro IV (Ba)	(Ca,Ba) <sub>2</sub> (Nb <sub>2</sub> O <sub>7</sub> )				■	
Pirocloro V (Pb)	(Pb)(Nb <sub>2</sub> O <sub>7</sub> )O				■	
Britolita-(La)	Ca(La,Ce)(SiO <sub>3</sub> PO <sub>3</sub> )(OH,F)		■			
Kutnohorita	Ca(Mn,Mg,Fe)(CO <sub>3</sub> ) <sub>2</sub>				■	
Estroncionita	SrCO <sub>3</sub>				■	
Barita	BaSO <sub>4</sub>				■	
Synchysita-(Nd)	Ca(Nd,Y,Gd)(CO <sub>3</sub> ) <sub>2</sub> F				■	
Synchysita-(Ce)	Ca(Ce,La,Pr)(CO <sub>3</sub> ) <sub>2</sub> F				■	
Hollandita	Ba(Mn <sup>2+</sup> ,Mn <sup>3+</sup> ) <sub>2</sub> O <sub>8</sub>				■	
Rabdofana-(Ce)	(Ce)(PO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O				■	
Rabdofana-(La)	(La,La,REE)(PO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O				■	
Gorceixita	BaAl <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH)·H <sub>2</sub> O				■	
Gibbsita	Al(OH) <sub>3</sub>				■	
Goethita (nióbbica)	(Fe,Nb)O(OH)				■	
Goethita	FeO(OH)				■	
Coronadita	Pb(Mn <sup>2+</sup> ,Mn <sup>3+</sup> ) <sub>2</sub> O <sub>8</sub>				■	

Fig. 17. Mineral sequence of a typical carbonatite: the Tchivira carbonatite in Angola (Bambi, 2015).

REEO have been evaluated. These are concentrated in the gorceixite and goyazite (Mariano, 1989a); in the Catalão I complex 2 Mt of lateritized carbonatite have been recognized, with 12% REEO in gorceixite (Mariano 1989a; Morteani and Preinfalk, 1996). Similar associations in Maicuru contain up to 17% REE (Costa et al., 1991).

In some cases, the karstification of carbonatites can favour the re-concentration of rare elements; either as paleoplacers in some cavities, as secondary minerals or in association with decalcification clays, like in the Tomtor massif in Siberia (Kravchenko and Pokrovsky, 1995).

In short, when the carbonatitic crystallization mineral sequence is observed, it can be seen that the major REE mineral concentrates are produced during the late hydrothermal and supergene stages. In figure 17, a synthesis of the crystallization sequence of the different phases of the Tchivira (Angola) carbonatites is presented. As it has previously been indicated, most part of the intrusion is made up by calcic

carbonatites which are affected by different hydrothermal alteration processes that produce a sequence of dolomitization, ankeritization and silicification-fluoritization processes, which can superimpose themselves in space; the host rock is strongly fenitized. As it can be appreciated, the zones affected by hydrothermal processes are those bearing the widest variety of REE minerals and, in fact, are those that posse the largest concentrations of these elements in the whole carbonatitic unit too. It is likewise important to point out that diverse generations of pyrochlore are produced, as well as other niobium minerals in association with these hydrothermal bodies. Moreover, these zones are full of other useful minerals such as fluorite, secondary apatite, barite and Sr minerals. Thus, these zones are usually critical when the economic interest of a carbonatite must be evaluated, especially in the case o REE. In addition, the supergene phenomenons are REE efficient re-concentrative, though only in zones affected by hydrothermal fluids, possibly because in these zones pre-concentrations, which are larger than in carbonatites



without hydrothermal alteration, take place (Fig. 17). Consequently, it is in these zones where the superposition between different processes can help to provide REE enrichments, which can lead to the formation of a truly economic deposit. However, it shall be taken into account when evaluating the deposits that the REE minerals, because of the same reason, can be distributed between mineral species with different behaviours during the mineral formation-processes. That is why a thorough cartography of the hydrothermal alteration zones and a detailed mineralogical study can be critical for the exploration design and for a correct ore treatment approach, in order to guarantee the success in the REE benefit in these bodies.

#### Postorogenic carbonatites

These include carbonatites disassociated from the clans previously cited. They are spatially associated with undersaturated or saturated alkaline intrusions, without clear genetic relationship, though in some cases they have been considered to be related to carbohydrothermal processes. This category includes rarer examples than those of rifting, but they are important as the few examples known tend to be especially enriched in REE. This happens in high economic interest deposits like the Maoniuping mine in China (Wang *et al.*, 2001), Mountain Pass in California (Olson *et al.*, 1954; Castor, 2008) and the carbonatite from Eden Lake (Manitoba, Canada; Chakhmouradian *et al.*, 2008). In fact, these carbonatites tend to be much more rich in REE minerals, especially in REE carbonates like bastnäsite, than its equivalents located in rift zones. On the other hand,

they are poor in Nb or Zr. In all the cases, the REE mineralization concentrates during the hydrothermal stages and tends to situate itself outside the carbonatitic intrusion, frequently in silicic veins in the host rock. In Mountain Pass, one of the largest deposits in North America and one of the biggest deposits of the West, the reserves are of 29 Mt of ore with 8,9 % of REE<sub>2</sub>O<sub>3</sub>, with a cut-off grade of 5% (Castor and Nason, 2004).

#### Oceanic carbonatites

In oceanic carbonatites mineralization processes and the minerals described can be, roughly, similar to those cited for the continental carbonatites (for example, Mangas *et al.*, 1997), even though the volume comprising its bodies is much lower and, therefore, do not seem to be strategic objectives.

#### Anatectic carbonatites

Though rare, in some places they can have developed important volumes of magma, like in the Bancroft zone (Ontario, Canada; Lentz, 1998) or in diverse localities of Oaxaca (Mexico; Melgarejo and Pro-Ledesma, 1999). In the first instance, they are generally carbonatite dikes hosted in granitoids affected by strong fenitization phenomena in the exocontact (Fig. 18). The mineralogy is not very varied and it does not present neither REE or Nb mineralization; in addition to calcite, there can be very variable quantities of apatite, fluorite, aegirine, amphiboles, biotite, sanidine and scapolite, being this one rarer than nepheline. In some places, uraninite has been found. Their crystals can be very large, euhedral and they use to be



Fig. 18. Some outcropping aspects of the anatectic carbonatites. Left, outcrop near Bancroft, Ontario, in which the fenitization on the hosting granite (to the left of the image) can be appreciated, as well as a simple mineralogy in the carbonatite, with aegirine-augite (green) and calcite. Right, outcrop of white carbonatites which are cutting the dark gneisses in the México-Oaxaca highway. Note the gneiss xenoliths in the carbonatite.

located at the contact between the body and the host rock, indicating earlier crystallization than calcite.

The Oaxaca carbonatites constitute bodies of stockwork morphology (Fig. 18) or dikes emplaced in gneissic rocks, composed of calcite with lesser proportions of fluorapatite, scapolite, zircon, titanite, potassic feldspar and augite. Locally, small quantities of monazite-(Ce) and xenotime occur, but they are nearly always very poor mineralizations. In fact, up to the moment, interesting evidence of REE related to this typology has not been described.

### 5. Deposits Associated to Granitoids

Generally, REE are concentrated in the less evolved granitic rock types in the structure of some common accessory minerals: apatite tends to concentrate LREE and titanite HREE. With larger concentrations, REE may produce accessory minerals, like monazite and xenotime, allanite and many others. This way, allanite does not only appear in pegmatites, but as accessory in granites with very different alkalinity grade, though in A-type granites it can be locally enriched in HREE and Y (Whalen *et al.*, 1987), like in Hungary (Buda and Nagy, 1995). In fact, monazite is a common accessory in very low proportions in a wide range of granitoids, charnockites and even migmatites and gneisses (Rapp and Watson, 1986). Generally, the typical calc-alkaline granites and their volcanic equivalents do not generate significant accumulations of these elements. Very evolved I or S type granites, including topaz-bearing granites and the greisen deposits, are not very enriched in REE (Vlasov, 1966; Manning and Hill, 1990). Enrichments in minerals of the monazite-huttonite-cherilite series do occur in greisens associated with S-type granites (Förster, 1998) as do oxyfluorides like håleniusite-(La)(Johan and Johan, 1994). It is also worth to mention the appearance of small, though abundant, monazite and xenotime crystals associated to zircon of early formation in the vein fillings of the Sn-W-Bi-Ag-Pb-Zn Bolivian type deposits, specially in the most proximal mineralizations in relation to the intrusions, ergo in the richest in Sn-W-Bi. This occurs, between others, in Viloco (Artiaga *et al.*, 2013), Llallagua, Huanuni (Arqués *et al.*,

2013), Poopó (Torres *et al.*, 2013), etc. In a possible similar way, both monazite and xenotime, associated with zircon and uraninite, occur in small quantities as fine grain crystals associated with cassiterite and diverse minerals bearing F and Be in the hydrothermal deposits associated with acid vulcanism. Deposits such as the diverse manto-type deposits from the Union zone, in Murcia, Spain (Pujol *et al.*, 2013; Sanmartí *et al.*, 2013; Soler *et al.*, 2013) can also be enriched in these minerals. However, the A-type granitoids are more favourable to concentrate REE, particularly the most evolved types and in those where late hydrothermal phenomenons take place, giving values higher than 0,2% wt.% of REE (being these either LREE or HREE) in bulk rock (Vlasov, 1966).

Like in the case of undersaturated rocks, the deposits of REE in alkaline rocks tend to develop in the most agpaitic rocks, thereby in the presence of accessory minerals like aegirine and alkaline amphiboles (mainly riebeckite and also arfvedsonite), even though fluorite usually appears. These are typical rocks located in extensional contexts (Bonin, 2007) and it is common for them to be associated with undersaturated alkaline rocks and carbonatites (Downes *et al.*, 2004).

Mineralizations of rare elements, including the REE, are produced in saturated alkaline rocks by a sequence of mineralizing phenomenons similar to those described in carbonatites and undersaturated alkaline rocks. Therefore, Boily and Williams-Jones, (1994) described in the Strange Lake deposit (Quebec, Canada) a sequence of mineralizing processes from an eminently magmatic stage to a hydrothermal one, each one with their mineral species.

Concentrations of rare element minerals already occur in the magmatic crystallization stages of the peralkaline granites. Thus, in the rare element deposit of Khaldzan-Buregtey massif (Occidental Mongolia), there are concentrations up to 25% of monazite and REE fluocarbonates, in association with large quantities of zircon and zirconosilicates like elpidite or gittinsite (Kovalenko *et al.*, 2004). These type of mineralizations become the rule in lots of A-type granitoids around the world, like those

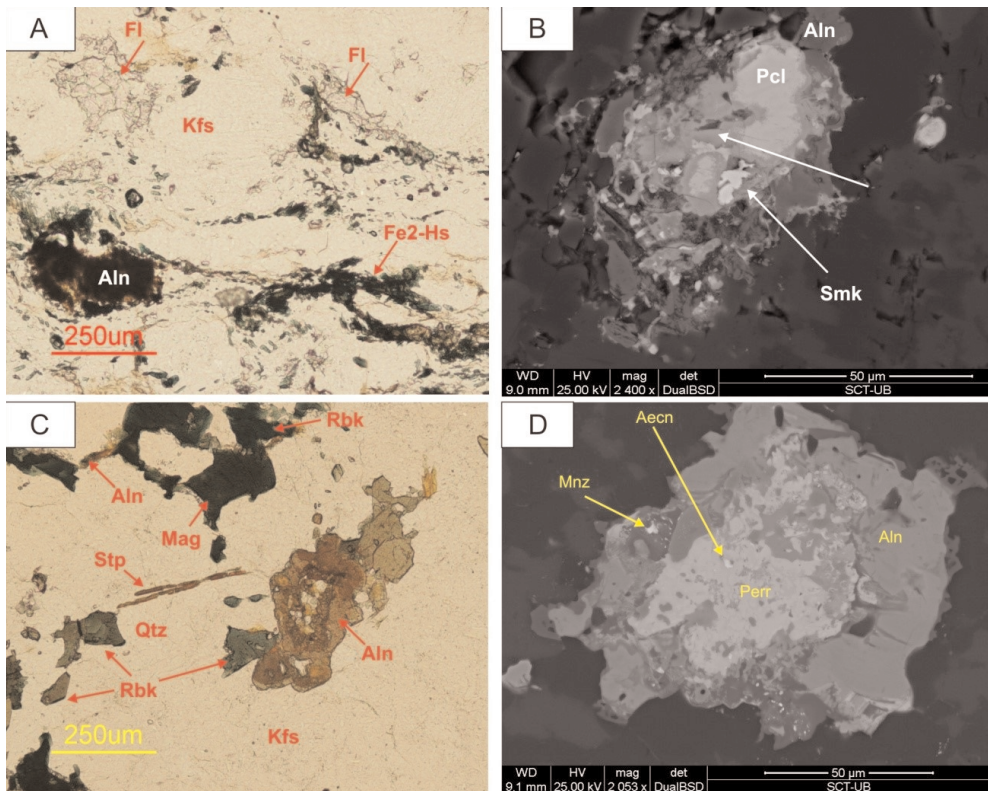


Fig. 19. Detail of some REE mineral associations in alkaline granitoids from Western Sahara. A) Gneissified alkaline granite from Gleibat Tieha, Mauritanides from Western Sahara, with planar polarized light without analyser. Fl, fluorite, Kfs, microcline, Aln, allanite-(Ce), Fe<sub>2</sub>-Hs, ferrosilite. B) Detail of allanite-(Ce) crystals, observed in image with scanning electron microscope with retrodispersed electron mode. Samarskite-(Y) (Smk) and pyrochlore (Pcl) replaced by allanite-(Ce) (Aln). C) Alkaline granite from Gleibat Lefhuda, with planar polarized light without analyser. Aln, allanite-(Ce), Rbk, riebeckite, Kfs, microcline, Mag, magnetite, Stp, stilpnomelane. D) Eburnean alkaline granites from Gleibat Musdar, in scanning electron microscopy with image obtained with retrodispersed electron mode. Perrierite-(Ce) (Perr) replaced by allanite-(Ce) (Aln), with monazite (Mnz) and aeschynite (Aecn).

from Western Sahara (RASD). In this case, REE minerals are in great part primary and crystallize with accessories such as amphiboles and alkaline pyroxenes; in many cases, allanite can be secondary, replacing primary oxides rich in Nb and REE like pyrochlore or samarskite (Fig. 19a, b), or other silicates such as perrierite (Fig. 19d). Fluorite is a common mineral in these granitoids; in addition, some silicates can also contain F in their structure.

Nevertheless, the subsolidus stages are much more fertile when producing REE mineralization in peralkaline granites, as it can be seen in the Strange Lake deposits in Canada (Salvi and Williams-Jones, 1990, 1996; Birkett et al., 1992). In very evolved alkaline granites, such as those in Kola Peninsula, high temperature hydrothermal alterations produce the replace-

ment of the primary paragenesis, generating rare element mineralizations, especially of REE; *Belolipetsky (1997)* details some of the most typical associations in the dome zones:

- \* Albitizations with zircon, aeschynite-(Y) and euxenite (the most common type), where these minerals form dense aggregates of dimensions ranging from centimetres to decimetres.

- \* Silicic albitizations, with zircon, with the following mineral sequence: chevkinite-(Ce), monazite-(Ce) and allanite-(Ce). This is the earliest association of the REE minerals and it is rich in LREE, though it tends to increase the HREE quantity to the end.

- \* Albitizations with mafic minerals: they consist of amphiboles-biotite-albite with allanite, gadoli-

nite and thorite. They are only found in contact zones between the granite and the host rock (amphibolite).

\* Silicifications with britholite-(Y), thalenite, danalite and thorite. These rocks are normally found forming the nucleus of the zoned metasomatic bodies and contain, nearly exclusively, late quartz and rare element minerals.

\* Silicifications with zircon, fergusonite and thorite: the zircon is an essential mineral (making up to 50%, or more of the bulk rock), in continuous and massive segregations of zoned crystals. Fergusonite and thorite occur in smaller proportions.

In addition to the previously mentioned associations, in the aplogranitic alkaline hydrothermal associations from different regions of Siberia, the following mineral associations of rare metals are observed (Belolipetsky, 1997):

\* High temperature sodic-potassic alterations with biotite-microcline-albite, with columbite, zircon and thorite: mainly formed by albite, generally of medium grain size, with diverse proportions of microcline, biotite and quartz. Columbite, thorite and quartz are found uniformly disseminated in the albite crystals.

\* Riebeckitic and aegirine-riebeckite-microcline-albite, with zircon, Ce pyrochlore, fluocerite and gagarinite. Zircon is usually found in form of bipyramidal crystals uniformly disseminated. Small Cerian pyrochlore crystals make up irregular disseminations. Gagarinite occurs as irregular segregations frequently replaced by REE fluorocarbonates. Fe-polythionite is also a common mineral.

\* Albitizations with polycrase and Th-rich zircon: they are mainly formed by albite, with small polycrase and Th-rich zircon grains irregularly disseminated. The largest concentrations of these minerals are observed between the contacts with the segregations, as veins or as cloudy aggregates. Large associations of polycrase and Th-rich zircon are associated with this late quartz. Other minerals such as pyrochlore, columbite, monazite, xenotime, gadolinite, fergusonite and gagarinite occur in lesser proportions.

\* Silicifications with zircon and Li micas: these metasomatites consist fundamentally in small tabular albite crystals and large thick quartz segregations. The mafic minerals are absent. The zircon occurs as zoned, well-formed bipyramidal crystals, generally red, brown or pink in colour. The Li micas occur in small veinlets cutting the rest of the minerals, and comprise from lithium biotite to zinnwaldite, lepidolite and polythionite. Columbite normally occurs as small crystals disseminated through the rock and may replace older pyrochlore crystals.

Some examples of currently important and highly altered deposits with economic interest can be cited. In first place, the Madeira mine in Pitinga (Amazon, Brasil), which is a Sn, Nb, Ta, Zr, Li, Y and HREE deposit on a global scale. It is emplaced in a highly fractionated alkaline granite with dispersed plumbopyrochlore and cassiterite as primary accessory minerals. It is also albitized, with F enrichments so high that it develops cryolite masses, resulting to be the only exploitable place nowadays for this mineral (Minuzzi *et al.*, 2003). Gagarinite-(Y) crystallizes towards the bottom of the body with fluocerite-(Ce) exsolutions. On the other hand, the high level of F activity has fostered the development of very complex phases, between them new fluorides like atroarite and waimirite. Waimirite has been recently accepted by the IMA (Atencio *et al.*, 2015) and is possibly much more common than expected. In addition, xenotime presents F replacing part of the oxygen when, at the same time, HREE enrichments occur (Neto *et al.*, 2009).

Saudi Arabia has some important Nb-Zr-REE deposits that have been poorly studied. The Jabal Tawlah microgranites and microsyenites are associated with Proterozoic alkaline intrusions and they form a highly mineralized sill of small size that contains 6.4Mt of ore with 1.2 % of REEYO (Drysdall *et al.*, 1984). The ores are really complex and they bear columbite, cassiterite, fergusonite, waimirite, xenotime and other indeterminate REE fluorides (Drysdall and Douch, 1986). Possibly, the deposit presents the highest Dy cutting-off grades of the world. The "rare" and uncharacterized minerals are precisely the carriers of 50% of Dy in the deposit, being the rest in the xenotime. Similar mineralizations associated with extreme F acti-

vities occur in Jabal Sayid (Harris et al., 1986).

## 6. Deposits Associated to Topaz Rhyolites

In the last years the topaz rhyolites have evolved from being a mineralogical or petrological curiosity to become a major target in mineral exploration, as a source for Fluor (one of the strategic elements for the EU), beryllium and gems (red beryl and topaz). These rocks are formed in extensional contexts and are an extrusive equivalent of the A-type granites (Manning and Hill, 1990).

Beryllium can appear in these rocks as primary beryl or as bertrandite. Bertrandite is actually the mineral which is exploited nowadays in the most important beryllium deposit in the world, in Spor Mountains, Utah. It consists of tufts associated with topaz rhyolites altered by hydrothermal fluids which are rich in F and Be. However, topaz rhyolites with topaz can also contain Sn, W, Ta and other resources including REE (Fig. 20). In the case of Spor Mountains the presence of allanite has been recognised as one of the components of the rock (Christiansen et al., 1986), and nowadays the REE potential as byproduct is being evaluated in these rocks (Kraulec, 2011). It should be noted that a good part of Be is contained in the hydrothermal alteration clays, so the possibility that these clays may have also fixated REE may be explored.

Some similar peraluminic rhyolites, even though formed in geotectonic contexts of continental

arc, can have even stronger enrichments in HREE, and can likewise produce REE minerals in the form of incompletely studied fluorides, like the laccolith ones in Sierra Blanca, Texas (Price et al., 1990).

## 7. Deposits Associated to NYF Pegmatites.

NYF type pegmatites (Niobium-Yttrium-Fluoride; Cerny and Ercit, 2005) are generally related with anorogenic magmatism (Martin and De Vito, 2005). They are relatively poorly evolved, and use to present mineralizations of rare earth elements, for which they have also been known by the name of "rare earth pegmatites" (Cerny, 1982, 1991a,b; Cerny et al., 1997; Ercit, 2005; London, 2008; Simmons and Webber, 2008; Linnen et al., 2012). In this group, Cerny and Ercit (2005) established three categories based on the accessory minerals of rare elements: the allanite-monzazite pegmatites, euxenite pegmatites and gadolinite pegmatites. However, these pegmatites are relatively poorly studied yet, and these groups are probably heterogeneous. LREE are dominant in the allanite-monzazite pegmatites, a LREE/HREE equilibrium occur in the euxenite pegmatites and HREE dominate in the gadolinite pegmatites. These differences can be determined by the F activity, which in its turn can come conditioned by the mineral composition of the zone of the lower crust in which the pegmatitic magma is produced (Simmons et al., 2012).

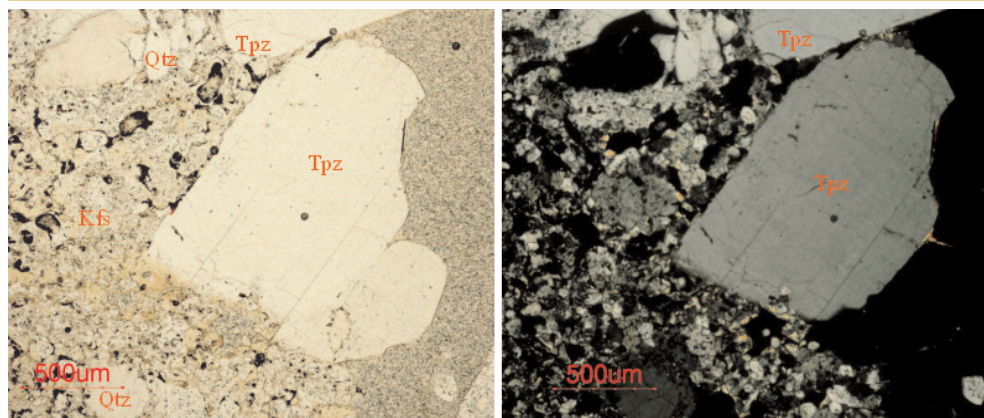


Fig. 20. General aspect of a topaz rhyolite thin section. Topaz is found in the lithophysae (implanted crystals in the right part of the pictures). Left side, in PPL; right, crossed nicols. Note the perfect cleavage {001} in topaz (Tpz). The REE minerals (mainly allanite) are of fine grain and are found in the matrix of the rock, with quartz (Qtz) and potassic feldspar of sanidine type (Kfs)

Allanite-Monazite pegmatites

The allanite-monazite pegmatites do not always include minerals rich in F, and are not

always associated with intrusive granites (Cerny, 1990). A very complete sequence of crystallization in allanite-monazite pegmatites can be found in the pegmatite from El

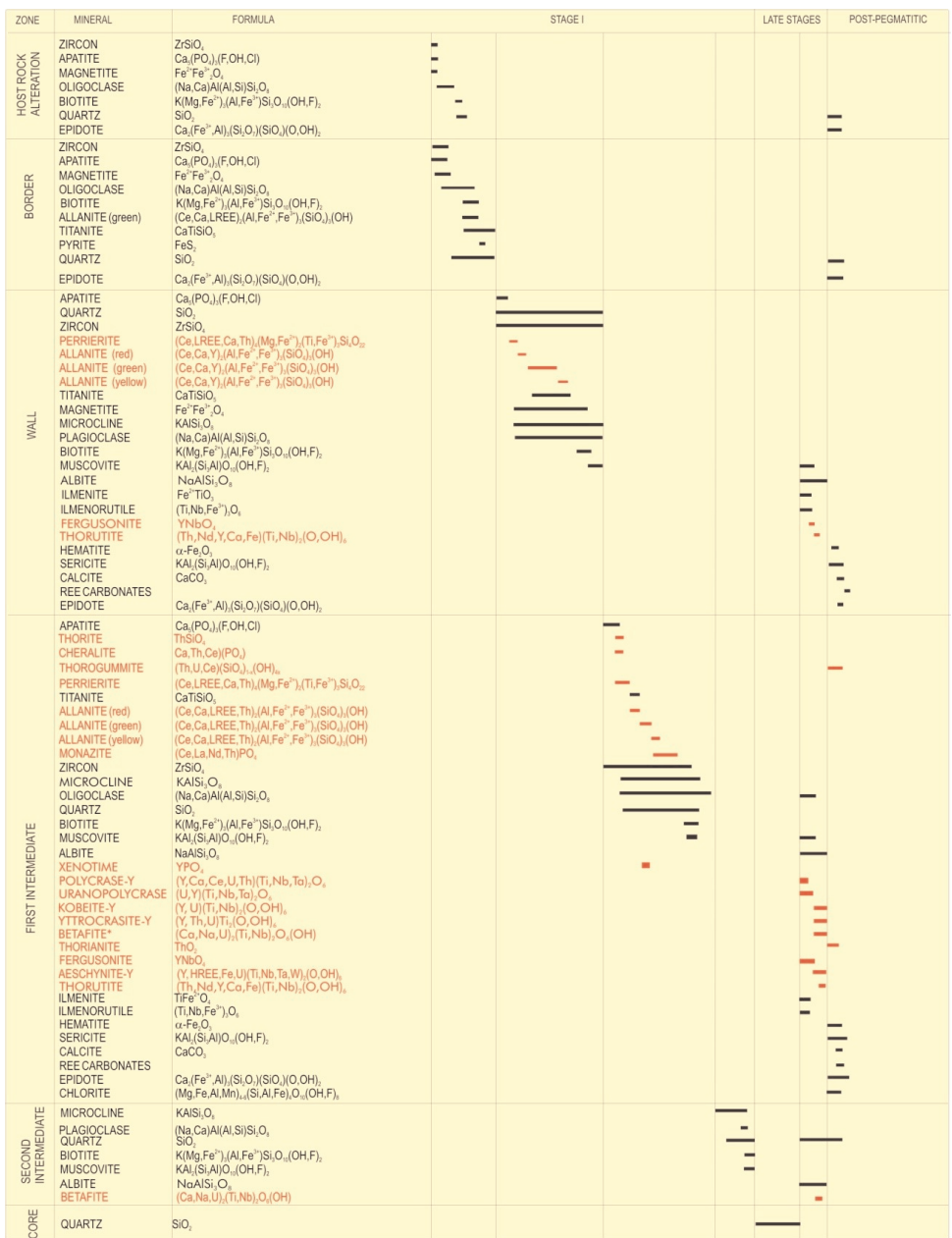
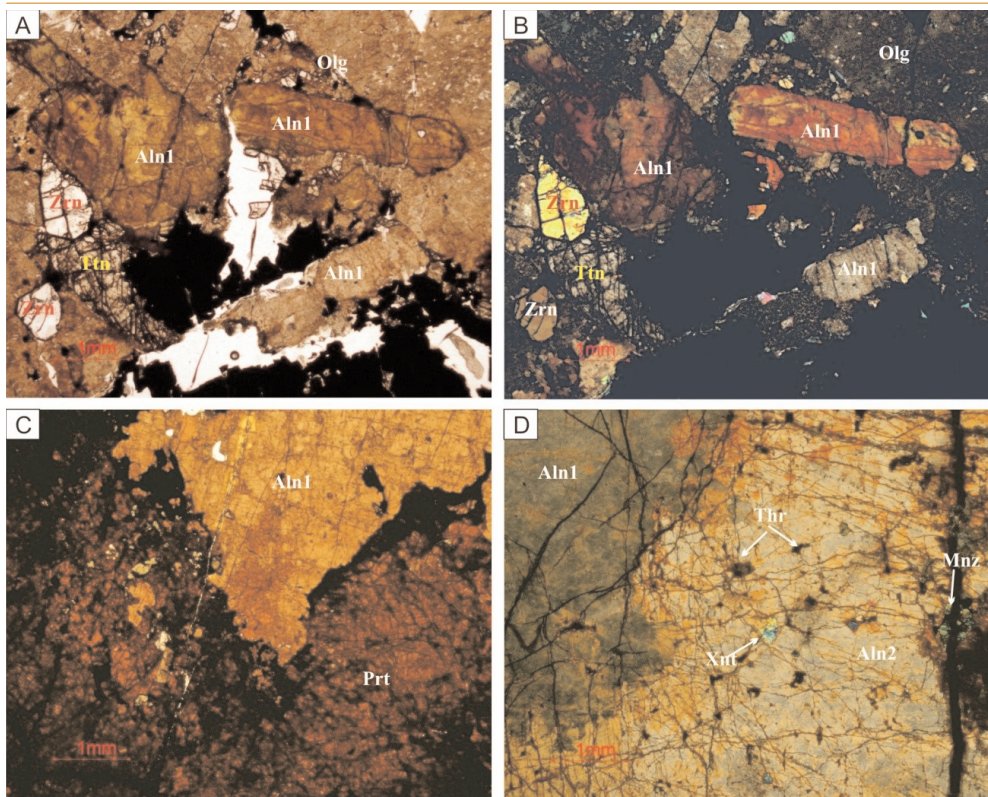


Fig. 21. Sequence of crystallization in the NYF pegmatites from el Muerto, San Pedro de Telixtlahuaca, Mexico. Note the crystallization of the LREE minerals in early stages and the HREE minerals in the late ones.

Muerto in Oaxaca (Mexico). The following units can be distinguished (*ProL-Ledesma et al., 2012; figure 21*):

- a) Border zone: primarily constituted by quartz and oligoclase with abundant biotite, magnetite, apatite, titanite and zircon, in millimetre-sized crystals.
- b) Wall zone: the mineral composition is similar to the previous unit, but with microcline accompanied by large quantities of perrierite-(Ce), which is almost totally pseudomorphed by various generations of allanite-(Ce). The crystals are of centimetre size and skeletal texture (*Fig. 22a,b*).
- c) First intermediate zone: there is a graphic intergrowth between quartz and microcline, or
- d) Second intermediate: giant microcline, oligoclase, quartz, biotite and muscovite crystals appear, with idiomorphic betafite crystals of centimetric size (the same unit also contains tourmaline in Czech pegmatites; *Skoda and Novák, 2007*).
- e) Core: it is made up exclusively by quartz.



**Fig. 22.** Thin section detail (PPL) of mineral associations in a pegmatite of the allanite-monazite subtype, from El Muerto in Oaxaca, Mexico. A) Detail of the wall zone, with centimetric skeletal crystals of allanite-(Ce) (Aln) intergrown with oligoclase (Olg), with zircon (Zrn), titanite (Ttn) and magnetite (opaque). B) The previous image, in crossed nicols. C) Detail of the first intermediate zone, PPL. Perrierite-(Ce) (Prt) replaced my metric crystals of allanite-(Ce) (Aln), accompanied by fine-grained thorite and titanite. D) Detail of the extrem of the allanite-(Ce) giant crystals in crossed nicols, with two generations of allanite-(Ce) (Aln 1 and Aln2); the second generation (Aln2) replaces the first and contains thorianite (Thr), xenotime-(Y) (Xnt) and monazite-(Ce).

f) Units of replacement (late stages): they are very fine, irregular veins with albite and which produce the albitization of the feldspars in their contacts. They contain minerals rich in HREE and Ta, of fine grain, which replace the previous minerals of Ti, Nb or REE, forming polycrase-(Y), uranopolycrase, kobeite-(Y), yttracrasite-(Y), thorianite, fergusonite, aeschynite-(Y), thorutite, ilmenite, ilmenorutile and hematite.

Similar sequences have been described in the Gloserheia pegmatites, near Arendal, Norway (Åmli, 1975, 1977), Colorado (Hanson et al., 1992), or in Slovakia (Uher and Broska, 1995); in all these mineralizations the major part of the Y-HREE minerals (like polycrase-(Y) or aeschynite-(Y)) are concentrated in the replacement units. The atelisite-(Y) appears likewise in late veins in the pegmatites of the Stetind quarry in Tysfjord, Norway (Malcherek et al., 2012); in the Evals-Lou quarry in Wakefield lake, Québec, Canada, late associations are also rich in HREE and are associated with quartz, hellandite, fergusonite, kainosite, tengerite, lokkaite, yttrian torogummite, yttrian spessartine, xenotime, wakefeldite-(Y), synchysite-(Y) and caysichite-(Y) (Hogarth et al., 1974).

Other pegmatites contain significant quantities of fluorite and other minerals rich in Fluor, like topaz, which favours the formation of other minerals of the pyrochlore group, microlite in particular, like in the Rutherford #2 mine in Virginia (Lumpkin, 1998). On the other hand, the composition of allanite is usually rich in Ce and LREE, which can be appreciated in the ensemble of the Grenville province pegmatites (Peterson and MacFarlane, 1993). Their impoverishment in Eu can be due to the fractioning of this element toward the plagioclase of granitic parental magmas (Möller, 1989b), while their HREE impoverishment can be due to crystallization with other phases which can easily collect these elements, like titanite, zircon and xenotime (Nagasawa, 1970; Yurimoto et al., 1990). Allanite is not always the REE dominant mineral, like in El Muerto. Mineral composition can come determined

by the host rock type, so for *Rapp and Watson (1986)* apatite + allanite + titanite + epidote + magnetite crystallization are typical in granitic systems contaminated by Ca.

As it can be seen, a problem for the benefit of the REE minerals is that they are concentrated in very refractory silicates. Nevertheless, meteorization and subsolidus hydrothermal processes usually produce the replacement of these silicates for fine grain carbonates, mainly bastnäsite (Sverdrup et al., 1959; Meintzer and Mitchell, 1988), as well as secondary monazite (which can be accompanied by other phosphates like florencite and rhabdophane), cerianite or lanthanite (Saebø, 1961) and goethite (which can capture part of the Th).

Few pegmatites of this type can be counted as having economic perspectives. Amongst them, those from Alice Springs, which are estimated in 1 Mt of ore with 4% allanite (Jackson and Christiansen, 1993).

### Euxenite Pegmatites

They seem to be rarer than the previous ones. The zonation described in the pegmatites associated with the pluton from Trebič in the Czech Republic (Skoda and Novák, 2007) consists of:

- a) Wall zone with a medium to thick size, with potassic feldspar, quartz, oligoclase, phlogopite and amphibole.
- b) Graphic unit with microcline (sometimes amazonitic), quartz and rarely albite.
- c) Zone of blocky crystals with potassic feldspar.
- d) Quartz core.

Many accessory minerals are scattered especially in the middle units, like tourmalines, beryl, minerals of the aeschynite and euxenite groups (Fig. 23), ilmenite, ilmenorutile, titanite, allanite, zircon, xenotime (Fig. 23) and monazite.



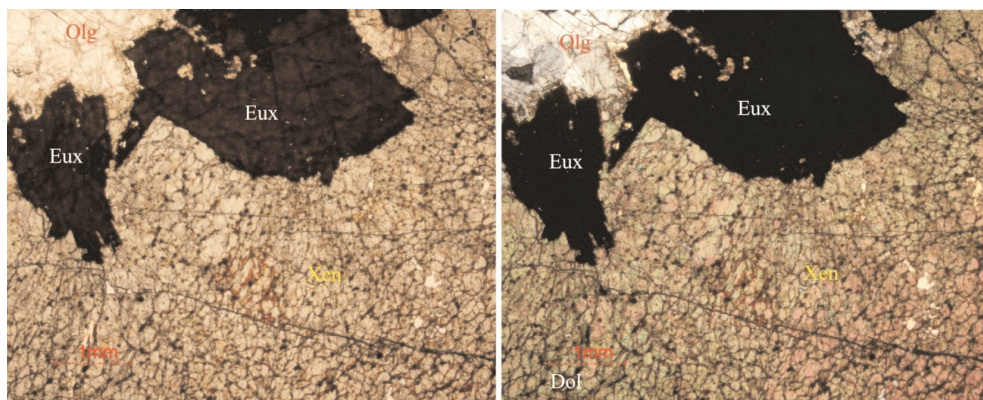


Fig. 23. Detail of an intermediate zone of a pegmatite representative of the euxenite subtype in thin section. To the left, in PPL; to the right, in crossed nicols. Eux, radial aggregates of idiomorphic crystals of euxenite; Xen, xenotime, Olg, oligoclase. The small dark dots inside the xenotime are of thorianite. Trout Creek Pass, Chaffee Co., Colorado, USA.

Similar pegmatites are found in some zones of the Evje-Iveland area, Norway (Smeds, 1990), Arvogno, Italia (Albertini and Andersen, 1989) and Trout Creek Pass (Hanson et al., 1992); these seem to be a transition with the allanite-monazite ones.

#### Rare earth pegmatites, gadolinite subtype

There are currently no developed exploitations on these occurrences, but they are of great historic importance, because in the Ytterby gadolinite many rare elements as Ta, Gd, Ho, Tm, Sc, Lu, Y, Yb, Tb and Er were discovered for the first time. In fact, the names of the last four elements mentioned derive from Ytterby. The most known examples of the gadolinite subtype are the Pyörönmaa pegmatites in Finland (Vorma et al., 1966) and the other locations near Stockholm,

Sweden (Smeds, 1990). Their structure is always simple with few replacements but the mineralogy is very varied. Even though the most part of the phases with rare earths are of small dimensions (less than 1cm), lots of minerals like gadolinite form nodules of more than a meter diameter. Their structure and mineralogy are formed by:

- a) Wall zone: formed by oligoclase, quartz, biotite and, in lesser proportion, microcline; as accessory minerals there is zircon, apatite and aluminosilicates (sillimanite, cordierite and almandine); sometimes allanite and magnetite are also present.
- b) Intermediate graphic zone: formed majorly by microcline, with quartz, oligoclase and biotite. Many times the microcline can be rich in Pb, of the amazonite variety.

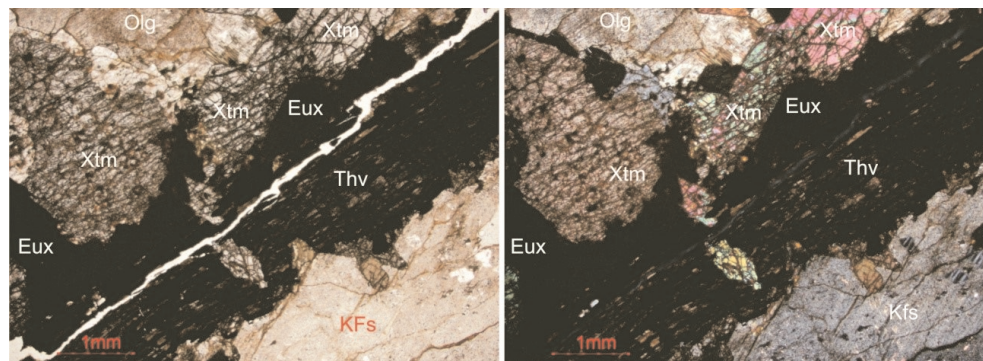


Fig. 24. Mineral association in a representative pegmatite belonging to the gadolinite subtype. Prismatic thortveitite (Thv) crystals are overgrown and replaced by xenotime (Xtm), euxenite (Eux). Olg, oligoclase; Kfs, perthitic potassic feldspar. Plane polarized light. Left, without analyser; right, with crossed nicols. Evje, Iveland, Norway.

c) Intermediate blocky zone: similar to the previous one but with a bigger grain size (metric), more albite and biotite proportion and less quartz. It can contain beryl, aluminosilicates, amphiboles (anthophyllite and hastingsitic hornblende) and scapolite, probably produced by contamination from metabasitic host rocks. It contains primary minerals with REE and U, which form big crystals implanted over biotite: Y-rich fluorite, allanite, zircon, gadolinite, britholite, thalenite, thorite, fergusonite, samarskite, aeschynite-(Y), davidite, uraninite, apatite and xenotime.

Thortveitite and tobarthite are also found in other pegmatites (Nilssen, 1971; Ewing y Ehlmann, 1973). Thortveitite can be so abundant that can become a Sc ore, like in Evje (Iveland, Norway; Fig. 24). The appearance of this mineral, preferably in pegmatites hosted in amphibolites, suggests that the Sc comes by contamination from the metabasitic host-rock (Neumann, 1961).

Both yttrian spessartine and muscovite have been named as a replacement product of the allanite, too. Locally, sulphurs can appear.

d) Core: exclusively constituted by quartz.

e) Fissure fillings: fluorite dikes with rare earth minerals (gadolinite, allanite and fergusonite) can exist and uraninite, with quartz and scarce feldspars (Nilssen, 1973). The fluorite can be rich in Y.

Similar pegmatites are found in Evje-Iveland, Norway (Smeds, 1990) and possibly in Western Keivy (Kola, Russia; Belolipetskii and Voloshin, 1996).

Synchysite can be formed by replacement of gadolinite during the late stage hydrothermal and supergene processes.

## 8. Deposits Associated to LCT Pegmatites

The LCT (Lithium- Caesium- Tantalum acronym) type pegmatites are much poorer in REE than the NYF type, and only occur in the latest replacement units of the most evolved pegmatites.

Therefore, in the most evolved beryl-columbite-phosphate or albite pegmatites of Cap de Creus, HREE minerals crystallize only in the latest stage units. Generally these units are quartz-muscovite replacement units. Tanteuxinite-(Y), fergusonite-(Y) and microlite (rich in Ta and with dominant HREE) replace the pre-existent columbite minerals (Alfonso et al., 1995). Nevertheless, these minerals are strictly confined inside those crystals that they are replacing. They are very fine grained in size and scarce. Similar enrichments occur in the latest stages of the pegmatites belonging to the Comechingones massif, in Argentina. In these late stage units highly evolved minerals, very rich in Cs, Rb, Ta Hf, occur. Nevertheless, the scarce microlite which is formed is poor in REE (less than a 5% in weight) and moreover, the REE belong predominantly to the LREE group (Demartis et al., 2014).

Allanite-(Nd) occurs as an accessory mineral in miarolitic pegmatites associated with type I granites of epizonal emplacement, as in La Cabrera in Madrid (González del Tánago, 1997). In a similar context, allanite-(Ce) also occurs in the pegmatites associated to epizonal calc-alkaline granites of the Catalonian Coastal Ranges (Melgarejo, 1992). However, all of these mineralizations are very poor.

Consequently, LCT type pegmatites cannot be expected to be prospectable for REE. However, even though minerals with attractive REE occur, sometimes as large size ones (for example, the famous microlites of the Ipê pegmatites in Brasil), these crystals are extremely rarely found in these pegmatites and have never been concentrated for their benefit.

## 9. Bodies of Nelsonitic Affinity

This typology is quite unclear, and of very recent creation. The monazite deposit of Steenkampskraal in South Africa can be the best example. In the years 1950 and 1960 50,000 tons of monazite were exploited in this mine. This was mainly due because of its Th contents (Neary y Highley, 1984), but has been currently revalued for the REE. It consists of almost massive monazite bodies (up to 75% modal), with minor proportions of apa-

tite, magnetite, chalcopyrite and quartz, located in a shear zone that cuts Proterozoic granitoids. *Andreoli et al. (1994)* proposed a magmatic fractioning model for those bodies that would derive from anorthositic magmas located in granulite facies.

The great nelsonitic deposits associated with the Kunene anorthosites (Angola) contain small quantities of monazite and xenotime, as trace minerals (*Villanova et al., 2011*). The REE contents in the apatite in the typical nelsonites, like those mentioned of Kunene, are generally very low. Therefore, it does not seem that significant resources can be expected from these deposits, neither as a subproduct of the Ti, V, Fe and apatite benefit.

## 10. Skarns

Skarn classifications based on the dominant element or, a priori, on the most interesting one, have been tried to be established (for example, *Meinert et al., 2005*), though this valuation is conjunctural. However, skarns do not seem to be a typology of deposit especially productive for REE, though some examples have been described as having a potential. The keyfactor for REE concentration in skarns appears to be the association with alkaline granites (*Lentz, 1998*). Thus, in the skarn developed in the contact between limestones and the alkaline granitic complex of Ambohimirahavavy (Madagascar), *Estrade et al. (2015)* found strong enrichments in REE minerals and rare metals. These include bastnäsite-(Ce), pyrochlore, niobiantitanite, zircon, elpidite and other zirconium silicates. The mineralization tends to concentrate in the endoskarn or in small dikes or veinlets localized in the host-rock.

On the other hand, it seems clear that the most significant enrichments are derived from Fluor-rich fluids (*Rubin et al., 1993*). In the Saima deposit in China, pyrochlore group minerals occur (*Wu et al., 1996*), which also agrees with a high F activity in mineralizing solutions. However, the Mina Monchi skarn in Burguillos del Cerro (Badajoz) contains allanite (*Álvarez and Domínguez Bella, 1995*) but borates such as ludwigite are the dominant volatile-rich minerals, instead of minerals enriched in F. Therefore, the ligand which

would have transported the REE could be boron in this case.

Some skarns can contain large REE reserves. The Mary Kathleen deposit in Australia contains up to 6 Mt of ore with 0.1% U<sub>3</sub>O<sub>8</sub> and 2.6% REE (*Kwak and Abeyasinghe, 1987*); LREE predominate, with La (33.5%), Ce (51.5%), Pr (4.0%), Nd (9.1%), Sm (1.1%); in addition to Th (0.64%). The mineral sequence of this deposit begins in a prograde stage with andradite + quartz + diopside-hedenbergite + scapolite, followed by a retrograde stage with development of ferrogastingsite + sulphides or allanite + stillwellite + uraninite + apatite; ends with the precipitation of late stage sulphides + chlorite + prehnite + calcite.

Unfortunately, lots of times the REE concentrate in skarns in some silicates related to early stages, which can be dominant in the skarn but are refractory for extraction metallurgy, like the garnets of the grossular-andradite series (up to 7,8% REE, *Smith et al., 2004; Kumral et al., 2007*), vesuvianite (up to 16,7% REE; *Fitzgerald et al., 1987*), epidote and allanite (*Smith et al., 2002*). Thus, the formation of retrograde REE carbonates by destabilization of the early stage silicates can be critical to enhance the economic value of the deposit.

On the other hand, very high concentrations of Sc have been described in muscovite (up to 0,6% Sc<sub>2</sub>O<sub>3</sub>), helvite (up to 0,1% Sc<sub>2</sub>O<sub>3</sub>) or magnetite associated with skarns, and their exploitation as Sc ore has been considered (*Vlasov, 1966*).

The cerium was originally discovered in the cerite at the Bastnäs mine, in Sweden, which initially was an iron mine where magnetite was the ore in a skarn-type deposit. This skarn was rich in LREE and was developed on carbonated rocks. In Bastnäs, the REE minerals fill decimetre-thick veins, which replaced amphibole skarns developed on dolomites. These veins were essentially constituted by cerite-(Ce) and bastnäsite-(Ce); cerite is being replaced by ferriallanite or västmanlandite + törnebohmitite + bastnäsite (*Fig. 25*).

There is a multitude of identical skarns in the region of Bastnäs, however, those in the close

area of Norberg are richer in HREE minerals and Y (Holtstam and Andersson, 2007). In this locality, the veins are early filled by Si-poor, REE-rich fluorbritholite. This mineral is replaced by västmanlandite, dissakisite–dollaseite, gadolinite, parisite, haleniusite-(Y) and fluorite (Holtstam et al., 2004).

In both cases, Bastnäs and Norberg, a high Fluor activity is reflected, in addition to the existence of fluorite, by the presence of humite group minerals in the host rocks. Holtstam and Andersson (2007) attribute the difference in the paragenesis and the separation of the REE in LREE and HREE in a district scale to differences in the F activity in the hydrothermal solutions.

### 11. Deposits in Metapelites

This category has been defined for a long time as “REE deposits in metamorphic

rocks”. However, the use of this large category can generate confusion. Evidently, the metamorphosed carbonatites, the orthogneisses derived from alkaline rocks or pegmatites or skarns have exploration guidelines very different of those that can be used in other metamorphic rocks. Probably, it is more correct to define the category as REE deposits in metapelites, which would possibly correspond to seabed metamorphosed deposits. Important deposits have not been found yet. Thus, it can be difficult to localize them, as it consists of more or less dense disseminations scattered in metamorphic rocks. The showings comprise a very simple mineralogy: xenotime, monazite or churchite with a very wide range of grain sizes; sometimes very fine-grained whilst in some occasions they can develop centimetric sized crystals, even if they do not stand out in the rock bulk. Nonetheless, they use to present Th contents

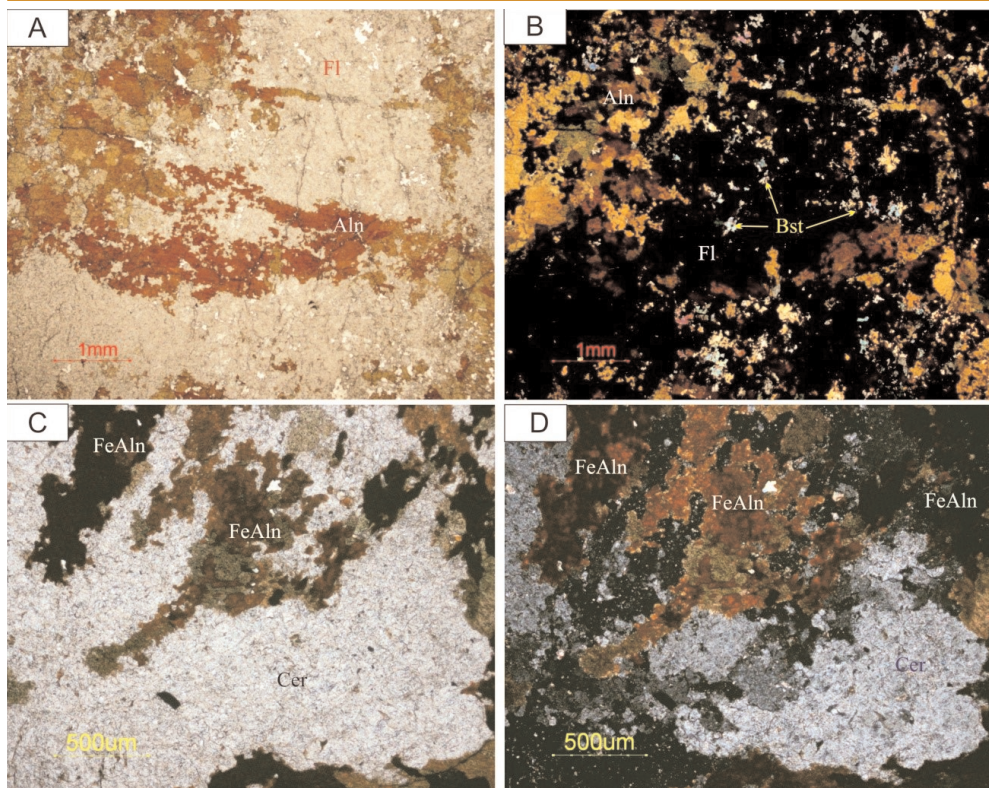


Fig. 25. Details of the mineralization in the REE skarn of Bastnäs (Sweden) in thin section with transmitted light. **A)** Plane polarized light, without analyser. Allanite crystals (Aln) cut fluorite (Fl). **B)** The previous image in crossed nicols. Note the bastnäsite-(Ce) (Bst) veinlets cutting the assemblage. **C)** Cerite-(Ce) (Cer) cut by ferriallanite-(Ce) (FeAln). Plane polarized light, without analyser. **D)** The previous image, in crossed nicols.

in their structure and, consequently, these mineralizations have been casually localized while prospecting for uranium deposits.

In such a way, the Music Valley anomalies in Riverside Co. (California) were discovered, for example (Evans, 1964). They consist of monazite and xenotime disseminations in gneisses, lacking tectonic control or an external hydrothermal or igneous source of the mineralization. Hence, it is supposed that REE were in the rock before the metamorphism. The bodies are not large and appear to present stratabound features. The deposit was prospected to evaluate the uranium resources, allowing to discover a resource of 0,05 Mt of ore with 8,6% REEO (Jackson and Christiansen, 1993). Similar associations, also in gneisses and migmatites, are found in Rock Corral, San Bernardino Co., California (Moxham et al., 1958), and in Colorado, in Central City, Gilpin Co. Xenotime can become the dominant mineral in some outcrops (Young y Sims, 1961).

The deposits of the so-called “grey monazites” or “dark monazites” can be included in this category. They are found in both primary deposits in metamorphic rocks and in the placers derived from their erosion, practically all around the world (Rosenblum y Mosier, 1983). The main mineral is monazite rich in Eu, which occurs as irregular grains, idiomorphic crystals or, most especially, in oolites,

peloids or nodules, which can reach centimetric sizes (Fig. 26). Since its discovery in diverse places in Western Europe (Donnot et al., 1973; Vaquero, 1979) systematic exploration studies have been undergone in many countries. Since the first moments, the possibility in which the monazite would have been formed due to the dehydration of diagenetic rhabdophane during the metamorphism was envisaged (Nagy et al., 2002). However, the composition of the REE minerals tends to be invariable during the metamorphism (Cullers et al., 1974), and the chemical composition of the rhabdophane in literature does not correspond to the one of these monazites. Thus, a specific crystallization mechanism of these monazites was necessary. It is noteworthy that, at least in the case of the monazite concentrations which we have localized in the late Ordovician series in the Central Pyrenees, these nodules are found in sedimentary units where the series is rich in sedex-type manifestations. In this way, the REE might have possibly accumulated in relation to exhalative processes; such as it is currently postulated for the REE mineralizations in the current ocean floor. The original REE phase is unknown, however, as it can be appreciated in the images (Fig. 26), these nodules are found deformed by the main schistosity stages. Consequently these could be diagenetic. These monazites are strongly radioactive, due to the presence of high Th contents in their structures.

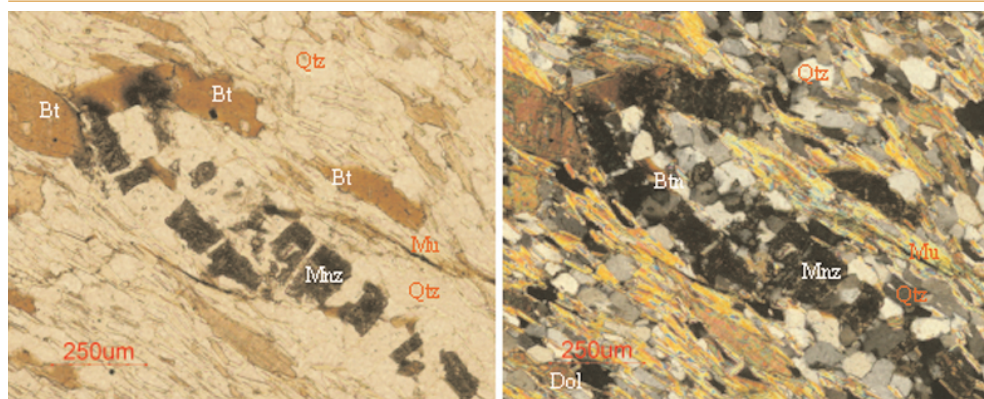


Fig. 26. Details in thin sections of monazite (Nd) nodules or “grey monazites” in intermediate-grade schists (cordierite-staurolite-almandine-andalusite zone) of the late Ordovician near the Victoria mine, in Bossòst (Vall d’Aran, Catalonia). Left, without analyser; note the metamictic aureoles developed in the biotite in contact with the monazite, due to the high Th contents in this mineral. Monazite is found affected by microboudinage processes, with development of pressure quartz-shadows. Right, crossed nicols. Take into account that the schistosity envelops the monazite. Mnz, monazite; Mu, muscovite; Bt, biotite, Qtz, quartz.

There are other deposits, though not economical, in which the occurrence of REE minerals can help understand the genesis of these deposits. A very interesting case is the emerald deposits of Colombia. These deposits are found in a series of Cenozoic black shales, slightly metamorphosed and without important igneous intrusions nearby (Giuliani *et al.*, 1992). The emeralds form pockets or veins in the shales in association with quartz, calcite, pyrite and parisite-(Ce). Parisite-(Ce) forms idiomorphic crystals, with hexagonal and pinacoid prism, of prismatic habit, with up to 3 cm of edge. It shall be noted that the hydrothermal alterations associated to this deposit produce strong albitions of the host-rock, sometimes confused with pegmatites (Beus, 1979). Consequently, it shall be highlighted the activity of hypersaline fluids, disassociated with magmatic activity, during the genesis of these emerald deposit and their REE minerals. These are basin or metamorphic fluids, which agrees with the homogenization temperature of 300°C of the fluid inclusions (Giuliani *et al.*, 1992). Moreover, the altered shales are depleted in REE, Be, Cr and V (Giuliani *et al.*, 1990). Concentrations of HFSE coming from the black shales can also be produced in these deposits.

### 12. Unconformity-related U Deposits

The uranium deposits associated to unconformities are a main source of this element. In general, the model requires a tectonized basement with pre-concentrations (like alkaline granites, pegmatites, etc.), over which an erosive unconformity surface occur, which is overlain by detrital series. The mineralization is localized in the basement or, partly, in the immediately overlying coverage, on top of fractures, in association, eventually, with low temperature hydrothermal alterations (see for example Marmont, 1990; Ruzicka, 1995; Kyser and Cuney, 2009). The main mineral is uraninite (locally altered to supergene minerals), with sulphides and Co-Ni-Cu arsenides. The REE are found in high concentrations in minerals of the crandallite, xenotime and apatite group, but also in the uraninite structure, in which the  $\Sigma$ REE can reach over 12000 ppm, being also enriched in HREE

(Fayek and Kyser, 1997). These high concentrations have determined that historically a recuperation of both Y and HREE from the uranium ores processing took place in Elliot Lake (Sinclair *et al.*, 1992).

### 13. IOCG

The IOCG deposits (acronym of Iron Oxide Copper Gold Deposits) are a very wide category including deposits of very diverse typologies and formed by very diverse processes too, mainly during the Proterozoic (Hauck, 1990) and typically in extensional tectonic contexts (Hitzman *et al.*, 1992). In the last few years they have evolved from being one of the worst understood deposits to probably be between one of the best studied. The name may be incorrect too, due to the fact that in some deposits some of these elements may lack, or they can even be mineralized in other elements, such as F, U and REE. Normally it consists of massive bodies of iron oxides (mainly magnetite or hematite) with a strong epigenetic feature, which can be stratabound (Slack, 2012) or appear in breccias (Oreskes and Einaudi, 2006). Normally, they are associated with a wide range of hydrothermal alterations, which mainly comprise diverse types of potassic, sodic-calcic, scapolization, albitization and sericitization alterations (Perring *et al.*, 2000). These processes are interpreted by means of the participation of diverse fluid types, strongly saline at high temperatures, being their origin basinal brine fluids (Gow *et al.*, 1994; Hunt *et al.*, 2007) or as degassing of intrusive rocks (Slack, 2012), or as diverse combinations of both (Barton, 2014). In any case, the contribution of magmatic fluids strongly enriched in F coming from the intrusive bodies, seems to have been determinant regarding the REE enrichment (McPhie *et al.*, 2011). Synthesis about the IOCG type deposits can be found for example in Hitzman (2000), Williams *et al.* (2005), Groves *et al.* (2010) and Richards and Mumin (2013).

In some cases, the relationship between the acid intrusions is very clear, as in the magmatic breccia bodies cemented by Fe oxides and apatite (subtype IOA), with economic quantities of Au, Co and REE of Pea Ridge, Missouri (Whitten and Yancey, 1990; Nuelle *et al.*, 1992). The REE minerals are mainly monazite, xenotime and britholite (Sidder *et al.*, 1993). The reserves of this

deposit, in addition to the 200 Mt of Fe ore, include 600.000 t of ore with 12% of REE, in large part of HREE (Gauch *et al.*, 2010).

as stratabound replacements of the adjacent hostrocks. So, the quartzites and the carbonates, as well as the conglomerates, are partially

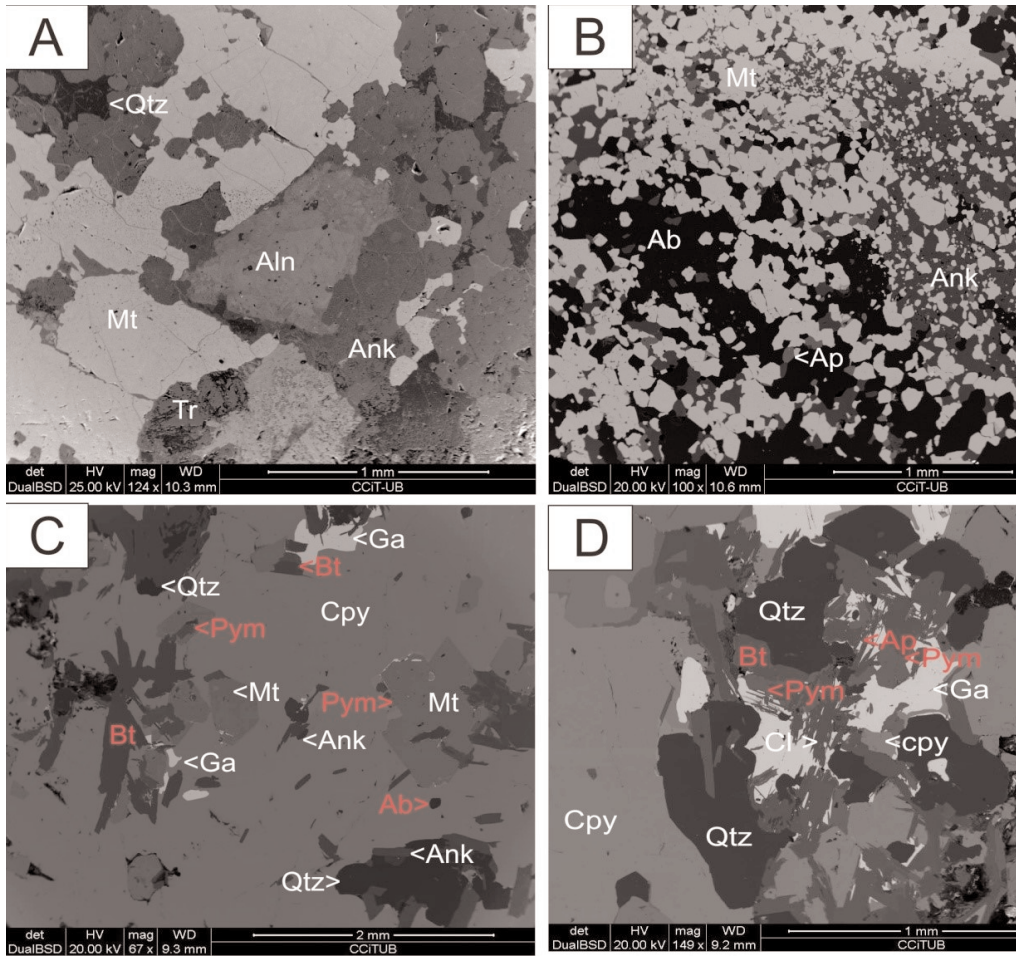
Mineral	Formula	ESTADIO			
		Sedimentación	IOCG-1	IOCG-2	Metamorfismo
Calcita	CaCO <sub>3</sub>	█			
Cuarzo	SiO <sub>2</sub>		█	█	
Apatito	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F		█		
Zircón	ZrSiO <sub>4</sub>		█		
Ilmenita	FeTiO <sub>3</sub>		█		
Magnetita	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> O <sub>4</sub>		█		
Albita	NaAlSi <sub>3</sub> O <sub>8</sub>		█		
Ankerita	CaFe(CO <sub>3</sub> ) <sub>2</sub>		█		
Allanita	(Ca,Ce)(Al <sub>2</sub> Fe)(Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> )O(OH)		█		
Tremolita-(Cl)	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH,Cl) <sub>2</sub>		█		█
Biotita-(Cl)	KAl <sub>2</sub> (Si <sub>2</sub> AlO <sub>10</sub> )(OH,Cl) <sub>2</sub>		█		█
Calcopirita	CuFeS <sub>2</sub>			█	
Pirita	FeS <sub>2</sub>			█	
Esfalerita	ZnS			█	
Galena	PbS			█	
Pirossmalita	(Fe,Mn) <sub>8</sub> Si <sub>6</sub> O <sub>15</sub> (OH,Cl) <sub>10</sub>				█
Epidota	(Ca) <sub>2</sub> (Al <sub>2</sub> Fe)(Si <sub>2</sub> O <sub>7</sub> )(SiO <sub>4</sub> )O(OH)				█
Clorita	(Fe,Mg) <sub>5</sub> Al(Si <sub>3</sub> AlO <sub>10</sub> )(OH) <sub>8</sub>				█
Greenockita	CdS				█

Tiempo

Fig. 27. Crystallization sequence in the Tsodilo IOCG. Note the presence of a chloride and alkaline metasomatic stage related to the IOCG development during the replacement of the carbonates from silica-rich protoliths (Cardona *et al.*, 2013).

Cardona *et al.* (2013) describe in the Tsodilo zone (Botswana) an ensemble of mineralizations, which recognition was based on a wide drilling network, that can fit in this scheme, even though BIF type mineralizations have been recognized in the same zone. The surveys, based on a previous geophysical campaign, reveal a sedimentary basin formed in a rift of Proterozoic age controlled by normal faults and with both strong lateral changes of facies and potential. In some areas, carbonate platform facies dominate, whereas other domains are made up of sequences of black shales and quartzites with minor metabasites and conglomerates. Sedimentary domains are limited by NNE-SSW trending thrusts. This type of geometrical relationships between tectonics and stratigraphy can be explained by PanAfrican tectonic inversion affecting an earlier Proterozoic cryptogenic basin. Moreover, these faults served as a mobilization channel for hydrothermal fluids. Therefore, mineralization formed as veins along the faults and

or completely replaced in the vicinity of the faults by a complex mineralization, forming stratabound bodies more or less massive. These are mainly constituted by magnetite, with chalcopyrite, pyrite and small quantities of uraninite, thorianite, allanite, monazite, xenotime and other REE minerals. These minerals are associated to the replacement of the pre-existing rocks for albite and ankerite, locally accompanied by Cl-rich tremolite and Cl-rich biotite (Fig. 27, Fig. 28a, and b). This assemblage is found deformed and foliated, and later affected by a contact metamorphism caused by the intrusion of calc-alkaline granitoids, which produced the recrystallization of these mineralizations with the development of metamorphic re-equilibrium textures with curved grain borders and triple points (Fig. 28 a, b). In a retrograde phase part of the previous minerals are replaced and veinlets are formed. In these veins epidote, chlorite and pyrossmalite (another mineral rich in Cl) and sulphides can be found (Fig. 28c, d).



**Fig. 28.** Detail of the mineral sequence found in the stratabound magnetite bodies of the Tsodilo IOCG, Botswana, SEM-BSE images. **A)** Disseminated allanite-(Ce) (Aln) in the magnetite bodies (Mt), with quartz (Qtz), ankerite (Ank) and Cl-rich tremolite (Tr). Note the presence of curved grain borders. **B)** Association with granoblastic texture of magnetite (Mt) with albite (Ab), ankerite (Ank) and apatite (Ap). **C)** Association with quartz (Qtz), magnetite (Mt), ankerite (Ank), albite (Ab) with Cl-rich biotite (Bt), galena (Ga), chalcopyrite (Cpy) and pyrosmalite (Pym). **D)** A detail of a similar association, including small quantities of late stage clinochlore (Cl) and apatite (Ap).

On the other hand, in the basins centres, occupied by black schist series, the faults contain polymetallic vein mineralization (bearing pyrrhotite, pyrite, chalcopyrite, galena, sphalerite, molybdenite, gold, diverse Bi-Te-Se minerals, uraninite and notable quantities of allanite, monazite, xenotime and other REE minerals). The host rocks are found likewise altered or impregnated by this mineralization. The host rocks are also altered by an intense albitization and scapolitization (with marialite, a member of the scapolite group rich in Cl and Na), eventually accompanied by Cl-rich tremolite, Cl-rich biotite and calcite which give evidence to intense hydrothermal alterations originated by hypersaline fluids (Fig. 29, Fig. 30). These mineralizations are found affected by a regional metamorphism of amphibolite facies and by the intrusion of post-tectonic granites. The biotite formed in this stage inherits the Cl derived from the pre-existing mineral associations. Despite they occur in all mineralizations with abundant REE proportions, these are mainly found in a refractory mineral (allanite), which would hinder its processing.



MINERAL	FORMULA	St1	St2	St3	St4	St5	St6
Albita	NaAlSi <sub>3</sub> O <sub>8</sub>	█					
Biotita-Cl	K(Mg,Fe) <sub>3</sub> (Si <sub>3</sub> AlO <sub>10</sub> )(OH,Cl) <sub>2</sub>	█					
Tremolita-Cl	Ca <sub>2</sub> Mg <sub>5</sub> (Si <sub>8</sub> O <sub>22</sub> )(OH,Cl) <sub>2</sub>	█					
Marialita	Na <sub>4</sub> Al <sub>3</sub> Si <sub>9</sub> O <sub>24</sub> Cl	█					
Cuarzo I	SiO <sub>2</sub>	█					
Calcita I	CaCO <sub>3</sub>	█					
Fluorapatito	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	-					
Monacita	(Ce,LREE)PO <sub>4</sub>	-					
Xenotima	(Y,HREE)PO <sub>4</sub>	-					
Cuarzo II	SiO <sub>2</sub>		█				
Pirrotita	Fe <sub>1-x</sub> S		█				
Clorita I	(Mg,Fe) <sub>5</sub> Al(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub>			█			
Molibdenita	MoS <sub>2</sub>			█			
Calcopirita	FeCuS <sub>2</sub>			█			
Hessita	AgTe <sub>2</sub>				█		
Altaita	PbTe				█		
Melonita	NiTe <sub>2</sub>				█		
Oro	Au				█		
Telurosos Bi	Bi <sub>x</sub> Te <sub>7</sub> S <sub>2</sub>				█		
Pirita	FeS <sub>2</sub>					█	
Esfalerita	ZnS					█	
Millerita	NiS					█	
Galena	PbS					█	
Uraninita	UO <sub>2</sub>					█	
Cuarzo III	SiO <sub>2</sub>						█
Clorita II	(Mg,Fe) <sub>5</sub> Al(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub>						█
Calcita II	CaCO <sub>3</sub>						█
Ankerita	Ca(Mg,Fe)(CO <sub>3</sub> ) <sub>2</sub>						-
Bastnäsita-(Ce)	(Ce,La)(CO <sub>3</sub> ) <sub>2</sub> F						-
Calcioancylita-(Ce)	(Ca,Sr)Ce(CO <sub>3</sub> ) <sub>2</sub> (OH).H <sub>2</sub> O						-
Ancylita-(Ce)	SrCe(CO <sub>3</sub> ) <sub>2</sub> (OH).H <sub>2</sub> O						-
Britholita-(Ce)	(Ce,Ca) <sub>5</sub> (SiO <sub>4</sub> ) <sub>3</sub> F						-
Yttrialita-(Y)	(Y,Th) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>						█
Barita	BaSO <sub>4</sub>						█

Fig. 29. Crystallization sequence in veins in thrusts associated with the Tsodilo IOCG. Note the presence of a stage with chlorine and alkaline metasomatism vinculated to the IOCG development during the replacement of the carbonate or silicic protoliths (Cardona et al., 2013).

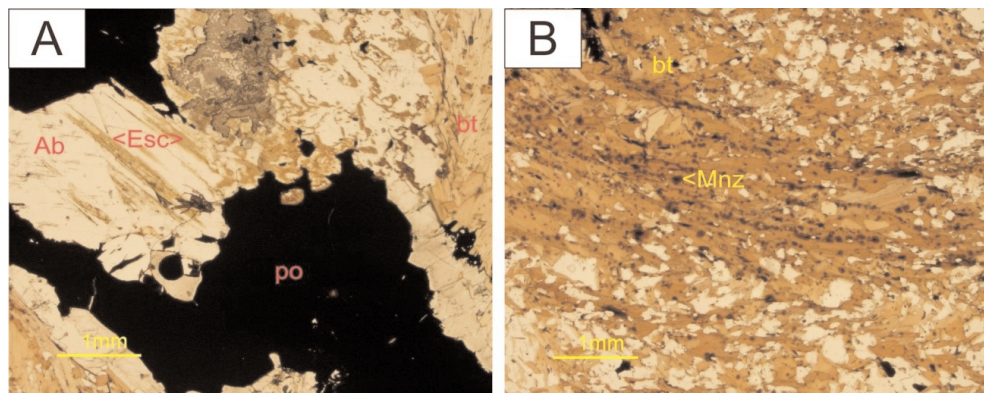


Fig. 30. Details of the mineral sequence in the veins following the thrusts associated with the Tsodilo IOCG, and the replacements of the hosting schists, under thin section microscopy, PPL. A) Pyrrhotite (Po) with albite (Ab) and marialite (Esc), at the contact of the vein with the schist, made up by Cl-rich biotite (Bt). B) Detail of the schist in the vicinity of the mineralized faults, with monazite-(Ce) grains (Mnz) scattered in Cl-rich biotite. Black aureolas in biotite are produced because monazite is Th-rich.

The Olympic Dam deposit in Australia is the most important regarding this category. It consists of a gigantic deposit strongly enriched in U and REE. The ore reserves are estimated in more than 2000 Mt with 0.24-0.45% La+Ce (Jackson and Christiansen, 1993). In this case, the mineralization occurs in breccia dikes embedded in granitic rocks (Oreskes and Einaudi, 2006). The breccias present interstitial hematite, accompanied by sulphides, mainly chalcopyrite; in addition, disseminations of REE minerals like bastnäsite, crandallite, xenotime, monazite and britholite are observed (Lottermoser, 1995).

Even though not all the IOCG type deposits are rich in REE, there are other examples around the world, like Kwijibo, in Quebec, Canada (Gauthier et al., 2004), Igarapé Bay, in Brazil (Tallarico et al., 2005), Mantoverde, in Chile (Rieger et al., 2010), Oued Belif, in Tunisia (Decrée et al., 2013), or Yinachang, in China (Li et al., 2015).

#### 14. Shear Zones

It has been verified that REE elements are mobilized in great crustal shear zones (for example, Condie and Sinha, 1996), with the chance of leaving these zones enriched in HREE or LREE, depending on the nature of the affected protoliths and on the types of fluids circulating through these zones. This can lead to enrichments of 5 to 1 regarding the original rock (Rolland et al., 2003).

Examples of such reconcentrations are found throughout the world. The talc deposits of the Pyrenees are among the most important, in a worldwide scale, and have been formed due to circulation of hydrothermal fluids between dolostones cut by regional shear zones. The mineral paragenesis, though in small proportions, contain simultaneously both LREE and HREE minerals; such as idiomorphic crystals of millimetric to centimetric size of allanite-(Ce), bastnäsite-(Ce), dissakisite-(Ce), parisite-(Ce), törnebohmitite-(Ce), gadolinite-(Y) and hingganite-(Y), between others (from Parseval et al., 1997). These are very late forming stage minerals and refill geodic porosity (Fig. 31).

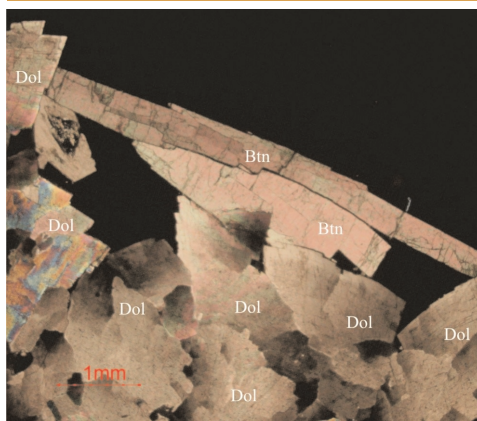


Fig. 31. Thin section detail of a mineralized shear zone (crossed nicols). Bastnäsite-(La) crystals, with a tabular habit (Btn), formed over euhedral geodic crystals of saddle dolomite (Dol); notice the curved faces and cleavages and the undulose extinction). Talc mines of Trimouns, Luzenac, France.

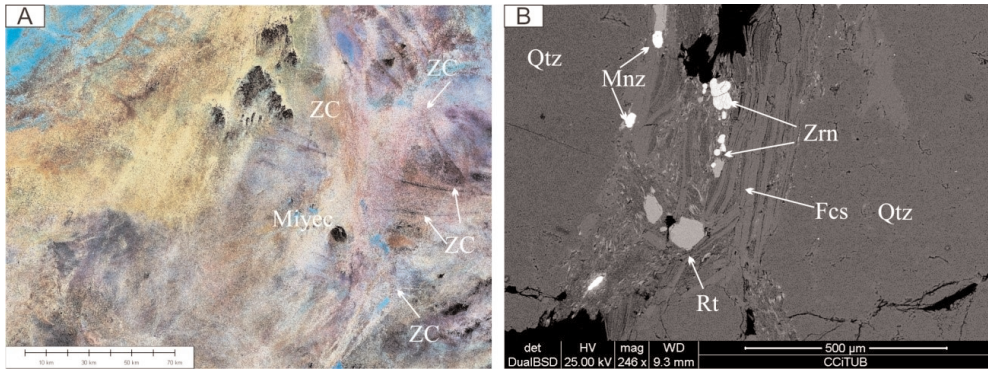


Fig. 32a. Regional shear zones (ZC), easily identified with satellite photos, in the Western Sahara (RASD), near Miyec. All of them are mineralized.  
 Fig. 32b. Details of the mineralization occurring in the shear zone. Qtz, quartz, Mnz, monazite-(Ce); Zrn, zircon, Fcs, fuchsite. SEM image, BSE mode.

The type of rocks affected by the fluid circulation control if a large REE deposit can be produced. In this way, some re-concentrations of REE elements similar to those described in Trimouns are found in regional shear zones, of hundreds of kilometres of longitude, which cut the materials of the Precambrian Reguibat shield in the Western Sahara (RASD, Fig. 32a). In this zone two types of mineralizations are found. The first type, similarly to the orogenic gold deposits, is found in the shear zones; zones of hydrothermal alteration with a broadness that can reach various hundreds of meters, even kilometres. It is constituted by a variable paragenesis, which depends on the type of altered rock, generally quartz with calcite and other carbonates, gold, chromite, zircon, chromium rich muscovite (fuchsite variety, easily recognized

in the field by its green emerald colour), epidote, niobian rutile, monazite and xenotime and divers sulphides (Fig. 32b). Tourmaline can also be present.

The second type of mineralization is produced when these shears cut the ultrabasic bodies, giving rise to a hydrothermal replacement of them, generating mineralizations denominated listwänites (Fig. 33a). These listwänites are ultrabasic rocks altered hydrothermally whose texture can sometimes be preserved (Fig. 33b), but the rock is mainly replaced by quartz (sometimes of chalcedony type) and fine grained calcite or dolomite. The rock exhibits a typical tobacco colour in the outcrop. These listwänites are slightly mineralized in LREE, U, HFSE and HREE, also EGP and gold (Lehbi 2015).

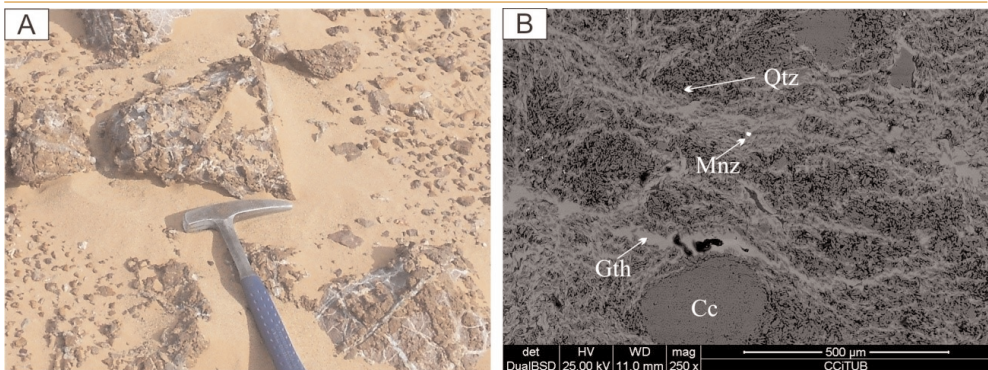


Fig. 33a. Aspect in the outcrop of the Zug listwänites, Western Sahara (RASD), partially covered by desert sand. The brownish areas correspond to peridotites replaced by calcite; the white veins are of quartz.  
 Fig. 33b. Detailed aspect of the previous rock, with olivine grains totally replaced by calcite (Cc) and the old serpentine matrix by mixtures of fine grained calcite, goethite (Gth) and quartz (Qtz); a monazite-(Ce) (Mnz) crystal outstands in the matrix. SEM image, BSE mode.

With all the reserves of the case, it is possible that the mineralizations of the Lemhi Pass in Idaho belong to this category. These consist of quartz and microcline veins, with thorite and eventually monazite and xenotime (with minor quantities of brockite; Mortimer et al., 1972). These authors highlight that the mineralization is enriched in MREE (reaching up to a 35% of Nd<sub>2</sub>O<sub>3</sub>, one of the highest values found in the world). Reserves are calculated as 39 Mt with 0.51% REO (Jackson and Christiansen, 1993). These mineralizations make up part of a belt which extends itself following the shear zones over more than 20 km, and which comprises other identical deposits like the Diamond Hill and Mineral Hill, in which 0,23 Mt of ore with 1.23%  $\Sigma$ REEO were also calculated (Jackson and Christiansen, 1993).

On the other hand, the small hydrothermal deposits in the zones classically denominated as “alpine veins” can share a common origin. Despite these showings do not have economical interest, they are a valuable help when studying the mobility of the REE elements, because the crystals are large. In these cases, carbonates and phosphates usually appear (including monazite-(Nd) and gasparite-(Ce); Graeser and Schwander, 1987), but also allanite, often enriched in HREE. It is symptomatic that in these cavities fluorite is typically found, which assures that during genesis of these mineralizations F rich fluids intervened. In some cases the paragenesis can be very complex, with silicates rich in As, like the cervandonite-(Ce) (Armbruster et al., 1988) or with Y arsenates like the chernovite-(Y) associated with niobian rutile, magnetite, asbecasite or cafarsite (Graeser and Roggiani, 1976).

### 15. MVT Deposits and Similar F-rich Veins

Data on possible REE mineralization are extremely scarce in these deposits, but in some fluorite mines, like the Clara mine in Germany, abundant species of supergene minerals, especially rich in REE, have been described. In addition to arsenates as agardite or phosphates as rhabdophane-(Ce), some minerals must be highlighted, including secondary REE sulphates like the chukhrovite-(Ce) (Walenta,

1979). These minerals are produced by supergene alteration of ores like galena, chalcopyrite, nickeline, etc. However, the origin of the REE is mysterious, but they could come from fluorite dissolution. If this is true, it is worthwhile to evaluate the REE contents in fluorites from this type of deposits, even though it does not seem to be as high as in the fluorites occurring in the igneous or high temperature hydrothermal deposits.

### 16. Sedimentary Phosphorites

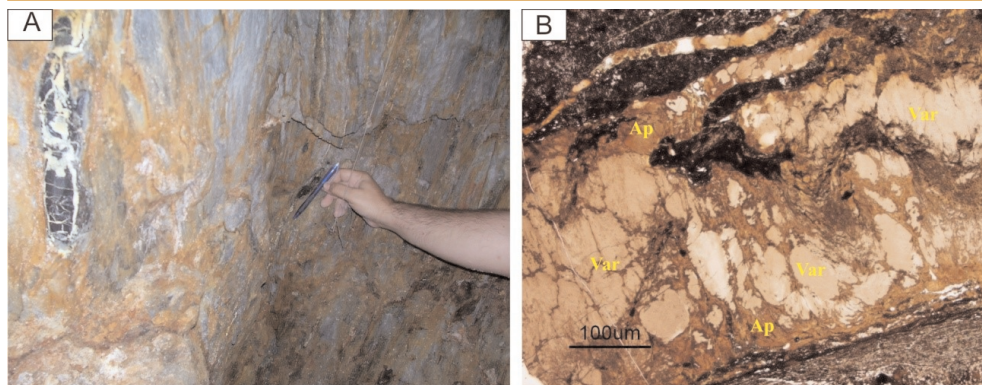
As in the case of the previous deposits, we will analyze the evolution of the REE contents from the primary deposits to those having experimented diagenetic re-concentration, metamorphic or supergene phenomena.

The phosphorites of sedimentary origin constitute a secondary reservoir of rare earth minerals. At the moment, there are no deposits of this category in exploitation, and they had not attracted much interest. Some authors (such as Altschuler et al., 1967; Altschuler, 1980) pointed out that the sedimentary phosphates are slightly enriched in  $\Sigma$ REE with respect to the classic patterns belonging to shales, even being the enrichment factor low, in the order 3-4. Notwithstanding, this enrichment is stronger in Y and in the HREE (but not in Sc). It should be considered that the phosphates treatment includes an acid lixiviation that can be used simultaneously to remobilize the REE. Following the same thematic thread, it should be taken into consideration that these types of rocks can present strong enrichments in actinides, which can be a penalizing. It would be desirable, and it is probable, that in the future a more efficient separation of the radioactive elements in phosphate will be performed. In this case, the REE minerals could be obtained as a by-product (Emsbo et al., 2015). These authors analyze the REE content in 23 phosphatic formations of the USA, which cover nearly all of the sedimentary register from the Proterozoic to the Miocene, and conclude that the REE proportions in colophane are highly variable during the geologic time. The variations can be from 0,1 to 100 in respect to the standard shales content, but can also be very different regarding

the different elements. In some episodes selective impoverishments in Ce are found, which can be the result of secular variations in the oxidizing conditions of the oceans. In general, a slight enrichment in MREE and HREE can be appreciated, but the deposits of late Carboniferous, Devonian and Silurian ages have enrichments in MREE of the order of 50-100, with high impoverishments in LREE and HREE.

The REE-bearing minerals in phosphorites are barely known, but it seems that they can

be exploited as a by-product of the phosphate production. The veins with secondary phosphates can be restricted to the phosphate formation or can penetrate other adjacent sedimentary formations. This process can also produce veins with scandium minerals, such as kolbeckite or aluminic phosphates enriched in this element, with  $\text{Sc}_2\text{O}_3$  proportions ranging from 0,01% to 1% in weight (crandallite, variscite, wavellite, millistite, wardite, goyazite, montgomeryite, gordonite, lehiite, etc.; *Frondelet et al., 1968*).



**Fig. 34.** Example of small-scale remobilization of sedimentary phosphates in the Silurian black shales of the Neolithic mines of Gavà (Catalonia). To the left, the aspect in the outcrop. The pyritic black shales near the surface have been altered; the pyrite has been oxidized and the oxidizing acid fluids resulting have reacted with the rock, leaching aluminium and oxidizing the organic matter, decolouring the rock. These fluids have reacted with the levels of apatite nodules (dark, on the left side image), replacing them by variscite veinlets of a pale-green-yellowish colour. To the right side; detail of one of these veins observed in transmitted light, PPL. Var, variscite, Ap, apatite.

occur in small proportions as a substitution to colophane. On the other hand, during the weathering of the phosphorite deposits, the REE can re-concentrate in secondary REE phosphates. These are very similar to those described in carbonatites (like rhabdophane, for example). REE can also be found in substitution of other elements in the aluminium phosphate structures, as in the variscite, crandallite and goyazite groups, among others (*Fig. 34*).

Supergene remobilizations that produce aluminium can give economic deposits. Thus, in the Zhijin deposit, in China, the REE have been re-concentrated in the secondary variscite (*Wu et al., 1996*). On the other hand, due to the fact that great deposits in which these supergene phosphates are exploited already exist (see *Melgarejo et al., 1997* and references therein), it seems logic to expect the existence of deposits in which REE can be

The guano deposits are another case. They consist of phosphate accumulations formed by reaction of relatively phosphate-rich excrements with a bedrock. The mineralogy formed depends on the type of excrement and the primary mineralogical composition of the bedrock. Thus, if the bedrock contains REE, these can be concentrated. In general, this does not happen when the bedrock is a limestone, resulting in the sequence of brushite – whittlockite – hydroxyapatite (*Flicoteaux and Lucas, 1984*). If the substratum is dolomitic, montgomeryite and crandallite are formed (*Trueman, 1965*). Hence, the lack of REE in the limestones also explains why REE concentrations are not produced in the guano phosphates found in Karstic environments. In fact, of the long list of minerals found in the Karstic cavities, none is of REE (*Hill and Forti, 1997*). Conversely, if the substratum is a REE-bea-

ring crystalline rock (as it is in the majority of cases), the sequence has Al-rich phosphates and is the following: leucophosphate \_ members of the variscite-strengite series (*Flicoteaux and Lucas, 1984*); thus, these minerals could contain REE. REE-rich crandallite can also be produced, like in the cavities found in the Ascension Island gabbros (*Harris, 1985*).

In general, the problem regarding the REE exploitation in most deposits of this type is that the process can be expensive and most especially, it may interfere in satisfying the rapid demand on superphosphates for the agrarian use. Notwithstanding, these deposits are enriched in radioactive elements, such as Po-210. This element, during the treatment of phosphates goes to superphosphates used as fertilizers in many mediums, particularly in the tobacco plantations. As the tobacco plant preferably absorbs the Po-210 in its leaves, the Po-210 has been revealed as the principal cause of pulmonary cancer (*e.g., Khater, 2004*). Thus, it would be desirable to find a viable process that could extract REE at the same time as radioactive elements.

### 17. Evaporites

The presence of REE minerals in evaporites is uncommon, but braitschite appears in nodules of millimetric to centimetric size in anhydrite levels included in an evaporitic sequence bearing sylvite in Cane Creek mine, in the Paradox Valley basin in Utah (*Raup et al., 1968*). These authors, in view of the REE spectrum, similar to the one belonging to the igneous rocks of the substratum, very different to the content of REE in seawater, propose that the accumulation derives from the leaching of rocks located at the border of the basin, and later diagenetic accumulation. It is not an anecdotic showing; taking into consideration that the mine is under exploitation, the possibility of benefiting the mineral as a sub-product has been valued (*Krahulec, 2012*). It should be taken into account that the presence of numerous borate species is abundantly documented in the major part of the European potash mines. They have been des-

cribed in Zechstein (*Garrett, 1998*) as in the Tertiary deposits located in the Ebro Depression (*Pardillo Vaquer, 1947*). It also should be taken into account that the boron complexes can be efficient transport agents of REE. Notwithstanding, the source of boron is not clear; Garrett (1998) proposes that it comes from hydrothermal contributions in relation to the fault activity, since the deposits bearing boron are scarce. However, it is possible that they could be much more common than they seem. The salt mines of Tuzla, in Bosnia, have important associations with borates, even though the presence of polymetallic mineralizations correspond in this case with an important hydrothermal contribution (*Sijaric et al., 2012*).

Continental evaporites can also contain minerals bearing REE, and their potential is still unknown. The Green River formation, in Wyoming, USA locally contains an Y and REE rich carbonate, the mckelveyite-(Y), associated with natron levels. Similar mineral associations have not been described in other continental evaporitic basins, and it is unknown if conditions for REE mineralization exist in the evaporitic deposits belonging to the enormous evaporitic deposits formed in the late Tertiary continental basins of the Iberian Peninsula (for example).

There is little information about the REE contents in the borate deposits in salars. Evidently, the hydrothermal fluids rich in B that nourish these salars could perfectly transport REE. *Chong et al. (2000)* offer data about the REE contents in some salars, though they are low (with total REE contents below 0,04%). It is unknown which is the mineralogical expression of these REE contents.

Obviously, the extraction of REE from evaporites is very simple taken into account that the hosting minerals are highly soluble and, on the other hand, are economically interesting too. Thus, these minerals could be easily concentrated in the insoluble residue and simply processed.

### 18. Residual Rocks

Bauxites are residual products of weathering,

lithified or not, rich in Al and poor in alkalis, Ca and Si (Gow and Lozej, 1993). Thus, they are constituted by Al and Fe hydroxides. The bauxite deposits are grouped into two big categories according to the nature of their bedrock (Bárdossy, 1982): a) bauxite deposits developed on carbonated rocks (karstic type or “terra rossa”), b) deposits developed on aluminium silicate rocks (laterites). These last ones, in turn, are subdivided in lateritic bauxites or bauxites Tikhvin type.

It is estimated that laterites can contain the most promising scandium resources, and they are also perspective for REE (Wang et al., 2011). In such a way, the Jamaican bauxites, developed on granitoids, are enriched in Sc and REE in respect to these ones and contain up to 100 ppm of Sc. Sc contents rises up to 150 ppm in the residue produced during the bauxite processing for the metallurgy of Al (Wagh and Pinnock 1987). In a similar way, the REEs are enriched too, especially in LREE: La reaches in residues more than 1000 ppm, although the Lu only achieves 10 ppm.

On the other hand, it is evident that the REE concentration grade largely depends of the existence of pre-concentrations in the protolith. In this way, the alteration of peridotitic or gabbroic rocks can favour scandium enrichment during the formation of laterites, being Sc extracted from the pyroxenes and amphiboles. The showing of the Lake Innes, in Australia, is of this type and count with 12.4 Mt with 0.004% Sc (Hedrick, 1998).

Lots of karstic bauxite deposits are relatively enriched in REE too (Mordberg, 1993) and in some bauxites in China, the REE contents reach industrial grades (Wang et al., 2010). In China, it is estimated that if the total REE content is higher than 500 ppm, the deposit is considered viable (Bao and Zaho, 2008; Klyucharev et al., 2013). However, the REE contents can be over values of 3500 ppm. For Wang et al. (2010) the main phases bearing REE are the clay group minerals (where the REE are found adsorbed in their surface), or the diasporite (where they can be adsorbed or substituting the aluminium in its structure). Moreover, REE minerals also

occur, especially minerals belonging to the bastnäsitegroup (Maksimovic and Pantó, 1985; Mariano, 1989b), though nearly always very fine grained sized. However, there can be other REE-bearing minerals likesynchysite, cerianite, parisite, churchite, xenotime, thorite, florencite and rhabdophane; and even some minerals like crandallite, goyazite, svanbergite-woodhouseite which can be enriched in these elements (Maksimovic and Pantó, 1996; Mongelli, 1997; Mordberg, 1999, 2000; Horbe and Costa, 1999; Laskou and Andreou, 2003; Mameli et al., 2007; Wang et al., 2010; Li et al., 2013). It has to be taken into account that in some deposits the minerals are enriched in MREE or HREE (Maksimovic and Pantó, 1985).

On the other hand, the Mediterranean bauxites are a promising REE resource for the UE. These deposits, commonly found in nearly all the Southern European countries, contain up to 100 ppm of REE and go up to 500 ppm in the red mud slurries produced after the aluminium extraction using the Bayer process, making viable its exploitation (Deady et al., 2014). In some cases, concentrations can reach higher values: up to several thousands of ppm in REE in the Parhari bauxites (Greece), at the contact between the laterites and the limestone protolith (Eliopoulos and Economou-Eliopoulos, 2000).

### 19. Calcretes and soils

The concentration of REE in soils is extremely variable, directly depending on the substrate composition and on the percolating solutions, which can make these selectively mobile or immobile. In this way, in levels of some soils, some REE can be specifically concentrated. In particular, this mechanism seems efficient for the Ce, or Nd separation from the rest of REE. Due to this, lantanite-(Nd) manifestations in calcrete are known from at least two sedimentary formations located in Brasil. The lantanite-(Nd) can develop tabular crystals up to 2 mm in longitude (Fig. 35; Roberts et al., 1980; Coimbra et al., 1989). It is noteworthy that such a simple mechanism is so effective in separating the REE.

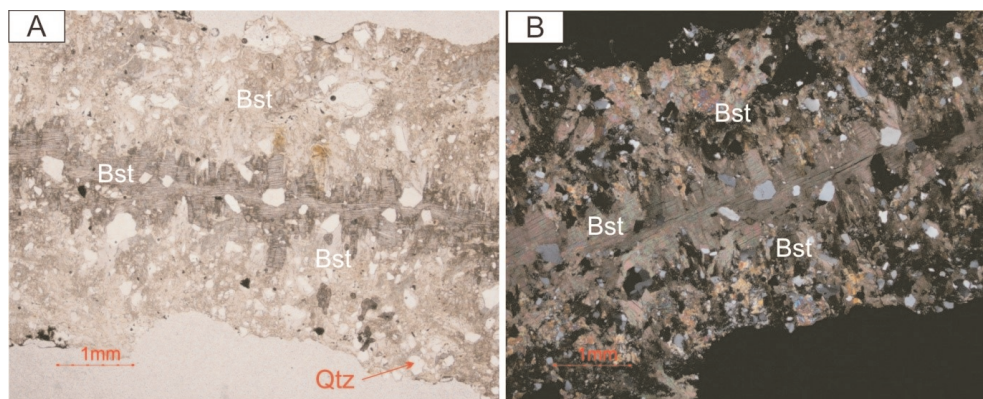


Fig. 35. Image taken with a transmitted light optical microscope of lanthanite-(Nd) pedogenetic mineralization of Curitiba, in Brazil. **A)** In PPL. **B)** The same image in crossed nicols. Note that lanthanite-(Nd) cements detrital quartz grains.

The rhabdophane concentrations developed on weathered limestones in Kazajstan (Dumler *et al.*, 1970) can have a similar origin.

The study of the REE minerals in paleosoils can help to understand the evolution processes of global change. Thus, in the Proterozoic paleosoils of the Flin Flon zone (Canada) the presence of cerianite, monazite-(Ce) and uraninite rich in REE has been recognized (Pan and Stauffer, 2000), supporting the theory that in this moment a change in the oxygen fugacity in the primitive atmosphere took place.

However, examples in which economic concentrations of these elements occurred remain so far unknown.

## 20. Clays

The ability of clays of fixing REE by adsorption has been known for a long time (Aagaard, 1974). Most of the worldwide resources are contained in clays (REE-bearing ion-adsorption clays) from the south of China (Bao and Zhao, 2007; Foley *et al.*, 2013). This type of deposit does not require more than a slight pre-concentration in REE in the protolith from which the clays derive.

The lateritic profiles consist of the following units, which have transitional limits (Bao and Zhao, 2008):

- a) a upper crust, poor in REE, with kaolinite + halloysite (7Å) ± gibbsite (horizon A)

- b) a totally weathered zone enriched in halloysite (7Å) + kaolinite + vermiculite (horizon B)
- c) a less weathered zone with halloysite (7Å) + kaolinite + montmorillonite + mica (horizon C)
- d) granitic protolith

The REE are found distributed in many components, though not all of them recoverable: as traces in residual minerals, as residual REE minerals, as secondary phases including colloids rich in REE, as trace components of Fe and Mn oxides, as interchangeable ions in clays (between 30% and 90%), or as traces in the structure of clay minerals (Chengyu *et al.*, 1996). In some areas, including Longnan and Pingyuan, the REE can be complexed by organic compounds.

From this assemblage, only the REE proportion that is found adsorbed in the clays can be easily separated by leaching. Even though, the simplicity of this process makes it very profitable.

On the other hand, the two main deposits produce different types of REE: the weathering of two mica granites produces laterites rich in Y-HREE, whilst the weathering of biotitic granites generate laterites rich in LREE (Chi and Tian, 2008). The reserves are not large in comparison with the resources of Bayan Obo, but are of 1 Mt of REE contents, and the reserves of some HREE are higher than those of Bayan Obo, being therefore the most important in a worldwide scale (Grauch and Mariano, 2008).



*Papangelakis and Moldoveanu (2014)* value this type of deposit as the key for the REE obtainment and, particularly for the HREE due to the fact that this type of deposits are abundantly distributed in subtropical environments and are of very easy benefit (localized in soft superficial levels). Moreover, the clays have an extremely high capacity of interchange. In addition, these authors have proven the performance of the clays extraction process (for different clay origins), demonstrating that the REE extraction from clays can be easily done by leaching.

## 21. Carbon and Petroleum

Systematic studies exist in regards to the analysis of the REE contents in carbon deposits belonging to several parts of the world, and it has been observed that the content of REE can vary from a few dozens of ppm to several hundreds of ppm (*Ekman, 2012*), forming differentiated mineral species or staying fixed in the organic material (*Zheng et al., 2007*). These authors mention the possibility that the concentrations could reach economic interest, especially in the case in which REE can be recovered as a by-product, either from the products of carbon combustion (*Hower et al., 1999*) or from the recovery from the associated clays. At the moment few studies of the carbons of the world have been done, and the most complete published data refer to USA, where the Geologic Service has performed a systematic study of the REE contents of all the carbon deposits. Roughly, it seems that the higher contents are found in the deposits of the United States east coast. The data available at the moment reflect relatively high content in HREE in several of these carbon deposits, with values higher than 1000 ppm of  $\Sigma$ REEO, but there is a wide variability in the LREE/HREE relationships and furthermore, the REE present little regularity in their distribution in the carbon levels (*Ekman, 2012*). Nevertheless, the volume of the extracted carbon is huge, so the separation of REE could provide large quantities of REE. So, these authors estimate that the recoverable REE+Y resources from the carbon deposits of the USA could reach 2 Mt, 5000000 of which would correspond to Y+REE. These

same authors estimate in more than 40000 t of REE the resources that are lost annually in the carbon extraction process.

On the other hand, carbon combustion evidently eliminates components and the ashes are relatively concentrated in REE. Therefore, some carbon deposits of Eastern Siberia present high contents of total REEO (300 to 100 ppm) but are rich in HREE; after the process of combustion, the HREE proportions in the ashes are of the 1% order in weight (*Seredin, 1995*), which makes them a true economic resource. *Hower et al. (2015)* remark that ashes from coal combustion are enriched in REE in an order of magnitude compared to the value at the original rock. However, it remains to be seen whether the mineralogical phase in which REE are in the ashes may allow removal easily.

Naturally, the processing of waste coal combustion is not the best source of REE if one considers that in the medium term coal combustion should be reduced to mitigate the effects of climate change. However, if accumulations of combustion residuals exist in thermal plants, it would be interesting to evaluate if the benefit of REE could help pay the costs of the residual treatment.

*Vlasov (1968)* comments that in some asphalts and ashes of petroleum combustion of some wells in the United States the REE can reach values of the 1% order (and so it would be convenient to examine the content of some ashes in thermal plants), but in many other deposits the values are below the detection limits.

## 22. Concentrations in Levels Rich in Organic Material in Intracontinental Basins

Little documentation exists on this subject. *Vlasov (1968)* cites enrichments in carbonaceous levels with U-V mineralization associated to red beds in the Colorado Plateau. In these rocks the proportions of Sc could reach 0,01%, Y up to 1%, Nd, 0,05%, Ce, 0,1%, Sm 0,05%, Dy, 0,05%, Er, 0,1%, Gd, 0,1%. It is unknown, however, what minerals contain these elements.

Strong concentrations of REE can also be found in the black shales hosting the stratabound Cu deposits of the Zechstein type, and Neogene shales from Russia return exceptionally high values ( $\Sigma\text{REE}=8\text{-}10\%$  weight), across a thickness of the mineralized layers of 1.3 m (Vlasov, 1968). The ores are rhabdophane, churchite, lanthanite and non-specified hydroxides, but it seems that part of the REE can be contained in asbolanes, pyrolusite, limonite, gummite and uraninite. Also, there can be a part absorbed in clays. In this sense, it is convenient to remember that the black shales enriched in HSFE (V, Cr, Mo, Se, As, U) and precious metals (Au, Ag, PGE) associated to exhalative levels of the Lower Silurian of Catalonia often present very high REE values, that reach mineralogical expression in the crystallization of several minerals during metamorphism, especially allanite rich in V and Cr, monazite and xenotime (Canet et al., 2003 a,b; Canet et al., 2004).

### 23. Gossan and Supergene Enrichment Zones

Though possibly it does not consist of more than a simple mineralogical showing, we cannot ignore the recent discovery of adamite rich in Ce (very possibly  $\text{Ce}^{4+}$ ), showing a beautiful shade of blue, in the weathering zones of the sulphide deposits in the Laurion mines, in Greece. This adamite appears with other secondary arsenates rich in Ce, like agardite-(Ce) (Fehr and Hochleitner, 1984). The agardite-(Y) has been cited in copper mines in Sardinia (Olmi et al., 1988) and in Mutoshi in Shaba, Congo (Deliens, 1989).

Many uranium mineralizations contain in their supergene enrichment zones a wide variety of REE minerals that can be produced by and alteration of uraninite and the subsequent liberation of REE from its structure. They are oxides and hydroxides, arsenates, phosphates, carbonates, silicates etc., often double, containing other elements in their structure. For example, in the Kamoto mine, Congo, numerous species have been described like françoisite-(Nd) in association with uraninite, schoepite, uranophane, curite, shabaite-(Nd), schuilingite-(Nd), kamotoite-(Y), astrocyanite-

(Ce) and masuyite (Deliens and Piret, 1986; Piret et al., 1988; Deliens and Piret, 1989). In Shinkolobwe, also in Congo, associations of uranyl and REE hydrated carbonates are recognised, as bijvoetite-(Y) and lepersonnite-(Gd), along with sklodowskite, curite, uranophane, becquerelite, rutherfordine, studtite, torbernite, soddyite, kasolite, schoepite and oursinite (Deliens and Piret, 1982); Sharp and Bertrand (1985) add gysinite-(Nd) to the list. Piret and Deliens (1982) find similar associations in the Kasompi mine, Congo. Also in the natural nuclear reactor of Bangombé, in Gabon, REE-rich coffinite has been described, as well as Ce-rich françoisite-(Nd) (Janeczek and Ewing, 1996).

Some REE phosphates like churchite-(Y) and rhabdophane are present in the hydrothermal alteration zones of several mineral deposits, especially those embedded in granitic rocks, but also in others, including deposits of Zambian Copper Belt type (Lefebvre and Gasparrini, 1980). The weathering of the feldspars of these rocks can add P, as well as the alteration of the accessory apatite.

In Paratoo, Australia, the weathering of a IOCG type deposit (with a primary mineralization of magnetite and chalcopyrite, and with zones of hydrothermal alteration by hypersaline fluids, enriched in volatiles and alkalis) has produced the formation of a very varied association of carbonates with Cl and REE, comprising decrespignyite-(Y), paratooite-(La), caysichite-(Y), donnayite-(Y), kamphaugite-(Y), along with malachite, nontronite, calcite, gypsum and limonite (Wallwork et al., 2002; Brugger et al., 2006). These species are very colourful and can facilitate the exploration of similar mineralizations. In addition, we cannot rule out that they can eventually produce economic accumulations.

More strangely, and possibly only in exceptional cases, the combined weathering of tungsten and REE minerals results in minerals like ytrotungstite or cerotungstite, like in Nyamulilo mine, in Uganda (Sahama et al., 1970). It is not common either that the simultaneous alteration of sulphides and REE minerals can lead to sulphates like chukrovite (Mathew et al., 1981), levinsonite-(Y),

and zugshunstone-(Ce) (*Lauf, 1997*). Finally, in some cases in which there are alterations of shales with monazite in acid soils rich in organic matter, REE sulphate-oxalates can be formed, like coskrenite-(Ce) (*Peacor et al., 1999*).

In any case, the presence of these minerals in the oxidation zones can open a query about the possible presence of minerals of significant quantities of REE in the corresponding primary ores.

It is necessary not to forget, on the other hand, that the presence of minerals of the agardite group is not strange in the oxidation zones of mineral deposits, even in some alkaline and carbonatite rocks (*Modreski, 1979*).

#### 24. Placers

For many years REE were only obtained as a by-product of the exploitation of other minerals (zircon, rutile, ilmenite, etc.) from placer deposits. REE are never the dominant mineral in these deposits, but they were easy to separate and hence these concentrates helped to cover the low REE demand.

Lots of the REE minerals are unstable in supergene conditions, whilst others are barely resistant to transport. Contrastingly, monazite and xenotime are very resistant minerals and are common in detrital sediments, and can be accumulated in alluvial placers and especially in lateral beach placers; additionally, even some offshore placers are also exploited. The problem for the exploitation of these deposits lies mainly in its relatively low grades, aspect that is partially compensated by the non-lithified character of the sediment. On the other hand, lots of these placers formed in older periods could have lithified and been converted to paleoplacers.

*Orris and Grauch (2002)* list more than 360 placer deposits around the world, which actually constitute a non-negligible resource.

Between the different types of monazite, in the last years an effort has been made to

localize re-concentrations of Eu rich monazites (grey monazites). These minerals are known as centimetric nodules disperse in metapelitic rocks of the Lower Paleozoic (*Donnot et al., 1973*), and since years ago projects have been done to localize alluvial re-concentrations of these minerals, which seem to have crystallized in the localization of a miner concession in Spain.

A problem for the metallurgical extraction of REE from concentrated minerals in these mediums is the high content of Th which monazite present.

#### 25. Geothermal Fluids

*Vlasov (1968)* reports contents of REE in superficial, poor saline waters, and as expected they have very low values. On the other hand, the potential that brines can suppose is starting to be valued very recently, as they are a mean that tends to transport REE easily. There is a diversity of environments more or less accessible. In general, the geothermal fluids present a salinity that increases with temperature, which can reach in some deep fluids salinities of more than 300.000 ppm (*Entingh and Vimmerstedt, 2005*). The first resource is the geothermal wells, in which the possibility of recovering REE in solution or from the recovery of the precipitates in the wells has been evaluated. If the recovery of silica, zinc, manganese, lithium, rubidium and caesium was already evaluated in recent years (*Gallup, 1998; Bourcier et al., 2003; Bloomquist, 2006*), the current demand of the industry make all eyes turn to REEs. On the other hand, as it is known, in oil traps the presence of brines is normal. Because of that, the geologic services of the United States are assessing the possibility of recovering REE from the brines of the petroleum wells, before their reinjection into the terrain (*Kruger, 2015*).

#### 26. Current Deep Oceanic Muds

Since the fulfilment of the first oceanographic projects it has been noticed significant REE-enrichment in ocean floor. For example, *Balashov and Girin (1969)* and *Balashov et al. (1970)* already highlighted these enrich-

ments; *Balashov et al. (1964)* prompted at climatic factors and sedimentary facies as critical for the development of these concentrations; furthermore, they already highlighted the enrichment in HREE in the marine sediments regarding the continental ones. According with these authors, the reasons should be that HREE should be more soluble than LREE in the superficial solutions; nevertheless, in addition to the incorporation of REE to the ocean as solution, it had to be considered that the continental clays accumulate a good part of REE (*Cullers et al., 1975*), so a part is transported towards marine depths inside the clays. Subsequent investigations demonstrated that there might be other mechanisms important in the supply of REE to the oceans, and particularly the hydrothermal venting in the ocean floor (for example, *Klinkhammer et al., 1983; Owen and Olivarez, 1988*).

However, the recent interest for REE has reactivated the study of REE behaviour in the marine environments. So, from the study of thousands of samples obtained in the oceanic depths of the Pacific, *Kato et al. (2011)* conclude that the muds formed in current deep sediments (generally metalliferous, zeolitic clays, pelagic red clays) are strongly enriched in REE. Thereby, these authors have located a total REE+Y values between 1.000-2,230 ppm ( $\Sigma$ REE+Y), 200-430 ppm of which correspond to the total HREE ( $\Sigma$ HREE). These values are comparable or even higher than those of the deposits of the ionic absorption clay type from South China ( $\Sigma$ REE+Y between 500-2,000 ppm;  $\Sigma$ HREE 50-200 ppm). The reserves are huge, as the thickness of the mineralized sediments, even though variable, can reach more than 70 m; REE can be found in the sediments in the sea bottom or in dozens of meters in depth. In these oceanic muds, the minerals that can accommodate the REE are Fe and Mn oxy-hydroxides or zeolites, like phillipsite. Thus, the extraction of these elements is easy with some simple acid leaching. These sediments are also enriched in HFSE like V, Co, Ni, Cu, Zn, Mo and Mn, so a simultaneous benefit of these elements can be envisaged; nevertheless, these authors do not clarify what minerals accommodate these elements (though presumably

some of them are concentrated in illites, which would make the extraction more difficult). Finally, yet another positive aspect is that Th and U proportions, which are penalizing elements, are much lower than in the classic REE deposits. This very important project raises lots of questions, like which are the REE sources (the authors propose that the origin is the REE incorporation to the ocean from hydrothermal plumes) and their mechanisms of accumulation, and the possible existence of analogous sediments in other seas or oceans. Currently the exploitation of these resources does not seem to be viable (or in an immediate future), because the environmental implications of their extraction are unknown, and the cost would be elevated. Possibly it is not worth following that lead, while other interesting and simpler possibilities have been posed. The question is: do analogous sediments of the current deposits exist in old sediments, outcropping now in the continents? The most probable answer is yes, and it opens an immense field for synthesis projects on earth sciences, combining sedimentological, tectonic, petrographic, mineralogical and geochemical aspects.

For example, it may be interesting to assess the possibility that the zeolitized volcanosedimentary submarine series could have REE resources. Enormous outcrops of these rocks exist in big regions of the planet, being exploited sometimes because of their zeolite content (for example *Orozco and Rizo, 1998*). In fact, possibly these pelagic REE are the precursor for some deposits that are found in deformed or metamorphosed sedimentary basins.

Actually, the presence of REE is not limited to clayish ferromanganiferous materials. *Rasmussen (1996)* has also cited the presence of phosphates with REE (florencite, gorceixite, crandallite and xenotime) as a diagenetic product in submarine sands.

### **27. Oxide Fe-Mn Crusts in Current and Ancient Hard-grounds**

On the other hand, not only pelagic muds contain REE in the oceanic floors. The famous submarine Mn nodules and the cobalt-rich

crusts, which exploitation has been evaluated as source of base metals, critical metals or precious metals (especially Mn and other HFSE like V, Ni, Cu, Zn, Co, Mo, W, Nb, in addition to Li and PGE; *Ross Heath, 1981*), are also enriched in REE and particularly in HREE (*Papavasileiou, 2014*). However, the crusts have three times more REE than the nodules, and contents of HREE equivalent to those of the clay deposits in China. Therefore, in short term they can become a better resource than the nodules (*Koschinsky et al., 2010; Hein et al., 2013*).

Nodules are currently formed in the surface of sea floors in which there is a low rate of terrigenous sedimentation, and present a complex internal structure (*Guo et al., 1990a*). The mineralogy is rich in paragenesis of opaque minerals, but its study is difficult due to the wide spectrum of phases and their poor crystallinity. The following minerals can be distinguished: vernadite, birnessite, todorokite, psilomelane, manganosite, nsutite, cryptomelane, rancieite, ferrihydrite, goethite, akaganeite, lepidocrocite, ferrosulphate, hematite, maghemite and magnetite (*Dubinín et al., 2008*). Transparent minerals tend to be detrital elements, although auto-genic minerals as zeolites (phillipsite and harmotome) and baritine are cited (see *Melgarejo and Alfonso, 1997* and their references). Silicates predominant at the core of the nodules are illite, montmorillonite, quartz and zeolites like phillipsite and harmotome; in the periphery the impurities are of quartz and phillipsite (*Guo et al., 1990b*).

The Fe-Mn crusts form coverings of up to 25 cm of width on seamount rocks and other domains that represent sedimentary highs where there is no sediment accumulation (*Papavasileiou, 2014*).

Both nodules and crusts grow at a very slow rate, 1mm per million years; they hijack numerous trace elements from the marine water column (*Hein et al., 2000, 2010*). Their high porosity and specific surface facilitate a very effective capacity of trace metals adsorption over the Fe-Mn oxyhydroxides (*Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003*).

On the other hand, the current seabottom crusts have their old equivalent in the deposits of ferruginous crusts of hard-ground type, eventually with phosphate. As it is known, these deposits represent events of hiatuses or low deposition rate in a stratigraphic series, and generally are horizons of Fe-Mn oxyhydroxides. Consequently, it can be interesting to effectuate a study for the rare elements where these crusts concentrate in small spaces various intervals of this type, especially where these levels are broad and their outcrop corresponds or is close to a structural surface.

### **28. Current and Old Stratiform Fe-Mn Deposits**

As it is known, deposits of iron and manganese minerals, of volcanic-sedimentary or sedimentary affinity, are also formed in sea bottom. These deposits can have large reserves and currently constitute the main source of manganese and iron. It is absolutely unknown if these deposits could have REE reserves; though it is known that extra European companies are effectuating a sampling at worldwide scale of some representative deposits. However, the results are unknown. On the other hand, *Sinisi (2015)* pointed out elevated concentrations of REE in VMS deposits of Mn in Sardinia; even though he does not give precise results, he indicates that the REE contents are similar to those found in the commercial clay deposits in China. However, it is not clear what phases can be the carriers; if the Mn mineral or the clays associated with them.

### **29. Mechanisms for Solubilization, Transportation and Precipitation of the REE: Experimental and Actualistic Data Versus Empirical Data**

To understand the formation mechanisms of a deposit of any element, it is essential to know the mechanisms of acquisition by the mean of transportation, the transportation mechanisms and precipitation; in any case, the experimental data should be in agreement with the empirical observations in the deposits. In the case of REEs, only in the last 20 years there have been experimental stu-

dies with this objective. As it can be deduced from the revision of the REE deposits, in good part of its deposits, REEs are concentrated by hydrothermal or supergene processes, including cases of deposits associated with igneous rocks (*Samson and Wood, 2005*). Consequently, the stability of REE in hydrothermal solutions must be studied.

### *(Pre)Concentration in magmas*

We have already seen that there are not important REE concentrations in most magmas, and that the higher concentrations occur in saturated and subsaturated alkaline rocks, in their pegmatites and in carbonatites; nelsonites are much rarer cases and are seldom mineralized.

Alkaline subsaturated rocks are formed from the partial melting of the previously metasomatized subcontinental lithosphere, under very low fusion rates (less than 1%, *Chakhmouradian and Zaitsev, 2012*); however, the incorporation of the REE mechanisms is still discussed, although it can also be conditioned by the presence of re-fertilization processes of the mantle.

In subsaturated peralkaline rocks the concentration of REE can be such that primary deposits can be produced from crystallization of liquidus minerals that can concentrate by the typical magmatic mechanisms, for example, by fractionated crystallization processes or cumulate formation. On the other hand, some mineral structures tend to select LREEs and others HREEs, which at the same time can favour REE separation mechanisms. However, many of the deposits including their pegmatites are enriched by subsolidus hydrothermal processes.

As noted above, carbonatites produce economic REE deposits only when hydrothermal fluids remobilize the REE pre-concentrations. The origin of saturated peralkaline magmas is less clarified, and these magmas tend to incorporate preferably HREE, while their concentration tends to be produced in the more evolved differentiates and almost always with participation of hydrothermal fluids.

Finally, as we have seen, there have been

important REE deposits associated to skarns or replacements (like IOCG), which sometimes can be related to another type of granites, including calcoalkaline rocks. In these deposits, nonetheless, there is an evident hydrothermal component and its origin should be explained by the solubilisation of the REEs in the hydrothermal fluids related to these granitoids.

### *Solubilization*

The number of REE mineral species is very broad and their stability is very variable. We are still in a very early stadium to assess the conditions of the solubility of this wide mineral population. Evidently, between the igneous minerals that present REE with more or less concentrations, carbonates and minerals belonging to the apatite group are easily removable in hydrothermal or even supergene conditions by very diverse fluids, especially in acid mediums. Instead, destruction of the structures of the immense majority of phosphates and REE silicates is more complicated and requires more complex fluids.

However, the first experimental data demonstrates that some REE minerals, like those of the monazite group, are very stable and have low products of solubility in the majority of natural fluids between 25 and 300°C (*Wood and Williams-Jones, 1994; Poitrasson et al., 2004; Cetiner et al., 2005*). Thus, it is not strange that monazite and xenotime are typical minerals accumulated in large quantities in placers, often showing idiomorphic forms. If we add that their structures are robust enough to become metamict, even in case of ancient Th-rich monazites, we can realize that these minerals can be used as storage of radioactive products. In addition, their low solubility does not facilitate their removal by hydrothermal fluids, especially in metamorphic conditions. In part because of these facts, for a long time the elements of REE have been considered as immobile elements during lots of geologic processes, and in particular, during metamorphism. Of course, this is a half-truth. It can be true for those rocks in which REEs are concentrated especially in monazite and xenotime, but we have already seen that lots of REE minerals of magmatic

formation are destroyed during the subsolidus hydrothermal processes that took place in these rocks, forming very complex paragenesis, and we know that REEs are transported by the hydrothermal fluids that alter the granitic peralkaline rocks and carbonatites, transporting the REEs to the host rock even at great distances.

### Transport mechanisms

On the other hand, a cursory examination of the mineral associations described draws a panorama in which the REE minerals occur in paragenesis rich in F-rich minerals (for example, villiaumite in alkaline subsaturated rocks, fluorite in lots of carbonatites and deposits associated to alkaline rocks, etc.). Therefore, a first impression is that the fluorine complexes could be very important for the transport of REEs, and that the precipitation of F minerals could help to precipitate REE minerals. In fact, Wood (1990a) already highlighted that up to 350°C the fluorine complexes dominated over chlorine complexes in terms of capacity of REE transportation. Early experimental data by Haas *et al.* (1997) indicated that in hydrothermal fluids rich in Cl, REE transport can be effectuated by the formation of chloride, fluoride and hydroxylate complexes, respectively in acid, neutral, and basic conditions. These authors also noted that HREEs form strongest complexes with fluoride and less by chloride than LREEs, while in alkaline pH HREEs and LREEs associated with hydroxyl have no fractionation. However, Migdisov *et al.* (2009) and Migdisov and Williams-Jones (2014) make a synthesis of the available experimental data in which they conclude that F does not seem to be the best complexing agent, and other agents like chlorides and sulphates form more effective complexes. In fact, experiments of the REE transportation in fluoride complexes do not seem to indicate that they are efficient mechanisms in the typical fluids associated to granitoids, especially in acid environments (Migdisov and Williams-Jones, 2007).

The reality may possibly be much more complex. In fact, it is long known that chloride solutions are an excellent REE complexing agent, especially at high salinity and tempe-

rature (see for example, Gammons *et al.*, 1996, 2002; Migdisov and Williams-Jones, 2002, 2006), conditions that happen in lots of magmatic fluids but also in basin brines and lots of other geological fluids, even superficial ones. So, this mechanism can be valid to explain REE transportation in skarn type deposits, IOCG or in discordances (remember the strong hydrothermal alterations with albitizations, scapolitizations and Cl enrichments in numerous minerals, as well as the data of fluid inclusions of, for example, Kwak and Abeysinghe, 1987; Groves *et al.*, 2010). The transportation by chlorides can also be valid to explain the associations in lots of igneous rocks (Salvi *et al.*, 2000, 2005), even carbonatites, but does not seem sufficient. In fact, a great part of the experimentation has been done in the case of fluids in acid conditions, but this is not the case in some magmatic-hydrothermal stages, like some pegmatitic stages or albitization processes, or in the cases with oversaturated F-rich Na-rich fluids or magmas. In these cases, the role of F and alkalis of REE as complexing agents does not seem negligible (Gieré, 1990). The efficiency of Na- and F-enriched fluids to transport Ti, Zr and REE was demonstrated at the Lovozero massif in waters of supergene origin, but of deep circulation, which have a pH > 12 (Kraynov *et al.*, 1969).

The role of double ligands of the fluorocarbonate type does not seem negligible either, as they could have had an important role in the formation of the Bayan Obo deposits, for example. Nevertheless, the role of F has been regained recently by several authors. Estrade *et al.* (2015) propose from the study of fluid inclusions of the skarn of Ambohimirahavavy (Madagascar) that the hydrothermal fluids with high Cl and F activity were decisive in the transportation of REE and HFSE, and the massive precipitation of minerals of these elements was favoured with the reaction with the carbonated host rock, the consequent increase of the pH and the loss of ligands by the precipitation of fluorite, resulting in the precipitation of REE F-carbonates and pyrochlore and a complex paragenesis.

The participation of sulphates in the hydro-

thermal REE transportation has been studied experimentally by *Migdisov et al. (2006)* and *Migdisov and Williams-Jones (2008)*, amongst others, and seems to be a very effective transportation mechanism. In particular, it could be effective in subsolidus carbonatitic processes in two forms. In first place, the fluid inclusions in hydrothermal minerals of lots of carbonatites and even kimberlites reveal the presence of fluids with alkaline sulphates. Thus, the hydrothermal carbonatitic phases could easily mobilize REEs, which would be dispersed in the structures of lots of primary carbonatitic minerals that are washed by these fluids. On the other hand, the precipitation of barite would eliminate the ligand, thus leading to what happens in the hydrothermal stages of carbonatites: a precipitation of quartz veinlets with barite and the simultaneous crystallization of great quantities of carbonates of the ancylite, bastnäsite, parisite, synchysite groups, etc. It is interesting, even though, that these carbonates have F in their structures. Moreover, the alteration of sulphides in supergene conditions can produce REE leaching too, which can be transported in part as sulphates or maybe as sulphates in many supergene contexts. This mechanism can be operative in the late carbonatite stages, but also in caliches, in soils, in phosphate deposits or in many other contexts. The precipitation of supergene barite or gypsum or anhydrite can, again, favour REE precipitation.

On the other hand, the hydrothermal fluids of black-smokers of ocean floors are enriched in REE, which are transported by saline fluids in the form of complex chlorides or fluorides (*Douville et al., 1999*), but also in form of sulphate complexes (*Bao et al., 2008*). Thus, these fluids play an important role in the supply of REE to the marine water for its subsequent enrichment in the nodules and Fe-Mn crusts and in the muds of the ocean depths. The transportation of REEs by carbonate complexes can be critical to produce REE enrichments in carbonatites in relation to other magmas, and in particularly in the REE enrichment of the fenites developed by fluid circulation of fluids rich in CO<sub>2</sub> of carbonatitic origin on the host rocks (*Wendlandt and Harrison, 1979*).

Even though there is not any experimental data on the role of the complexes with boron in the transportation of REE, we have already indicated that these complexes may develop a role in the diagenetic fluids of saline deposits. On the other hand, *Alderton et al. (1980)* highlight the REE mobilisation during the processes of turmalinization in the granitoids of SW of England.

The presence of methane and oxalates in some highly evolved alkaline subsaturated magmas cannot be forgotten either, in which the REE ligand could be the presence of oxalate or methane.

An observation of volcanologists in the carbonatite lavas of Oldoinyo Lengai demonstrates the different behaviour of REE in active fumaroles. Those with vapours of volcanic carbonatitic origin precipitate REE-rich crusts, while other crusts precipitated from reheated supergene aqueous fluids are poor in REE. These observations suggest that REE are transported in a gaseous phase at high temperature (*Gilbert and Williams-Jones, 2008*), while the reheated meteoric fluids seem to not have enough temperature to transport REE. Consequently, it is possible that some late concentrations in carbonatite cracks could have been formed by this mechanism; in this case, the late invasion of the carbonatitic systems by meteoric water, extensively demonstrated in carbonatites with stable C and O isotopes (for example, *Campeny et al., 2015*) could not be a good mechanism to re-concentrate REE.

*Wood (1990b)* analyses the roles of different possible ligands as complexing agents in supergene solutions. A first conclusion is that the nitrate anion is not effective, which would correspond with the absence of REE minerals in the nitrate deposits of Chile, even though the regional rocks can carry minerals with these elements. Under these low temperatures chloride complexes are not effective either, even in very saline waters. On the other hand, fluoride, phosphate and sulphate complexes are effective at a low pH, or even transportation as a simple ion, while carbonates or bicarbonates are effective in more alkaline mediums. So, the presence of cali-



ches with REE can be favoured in saline soils if they are developed over rocks where pre-concentrations of REE exist. These experiments also help to understand how REE transport can work in supergene environments in presence of phosphate anion, like in the supergene enrichments in carbonatites or the sedimentary phosphate deposits. There is not much information about REE transport by phosphate complexes, but *Kerr (1998)* proposes that REE transportation in the apatite-rich IOCG deposit of Pea Ridge (Missouri) was produced due to a high phosphate activity in mineralizing solutions.

*Ding and Wood (2002)* have analysed the possible role of acetate as complexing agents at low temperatures and pressures, circumstance that could happen in brines associated with petroleum deposits or in fluids associated with some exhalative submarine deposits, and in some soils; in some conditions acetate can be more effective than chloride anions.

Finally, there are still lots of open questions regarding to the REE fractionation during transport. *Smith et al. (2000)* propose that elevated values in the La/Nd ratios (or even La/Lu) in the early stages (of high temperature), of the mineralization of Bayan Obo (rich in monazite) can be related to high CO<sub>2</sub> activities in fluids, while lower values can be due to the presence of eminently aqueous solutions; in the later stages, rich in fluorocarboxylates, this ratio tends to have lower values, due to the fact that MREE and HREE complexes are more soluble at low temperatures (250-150°C).

### Precipitation

It must be taken into account that the fractionation of REEs can be controlled by the type of structure of the minerals that are formed in the deposit. As indicated before, LREEs tend to accumulate in monazite and HREE and Y in xenotime (*Ni et al., 1995; Franz et al., 1996*); nonetheless, the quantity of Y that can be accepted by the monazite that co-crystallizes with xenotime is function of the temperature, so it can be a good geothermometer (*Gratz y Heinrich, 1997*).

In the major part of hydrothermal deposits the precipitation mechanism is often the loss of the complexing ligand, which is generally produced fixing the anion to the structure of a mineral. In this sense, the crystallization of minerals rich in chlorine or fluorine (amphiboles, micas, scapolite, fluorite, villiaumite, etc.) seems to be the most efficient mechanism of crystallization of REE minerals.

### 30. Conclusion

The reassessment of REE has produced a systematic exploration that has given as a result the appearance of new types of deposits, which potential is far from being currently explored in its whole. In this aspect, China has been much more diligent than occidental countries, whose endemic lethargy in the investigation of mineral resources during this last half century can result in problems in the supply of raw materials.

Decidedly, the great progress in the localization of REE mineral deposits has been done in China in the last 15 years, and since then, little significant data has been contributed from Western countries further than the timid application of these criteria to the exploration of resources in Europe.

Most of the REE deposits known in Europe are of a more dubious profitability or of few real reserves (we have to disregard the immense areas affected by protection programs or with a high environmental or social impact) and often there is a lack of mechanisms for their benefit (for example, bauxites). It can take years to resolve most of these problems. Because of this, the EU should bet at short term on the study and exploitation of the most wellknown deposits, almost always situated in developing countries, while the methodology for exploiting their own resources is being prepared.

REE are found in minerals that are generally only slightly showy or of a fine grain size, which makes hard to recognize them in the field; furthermore they are found in low proportion compared to other minerals. Because of that, locating new deposits needs the use of systematic geochemical analysis. Nevertheless, as it has

been seen plenty of times, REE are found in the structure of minerals which are very refractory to metallurgical treatment, which limits its benefit. Thus, the valorisation of the REE deposits decidedly requires careful mineralogical studies. In many cases the economic REE minerals are species that have been recently discovered, even without characterization as a species. Therefore, efforts must not only be destined to investigate these deposits but also to characterize these minerals and study their stability and formation conditions. Because of all this, without a doubt, pure mineralogy projects are needed in the study of REE minerals, including structure determination, characterization of physical properties (and, particularly, the optical), mineral associations and evidently studies of their stability and methods for their benefit.

Concerning the concentration mechanisms to produce deposits of REE; some big master lines can be drawn, which are those that allow to extrapolate new deposit models. In general, magmatic REE deposits, whether in carbonatites, in saturated or in supersaturated alkaline rocks, have in common to have been formed in relation to highly fractionated mediums, with highly saline fluids and sometimes rich in F or B (magmatic fluids of high temperature in orthomagmatic, pegmatite and skarns deposits). Hypersaline fluids like the basin hypersaline fluids have a similar effectiveness (in deposits linked to discordances, IOCG, etc.).

Many of the initial deposits, nonetheless, are far from being economic unless a supergene re-concentration process is produced. REEs are relatively immobile during supergene processes; so they can re-concentrate in laterites or bauxites, accumulate in clays or possibly, in Fe and Mn oxides, in both subaerial and submarine deposits. The submarine deposits might be of economic interest in the future; however, in short-term, one of the REE resources until now completely unexplored is probably hidden in the old sedimentary series equivalent to these deposits.

### 31. Acknowledgements

This work has been supported by the pro-

jects2014 SGR1661 Consolidated Research Group (Generalitat de Catalunya), CGL2009-13758 and 2014/100820 (AJGA-Ayuntamiento de Gavà). I must thank J. Proenza, J. Mangas, E. Tauler, M. Campeny, L. Torró, C. Villanova, M. Castillo, S. Amores, S. Lehib, A.C.J.M. Bambi, A.O. Gonçalves, A. Camprubí, C. Canet, J. Bosch, P. Alfonso, A. Castellano, Jingyao Xu and S. Galí for having provided plenty of data, samples or their experience in this topic. S. Baurier made the translation to English.

### 7. References

- Aagaard, P. (1974): *Rare earth element adsorption on clay minerals*. Bull. Gr. Fr. Argiles 26, 193-199.
- Aide, M.T., Aide, Ch. (2012): *Rare Earth Elements: Their Importance in Understanding Soil Genesis*. International Scholarly Research Network ISRN Soil Science Volume 2012, Article ID 783876, 11 p.
- Albertini, C., Andersen, T. (1989): *Non-metamict orthorhombic AB<sub>2</sub>O<sub>6</sub> Y-Nb-Ta-Ti oxides from a pegmatite in Arvogno, Crana Valley (Toceno, Vigizzo Valley, Northern Italy)*. Rend. Soc. Ital. Mineral. Petrol. 43, 773-779.
- Alderton, D.H.M., Pearce, J.A., Potts, P.J. (1980): *Rare earth element mobility during granite alteration: Evidence from south-west England*, Earth Planet. Sci. Lett. 49, 149-165.
- Alfonso, P., Melgarejo, J.C., Corbella, M. (1995): *Nb-Ta-minerals from the Cap de Creus pegmatite field, eastern Pyrenees: distribution and geochemical trends*. Mineral. Petrol 55, 53-59.
- Allègre, C.J., Pineau, F., Bernat, M., Javoy, M. (1971): *Evidence for the Occurrence of Carbonatites on the Cape Verde and Canary Islands*. Nature 233, 103-104.
- Altschuler, Z.S. (1980): *The geochemistry of trace elements in marine phosphorites. Part I. Characteristic abundances and enrichment*. In: Y.K. Bendor (ed). *Marine phosphorites-geochemistry, occurrence, genesis*. Spec. Publ. Soc. Econ. Paleontol. Mineral. 29, 19-30.

- Altschuler, Z.S., Berman, S., Cuttitta, F. (1967): *Rare earths in phosphorite-Geochemistry and potential recovery*. U.S. Geol. Surv. Prof. Paper 575-B.
- Álvarez, M.A., Domínguez Bella, S. (1995): *Estudio mineralógico de allanitas de Burguillos del Cerro (Badajoz)*. Bol. Soc. Esp. Min 18,2, 37-38.
- Åmli, R. (1975): *Mineralogy and Rare Earth Geochemistry of apatite and Xenotime from the Gloserheia Granite pegmatite, Froland, southern Norway*. Amer. Mineral. 60, 607-620.
- Åmli, R. (1977): *Internal structure and mineralogy of the Gloserheia granite pegmatite, Froland, southern Norway*. Norsk. Geol. Tidss. 57, 243-262.
- Andreoli, M.A.G., Smith, C.B., Watkeys, M., Moore, J.M., Ashwal, L.D., Hart, R.J. (1994): *The geology of the Steenkampskraal monazite deposit, South Africa: Implications for REE-Th-Cu mineralization in charnockite-granulite terranes*. Economic Geology 89, 994-1016.
- Arden, K.M., Halden, N.M. (1999): *Crystallization and alteration history of britholite in rare-earth-element enriched pegmatitic segregations associated with the Eden Lake Complex, Manitoba, Canada*. Can. Mineral. 37, 1239-1253.
- Armbruster, T., Böhler, C., Graeser, S., Stalder, H.A., Amthauer, G. (1988): *Cervandonite-(Ce), (Ce,Nd,La)(Fe<sup>3+</sup>,Fe<sup>2+</sup>,Ti<sup>4+</sup>,Al)3SiAs(Si,As)O13; a new Alpine fissure mineral*. Schweiz. Mineral. Petrog. Mitt. 68, 125-132.
- Armbustmacher, T.J. (1988): *Geology and resources of thorium and associated elements in the Wet Mountains area, Fremont and Custer Counties, Colorado*. U.S. Geol. Surv. Prof. Paper 1049-F, 34 p.
- Arqués Farré, L., Cacho Amorós, A., Artiaga Torres, D., Torres Cueva, B., Torró, L., Melgarejo, J.C., Ramiro Condori, R., Guevara, N., Arce, O. (2013): *The Huanuni Sn-W-Pb-Zn-Ag vein deposits, Bolivia: structure and mineralogy*. In E. Jonsson, et al. (ed). *Mineral deposit research for a high tech world 3, Proceedings of the 12th Biennial SGA Meeting, 12-15 August 2013, Elanders Sverige AB Uppsala, Sweden,1236-1238*.
- Artiaga, D., Torres, B., Torró, L., Tauler, E., Melgarejo, J.C. (2013): *The Viloco Sn-W-Mo-As deposits, Bolivia: geology and mineralogy*. In E. Jonsson et al. (ed). *Mineral deposit research for a high tech world 3, Proceedings of the 12th Biennial SGA Meeting, 12-15 August 2013, Elanders Sverige AB Uppsala, Sweden,1239-1242*.
- Arzamastsev, A.A., Bea, F., Arzamastseva, L.V., Montero, P. (2002): *Rare earth elements in rocks and minerals from alkaline plutons of the Kola Peninsula, NW Russia, as indicators of alkaline magma evolution*. Rus. J. Earth Sci. 4, 187-209.
- Arzamastsev, A.A., Yakovenchuk, V., Pakhomovsky, Y., Ivanyuk, G. (2008): *The Khibina and Lovozero alkaline massifs: Geology and unique mineralization*. Guidebook 33 IGC excursion No 47, 58 pp.
- Arzamastsev, A.A., Arzamastseva, L.V., Zhirova, A.M., Glaznev, V.N. (2013): *Model of formation of the Khibiny-Lovozero ore bearing volcanic-plutonic complex*. Geol. Ore Deposits 55, 341-356.
- Atencio, D., Bastos Neto, A.C., Pereira, V.P., Ferron, J.T.M.M., Hoshino, M., Moriyama, T., Watanabe, Y., Miyawaki, R., Coutinho, J.M.V., Andrade, M.B., Domanik, K., Chukanov, N.V., Momma, K., Hirano, H., Tsunematsu, M. (2015): *Waimirite-(Y), orthorhombic YF<sub>3</sub>, a new mineral from the Pitinga mine, Presidente Figueiredo, Amazonas, Brazil, and from Jabal Tawlah, Saudi Arabia: Description and crystal structure*. Mineral. Mag. 79 (en prensa).
- Balashov, Yu.A., Dmitriev, L.V., Sharas'kin, A.Ya (1970): *Distribution of the rare earths and yttrium in the bedrock of the ocean floor*. Geochem. Intern. 7, 456-468.
- Balashov, Yu.A., Ronov, A.B., Migdisov, A.A., Turanskaya, N.V. (1964): *The effect of climate and facies environment of the rare earths during sedimentation*. Geochem. Intern. 1, 951-969.
- Balashov, Yu.A., Girin, Yu.P. (1969): *On the reserve of mobile rare-earth elements in sedimentary rocks*. Geochem. Intern. 6, 649-659
- Bambi, A.C.J.M., Costanzo, A., Gonçalves, A.O., Melgarejo, J.C. (2012): *Tracing the chemical evolution of primary pyrochlore from plutonic to vol-*

- canic carbonatites: the role of fluorine. *Mineral. Mag.* 76, 377-392.
- Bao, Z., Zhao, Z. (2007): Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in south China. *Ore Geol. Rev.* 33, 519-535.
- Bardossy, G. (1982): *Karst bauxites*. Elsevier, 441 p.
- Bao, S.-X., Zhou, H.-Y., Peng, X.-T., Ji, F.-W., Yao, H.-Q. (2008): Geochemistry of REE and yttrium in hydrothermal fluids from the Endeavour segment, Juan de Fuca Ridge. *Geochem. J.* 42, 359-370.
- Barker, D. (1989): Field relations of carbonatites. In K. Bell (ed.): *Carbonatites: Genesis and Evolution*. London: Unwin Hyman, 38-69.
- Barker, D. (1996): Carbonatite volcanism. In R.H. Mitchell (ed.): *Undersaturated alkaline rocks: mineralogy, petrogenesis and economic potential*. MAC Short Course 24, Winnipeg, Manitoba, 45-61.
- Barton, M.D. (2014): Iron oxide (-Cu-Au-REE-P-Ag-U-Co) systems. In H. Holland y K. Turekian (eds.). *Treatise on geochemistry*, Vol. 13: *Geochemistry of Mineral Deposits*, 515-541.
- Bastos Neto, A.C., Pereira, V.P., Ronchi, L.H., de Lima, E.F., Frantz, J.C. (2009): The world-class Sn, Nb, Ta, F (Y, REE, Li) deposit and the massive cryolite associated with the albite-enriched facies of the Madeira A-type granite, Pitinga mining district, Amazonas State, Brazil. *Can. Mineral.* 47, 1329-1357.
- Belolipetskii, A.P., Voloshin, A.V. (1996): Yttrium and rare earth element minerals of the Kola Peninsula, Russia. In A.P. Jones, F. Wall, C.T. Williams (eds.), *Rare earth minerals-chemistry, origin and ore deposits*: New York, Chapman and Hall, *Mineral. Soc. Series 7*, 311-326.
- Belolipetskii, A.P. (1997): asociaciones minerales en metasomatitas alcalinas de elementos raros. In J.C. Melgarejo (Ed.), *Atlas de asociaciones minerales en lámina delgada*. Edicions UB, Barcelona, 161-166.
- Berger, V.I., Singer, D.A., Orris, G.J. (2009): *Carbonatites of the world, explored deposits of Nb and REE-Database and grade and tonnage models*: U.S. Geological Survey Open-File Report 2009-1139, 17 p. and database. (Also available at <http://pubs.usgs.gov/of/2009/1139/>).
- Beus, A.A. (1979): Sodium: a geochemical indicator of emerald mineralization in the Cordillera Oriental, Colombia. *J. Geochem. Explor.* 2, 195-208.
- Birkett, T.C., Miller, R.R., Roberts, A.C., Mariano, A.N. (1992): Zirconium-bearing minerals of the Strange Lake intrusive complex, Québec-Labrador. *Can. Mineral.* 30, 191-205.
- Birkett, T.C., Sinclair, W.D. (1998): Rare-metal replacement deposits (skarn and fenites) associated with alkalic and carbonatite complexes. In D.R. Lentz (Ed.), *Mineralized Intrusion-Related Skarn Systems*. Mineralogical Association of Canada Short Course, vol. 26, 445-473.
- Bloomquist, R.G. (2006) *Economic benefits of mineral extraction from geothermal brines*: Washington State University Extension Energy Program. <https://pangea.stanford.edu/ERE/pdf/IGAstandard/Russia/MEGB-2006/20Bloomquist.pdf>
- Boily, M., Williams-Jones, A.E. (1994): The role of magmatic and hydrothermal processes in the chemical evolution of the Strange Lake plutonic complex, Québec-Labrador. *Contrib. Mineral. Petrol.* 118, 33-47.
- Bonin, B. (2007): A-type granites and related rocks: Evolution of a concept, problems and prospects. *Lithos* 97, 1-29.
- Bourcier, W., Lin, M., Nix, G. (2003): *Recovery of Minerals and Metals from Geothermal Fluids*. Lawrence Livermore National Laboratory, Livermore, CA, USA, 18pp.
- Braun, J.-J., Pagel, M., Muller, J.-P., Bilong, P., Michard, A., Guillet, B. (1990): Cerium anomalies in lateritic profiles. *Geochim. Cosmochim. Acta* 54, 781-795.
- Brugger, J., Ogierman, J., Pring, A., Waldron, H., Kolitsch, U. (2006): Origin of the secondary REE-minerals at the Paratoo copper deposit near Yunta, South Australia. *Mineral. Mag.* 70, 609-627.
- Buda, G., Nagy, G. (1995): Some REE bearing

- accessory minerals in two types of variscan granulites, Hungary. *Geol. Carpathica* 46, 67-78.
- Bulakh, A.G., Le Bas, M.J., Wall, F., Zaitsev, A.N. (1998): Ancylyte-bearing carbonatites of the Sebyavr massif, Kola Peninsula, Russia. *Neues Jahrb. Mineral. Monatshefte* 4, 171-192.
- Campeny, M., Mangas, J., Melgarejo, J.C., Bambi, A., Alfonso, P., Gernon, Th., Manuel, J. (2014): The Catanda extrusive carbonatites (Kwanza Sul, Angola): an example of explosive carbonatitic volcanism. *Bull. Volcanol.* 76, 1-15.
- Campeny, M., Kamenetsky, V., Melgarejo, J.C., Mangas, J., Manuel, J., Alfonso, P., Kamenetsky, M., Bambi, A.C.J.M., Gonçalves, A.O. (2015): Carbonatitic lavas in Catanda (Kwanza Sul, Angola): Mineralogical and geochemical constraints on the parental melt. *Lithos* 232, 1-11.
- Canet, C., Alfonso, P., Melgarejo, J.C., Jorge, S.E. (2003a): V-rich minerals in contact-metamorphosed Silurian sedex deposits in the Poblet area, southwestern Catalonia, Spain. *Can. Mineral.* 41, 561-579.
- Canet, C., Alfonso, P., Melgarejo, J.C., Jorge, S.E. (2003b): PGE-bearing minerals in Silurian sedex deposits in the Poblet area, southwestern Catalonia, Spain. *Can. Mineral.* 41, 581-595.
- Canet, C., Alfonso, P., Melgarejo, J.C., Belyatsky, B.V. (2004): Geochemical evidences of sedimentary-exhalative origin of the shale-hosted PGE-Ag-Au-Zn-Cu occurrences of the Prades Mountains (Catalonia, Spain): trace-element abundances and Sm-Nd isotopes. *J. Geochem. Explor.* 82, 17-33.
- Cardona, S., Torró, L., Campeny, M., Andreu, E., Melgarejo, J.C., Proenza, J.A., De Witt, M., Bruchs, J.M., Lewis, J.F. (2013): Proterozoic metallogeny in the NW border of Botswana. In E. Jonsson et al. (ed). *Mineral deposit research for a high tech world 3*, Proceedings of the 12th Biennial SGA Meeting, 12-15 August 2013, Elanders Sverige AB Uppsala, Sweden, 1247-1250.
- Castellano, A., Melgarejo, J.C., Bambi, A.C.J.M., Gonçalves, A.O., Alfonso, P. (2011): Nb and REE at the Bailundo carbonatite, Angola. *Biennial Meeting SGA*, 675-677.
- Castor, S.B. (2008): The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California. *Can. Mineral* 46, 779-806.
- Castor, S.B., Nason, G.W. (2004): Mountain Pass Rare Earth Deposit, California. In S.B. Castor, K.G. Papke, R.O. Meeuwig (eds.): *Proceedings of the 39th Forum on the Geology of Industrial Minerals: Nevada Bureau of Mines and Geology Special Publication* 33, 68-81.
- Cerny, P. (1982): Anatomy and classification of granitic pegmatites. In P. \_ern\_ (ed): *Granitic pegmatites in science and industry. MAC Short course Handbook* 8: 1-39.
- Cerny, P. (1990): Distribution, affiliation and derivation of rare-element pegmatites in the Canadian Shield. *Geol Rundschau* 79: 183-226.
- Cerny, P. (1991a): Rare-element granitic pegmatites. Part I: Anatomy and internal evolution of pegmatite deposits. *Geoscience Canada* 18, 49-67.
- Cerny, P. (1991b): Rare-element granitic pegmatites. Part II: Regional to global environments and petrogenesis. *Geoscience Canada*, 18,2: 68-81.
- Cerny, P., Alfonso, P., Melgarejo, J.C. (1997): *Pegmatitas graníticas*. In J.C. Melgarejo (Ed.), *Atlas de asociaciones minerales en lámina delgada*. Edicions UB, Barcelona, 129-152.
- Cerny, P., Ercit, T.S. (2005): The classification of the granitic pegmatites revisited. *Can. Mineral.* 43, 2005-2026.
- Cetiner, Z., Wood, S.A., Gammons, C.H. (2005): The aqueous geochemistry of the rare earth elements. Part XIV. The solubility of rare earth element phosphates from 23 to 150 °C. *Chem. Geol.* 217, 147-169.
- Chakhmouradian, A.R., Mitchell, R.H. (1998): Lueshite, pyrochlore and monazite-(Ce) from apatite - dolomite carbonatite, Lesnaya Varaka complex, Kola Peninsula, Russia. *Mineral. Mag.* 62, 769 - 782.
- Chakhmouradian, A.R., Mitchell, R.H. (2002): The mineralogy of Ba- and Zr-rich alkaline pegmatites from Gordon Butte, Crazy Mountains (Montana, USA): comparisons between potassic

- and sodic agpaitic pegmatites. *Contrib. Mineral. Petrol.* 143, 93-114.
- Chakhmouradian, A.R., Mumin, A.H., Demény, A., Elliott, B. (2008): Postorogenic carbonatites at Eden Lake, Trans-Hudson Orogen (northern Manitoba, Canada): Geological setting, mineralogy and geochemistry. *Lithos* 103, 503-526.
- Chakhmouradian, A.R., Wall, F. (2012): Rare earth elements: minerals, mines, magnets (and more). *Elements* 8, 333-340.
- Chakhmouradian A.R., Zaitsev A.N. (2012) Rare earth mineralization in igneous rocks: Sources and processes. *Elements* 8, 347-353.
- Chakhmouradian A.R., Smith, M.P., Kynicky J. (2015a): From "strategic" tungsten to "green" neodymium: A century of critical metals at a glance. *Ore Geol. Rev.* 64, 455-458.
- Chakhmouradian A.R., Reguir E.P., Kressall R.D., Crozier J., Pisiak L.K., Sidhu R., Yang P. (2015b): Carbonatite-hosted niobium deposit at Aley, northern British Columbia (Canada): mineralogy, geochemistry and petrogenesis. *Ore Geol. Rev.* 64, 642-666.
- Chao, G.Y., Mainwaring, P.R., Baker, J. (1978): Donnayite,  $\text{NaCaSr}_3\text{Y}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$ , a new mineral from Mont St.-Hilaire, Québec. *Can. Mineral.* 16, 335-340.
- Chao, E.C.T., Back, J.M., Minkin, J.A. (1992): Host-rock controlled epigenetic, hydrothermal metasomatic origin of the Bayan Obo REE-Fe-Nb ore deposit, Inner Mongolia, PRC. *Appl. Geochem.* 7, 443-458.
- Chao, E. C. T., Back, J. M., Minkin, J. A., Tatsumoto, M., Junwen, Wang, Conrad, J. E., McKee, E. H., Zonglin, Hou, Qingrun, Meng, Shengguang, Huang (1997): Sedimentary carbonate-hosted giant Bayan Obo REE-Fe-Nb ore deposit of Inner Mongolia, China; a cornerstone example for giant polymetallic ore deposits of hydrothermal origin. *U.S. Geological Survey Bulletin*, 65 pp.
- Chengyu, W., Yuan, Z., Bai, G. (1996): Rare earth deposits of China. In A.P. Jones, F. Wall, C.T. Williams (eds.), *Rare Earth Minerals: Chemistry, origin and ore deposits. Mineral. Soc. Series* 7, Chapman and Hall, London, 281-310.
- Chi, R., Tian, J. (2008): *Weathered Crust Elution-deposited Rare Earth Ores*. Nova Science Publishers, New York, 288 p.
- Chong, G., Pueyo, J.J., Demergasso, C. (2000): Los yacimientos de boratos de Chile. *Rev. Geol. Chile* 27, 99-119.
- Christiansen, E.H., Sheridan, M.F., Burt, D.M. (1986): *The geology and geochemistry of Cenozoic topaz rhyolites from the western United States: Geological Society of America Special Paper* 205, 82 p.
- Coimbra, A.M., Coutinho, J.M.V., Atencio, D., Iwanuch, W. (1989): Lanthanite-(Nd) from Santa Isabel, state of Sao Paulo: second brazilian and world occurrence. *Can. Mineral.* 27, 119-123.
- Condie, K.C., Sinha A.K. (1996): Rare earth and other trace element mobility during mylonitization: a comparison of the Brevard and Hope Valley shear zones in the Appalachian mountains, USA. *J. Metamorph. Geol.*, 14, 213-226.
- Cullers, R.L., Yeh, L.-T., Chaudhuri, S., Guidotti, C.V. (1974): Rare earth elements in Silurian pelitic schists from N.W. Maine: *Geochim. Cosmochim. Acta* 38, 389-400.
- Cullers, R.L., Chaudhuri, S., Arnold, B., Lee, M., Wolf, C.W.Jr. (1975): Rare earth distributions in clay minerals and in the clay-sized fraction of the Lower Permian Havensville and Eskridge shales of Kansas and Oklahoma: *Geochim. Cosmochim. Acta* 39, 1691-1703.
- Costa, M.L., Fanesca, L.R., Angelica, R.S., Lemos, V.P., Lemos, R.L. (1991): Geochemical exploration of the Maicuru alkaline ultramafic-carbonatite complex, northern Brazil. *J. Geochem. Explor.* 40, 193-204.
- Deady, E., Mouchos, E., Goodenough, K., Williamson, B., Wall, F. (2014): Rare Earth Elements in karst bauxites: a novel untapped European resource?. *ERES2014: 1st European Rare Earth Resources Conference, Milos*, 1-12.
- Decrée, S., Maignac, Ch., De Putter, Th., Yans, J., Clauer, N., Dermech, M. Aloui, K., Baele, J.M.

- (2013): *The Oued Belif Hematite-Rich Breccia: A Miocene Iron Oxide Cu-Au-(U-REE) Deposit in the Nefza Mining District, Tunisia*. *Econ. Geol.* 108, 1425-1457.
- de Ignacio, C., Muñoz, M., Sagredo, J. (2008): *Relaciones de campo y geoquímica de las carbonatitas de Esquinzo-Agua Salada, NW de Fuerteventura, Islas Canarias*. *Geogaceta* 44, 11-14.
- Deliens, M. (1989): *L'agardite-(Y) de Mutoshi, Shaba, Zaïre*. *Ann. Soc. Geol. Belg.* 112, 207-213.
- Deliens, M., Piret, P. (1982): *Bijvoetite et leperonnite, carbonates hydratés d'uranyle et de terres rares de Shinkolobwe, Zaïre*. *Can. Mineral.* 20, 231-238.
- Deliens, M., Piret, P. (1986): *La kamotoïte-(Y), un nouveau carbonate d'uranyle et de terres rares de Kamoto, Shaba, Zaïre*. *Bull. Minéral.* 109, 643-647.
- Deliens, M., Piret, P. (1989): *La shabaïte-(Nd), Ca(Tr)2(UO2)(CO3)4(OH)2.6H2O, nouvelle espèce minérale de Kamoto, Shaba, Zaïre*. *Eur. J. Mineral.* 1, 85-88.
- Demartis, M., Melgarejo, J.C., Colombo, F., Alfonso, P., Coniglio, J.E., Pinoglio, L.P., D'Eramo, F.J. (2014): *Extreme F activities in late pegmatitic events as a key factor for LILE and HFSE enrichment: the Angel pegmatite, Central Argentina*. *Can. Mineral.* 52, 247-269.
- De Parceval, Ph., Fontan, F., Aigouy, T. (1997): *Composition chimique des minéraux de terres rares de Trimouns (Ariège, France)*. *C.R. Acad. Sci. Paris, Ser.1a*, 324, 625-630.
- Ding, R., Wood, S.A. (2002): *The aqueous geochemistry of the rare earth elements and yttrium. Part X. Potentiometric determination of stability constants of acetate complexes of La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup> and Yb<sup>3+</sup> at 25-70°C and 1 bar*. In R. Hellmann y S.A. Wood (eds): *Water-rock interactions, ore deposits, and environmental geochemistry: A tribute to David A Crerar*. *Geochem. Soc., Spec. Publ.* 7, 209-227.
- Donnot, M., Guigues, J., Lulzac, Y., Magnien, A., Parfenoff, A., Picot, P. (1973): *Un nouveau type de gisement d'euporium: la monazite grise à europium en nodules dans les schistes paléozoïques de Bretagne*. *Mineralium Deposita* 8,1, 7-18.
- Doroshkevich, A.G., Viladkar, S.G., Ripp, G.C., Burtseva, M.V. (2009). *Hydrothermal REE mineralization in the Amba Dongar carbonatite complex, Gujarat, India*. *Can. Mineral.* 47, 1105-1116.
- Douville, E., Bienvenu, P., Charlou, J.L., Donval, J.P., Fouquet, Y., Appriou, P., Gamo, T. (1999): *Yttrium and rare earth elements in fluids from various deep-sea hydrothermal systems*. *Geochim Cosmochim Acta* 63, 627-643.
- Downes, H., Balaganskaya, E., Beard, A., Liferovich, R., Demaiffe, D. (2005): *Petrogenetic processes in the ultramafic, alkaline and carbonatitic magmatism in the Kola Alkaline Province: a review*. *Lithos* 85, 48-75.
- Drew, L.J., Qingrun, M., Weijun, S. (1990): *The Bayan Obo iron-rare-earth-niobium deposits, Inner Mongolia, China*. *Lithos* 26, 43-65.
- Drysdall, A.R., Jackson, N.J., Ramsay, C.R., Douch C.J., Hackett, D. (1984): *Rare element mineralization related to Precambrian alkali granites in the Arabian Shield*. *Econ. Geol.* 79, 1366-1377.
- Drysdall, A.R., Douch, C.J. (1986): *Nb-Th-Zr mineralization in microgranite-microsyenite at Jabal Tawlah, Midyan region, Kingdom of Saudi Arabia*. *J. African Earth Sci.* 4, 275-288.
- Dubinina, A.V., Uspenskaya, T.Yu., Gavrilenko, G.M., Rashidov, V.A. (2008): *Geochemistry and genesis of Fe-Mn mineralization in island arcs in the West Pacific Ocean*. *Geochem. Intern.* 46, 1206-1227.
- Dudkin, O.B. (1997): *Asociaciones minerales agpaíticas*. In J.C. Melgarejo (Ed.), *Atlas de asociaciones minerales en lámina delgada*. Edicions UB, Barcelona, 153-160.
- Dumler, F.L., Skorniyakova, K.P., Shul'ga, G.G. (1970): *Lanthanum rhabdophane in the weathered mantle on limestones; a new type of rare earth mineralization*. *Intern. Geol. Rev.* 12, 1140-1145.
- Eby, G.N. (1975): *Abundance and distribution of the rare earth elements and yttrium in the rocks*

- and minerals of the Oka carbonatite complex, Quebec. *Geochim. Cosmochim. Acta* 39, 597-620.
- Ekman, J.M. (2012): Rare earth elements in coal deposits – a prospectivity analysis: Search and Discovery Article #80270. AAPG. Eastern Section meeting, Cleveland, Ohio, 22-26 September 2012. [http://www.searchanddiscovery.com/documents/2012/80270ekmann/ndx\\_ekmann.pdf](http://www.searchanddiscovery.com/documents/2012/80270ekmann/ndx_ekmann.pdf).
- Eliopoulos, D.G., Economou-Eliopoulos, M. (2000): Geochemical and mineralogical characteristics of Fe-Ni- and bauxitic-laterite deposits of Greece. *Ore Geol. Rev.* 16, 41-58.
- Emsbo, P., McLaughlin, P.I., Breit, G.N., du Bray, E.A., Koenig, A.E. (2015): Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis? *Gondwana Res.* 27, 776-785.
- Entingh, D., Vimmerstedt, L. (2005): Geothermal studies and analysis; geothermal chemical byproducts recovery: markets and potential revenues. Princeton Energy Resources International, LLC, Rockville MD, USA, 55 pp.
- Ercit, T.S. (2005): REE-enriched granitic pegmatites. In R.L. Linnen y I.M. Samson (Eds.), *Rare-element Geochemistry and Ore Deposits*. Geol. Assoc. Canada Short Course Notes 17, 257-296.
- Estrade, G., Salvi, S., Béziat, D., Williams-Jones, A.E. (2015): The origin of Skarn-hosted rare-metal mineralization in the Ambohimirahavavy alkaline complex, Madagascar. *Econ. Geol.* 110, 1485-1513.
- Evans, J.R. (1964): Xenotime mineralization in the southern Music Valley area, Riverside County, California. California Division Mines and Geol. Spec. Report 79, 24 p.
- Ewing, R.C., Ehlmann, A.J. (1973): Yttrialite and uraninite, additional minerals from the Rode Ranch Pegmatite, Central Mineral Region, Texas. *Amer. Mineral.* 58, 545-547.
- Fayek, M., Kyser, T.K. (1997): Characterization of multiple fluid-flow events and rare-earth-element mobility associated with formation of unconformity-type uranium deposits in the Athabasca Basin, Saskatchewan. *Can. Mineral.* 35, 627-658.
- Fehr, R., Hochleitner, R. (1984): Agardit-(Ce), ein neues mineral von Lavrion, Griechenland. *Lapis* 1, 22-37.
- Fitzgerald, Sh., Leavens, P.B., Rheingold, A.L., Nelen, J.A. (1987): Crystal structure of a REE-bearing vesuvianite from San Benito County, California. *Am. Mineral.* 72, 625-628.
- Flicoteaux, R., Lucas, J. (1984): Weathering of phosphate minerals. In J.O. Nriagu, P.B. Moore (eds.): *Phosphate minerals*. Springer-Verlag, Berlin: 292-317.
- Foley, N.K., De Vivo, B., Salminen, R. (2013): Rare Earth Elements: The role of geology, exploration, and analytical geochemistry in ensuring diverse sources of supply and a globally sustainable resource. *J. Geochem. Explor.* 133, 1-5.
- Förster, H.J. (1998): The chemical composition of REE-Y-Th-U-rich accessory minerals from peraluminous granites of the Erzgebirge-Fichtelgebirge region, Germany. I. The monazite-(Ce) - brabantite solid solution series. *Am. Mineral.* 83, 259-272.
- Franchini, M., Lira, R., Meinert, L., Ríos, F.J., Poklepovic, M.F., Impiccini, A., Millone, H. (2005): Na-Ca-Fe Alteration and LREE (Th-Nb) Mineralization in Marble and Granitoids of Sierra de Sumampa, Santiago del Estero, Argentina. *Econ. Geol.* 100, 733-764.
- Franz, G., Andrehs, G., Rhede, D. (1996): The crystal chemistry of natural monazite and xenotime from metamorphic rocks—a case study from the Saxothuringian-Moldanubian area in NE Bavaria, Germany. *Eur. J. Mineral.* 8, 1097–1118.
- Fron del, C., Marvin, U.B. (1959): Cerianite, CeO<sub>2</sub>, from Poços de Caldas, Brazil. *Amer. Mineral.* 44, 882-884.
- Fron del, C., Ito, J., Montgomery, A. (1968): Scandium content of some aluminum phosphates. *Amer. Mineral.* 53, 1223-1231.
- Gallup, D. (1998): Geochemistry of Geothermal Fluids and Well Scales, and Potential for Mineral Recovery. *Ore Geol. Rev.* 12, 225-236.
- Gammons, C.H., Wood, S.A., Williams-Jones, A.E. (1996): The aqueous geochemistry of the rare



- earth elements and yttrium: VI. Stability of neodymium chloride complexes from 25 to 300°C. *Geochim. Cosmochim. Acta* 60, 4615-4630.
- Gammons, C.H., Wood, S.A., Li, Y. (2002): Complexation of the rare earth elements with aqueous chloride at 200 C and 300 C and saturated water vapor pressure. *Geochem. Soc. Spec. Publ.* 7, 191-207.
- Garrett, D.E. (1998): *Borates. Handbook of deposits, processing, properties, and use.* Academic press, 483 pp.
- Gauthier, M., Chartrand, F., Cayer, A., David, J. (2004): The Kwajibo Cu-REE-U-Au-Mo-F property, Quebec; a Mesoproterozoic polymetallic iron oxide deposit in the north-eastern Grenville Province. *Econ. Geol.* 99, 1177-1196.
- Gieré, R. (1990): Hydrothermal Mobility of Ti, Zr and REE: Examples from the Bergell and Adamello Contact Aureoles (Italy). *Terra Nova* 2, 60-67.
- Gilbert, C.D., Williams-Jones, A.E. (2008): Vapour transport of rare earth elements (REE) in volcanic gas: Evidence from encrustations at Oldoinyo Lengai. *J. Volcanol. Geothermal Res.* 176, 519-528.
- Gittins, J. (1989): The origin and evolution of carbonatite magmas. In K. Bell (ed.): *Carbonatites: Genesis and Evolution.* London: Unwin Hyman, 580-600.
- Gittins, J., McKie, D. (1979): Alkalic carbonatite magmas: Oldoinyo Lengai and its wider applicability. *Lithos* 13, 213-215.
- Giuliani, G., Rodríguez, C.T., Rueda, F. (1990): Les gisements d'émeraude de la Cordillère orientale de la Colombie: nouvelles données métallogéniques. *Mineralium Deposita* 25: 105-111.
- Giuliani, G., Sheppard, S.M.F., Cheilletz, A. (1992): Fluid inclusions and 180/160, 13C/12C isotope geochemistry contribution to the genesis of emerald deposits from the Oriental Cordillera of Colombia. *C. R. Acad. Sci. Paris* 314,II, 269-274.
- González del Tánago, J. (1997): Allanita-(Nd) y minerales de elementos raros en las pegmatitas graníticas de La Cabrera, Madrid (Sistema Ibérico Central). *Rev. Soc. Geol. España* 10, 83-105.
- Gow, N.N., Lozej, G.P. (1993): Bauxite. *Geosc. Canada* 20, 9-16.
- Gow, P.A., Wall, V.J., Oliver, N.S., Valenta, R.K. (1994): Proterozoic iron oxide (Cu-U-Au-REE) deposits: Further evidence of hydrothermal origins. *Geology* 22, 633-636.
- Graeser, S., Roggiani, A.G. (1976): Occurrence and genesis of rare arsenate and phosphate minerals around Pizzo Cervandone, Italy/Switzerland. *Rend. Soc. Ital. Mineral. Petrol.*, 32, 279-288.
- Graeser, S., Schwander, H. (1987): Gasparite-(Ce) and monazite-(Nd): two new minerals to the monazite group from the Alps. *Schweiz. Mineral. Petrog. Mitt.* 67, 103-113.
- Gratz, R., Heinrich, W. (1997): Monazite-xenotime thermobarometry: Experimental calibration of the miscibility gap in the binary system CePO<sub>4</sub>-YPO<sub>4</sub>. *Am. Mineral.* 82, 772-780.
- Grauch, R.I., Mariano, A.N. (2008): Ion-adsorption type lanthanide deposits[abs]: Society of Mining, Metallurgy and Exploration Annual Meeting and Exhibit Preliminary Program, p. 40.
- Grauch, R.I., Verplanck, Ph.L., Seeger, Ch.M., Budahn, J.R., Van Gosen, B.S. (2010): Chemistry of selected core samples, concentrate, tailings, and tailings pond waters: Pea Ridge Iron(-Lanthanide-Gold) ceposit, Washington County, Missouri. *U.S. Geol. Surv. Open-File Report* 2010-1080, 1-15.
- Grice, J.C., Chao, G.Y. (1997): Horváthite-(Y), a rare-earth fluorocarbonate, a new mineral species from Mont Saint-Hilaire, Quebec. *Can. Mineral.* 35, 743-749.
- Grice, J.D., Rowe, R., Poirier, G., Pratt, A., Francis (2009) Bussyite-(Ce), a new beryllium silicate mineral species from Mont Saint-Hilaire, Quebec. *Can. Mineral.* 47, 193-204.
- Groves, D.I., Bierlein, F.P., Meinert, L.D., and Hitzman, M.W. (2010): Iron Oxide-Copper-Gold (IOCG) Deposits Through Earth History: Implications for Origin, Lithospheric Setting and

- Distinction from Other Epigenetic Iron Oxide Deposits: Econ. Geol.* 105, 641-654.
- Guo, S., Sun, W., Chen, Y. (1990a): Structure and texture characteristics of deep sea manganese nodules and their diagenesis. Abstracts 15th General Meeting IMA, vol. 2, Beijing: 719-720.
- Guo, S., Sun, W., Xiao, X., Lin, Y., Yang, M., Chen, Y. (1990b): Mineralogy of manganese nodules from Northern Equatorial Pacific Ocean. Abstracts 15th General Meeting IMA, vol. 1, Beijing: 253-254.
- Haas, J.R., Shock, E.L., Sassani, D.C. (1995): Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. *Geochim. Cosmochim. Acta.* 59, 4329-4350.
- Haggerty, S.E., Mariano, A.N. (1983): Strontianloparite and strontiochevkinite: two new minerals in rheomorphic fenites from the Parana Basin carbonatites, South America. *Contrib. Mineral. Petrol.* 84, 365-381.
- Hatch, G.P. (2012): Dynamics in the global market for Rare Earths. *Elements* 8, 341-346.
- Hanson, S.L., Simmons, W.B., Webber, K.L., Falster, A.U. (1992): Rare-earth-element mineralogy of granitic pegmatites in the Trout Creek Pass District, Chaffee County, Colorado. *Can. Mineral.* 30, 673-686.
- Harris, N.B.W., Marzouki, F.M.H., Alí, S. (1986): The Jabal Sayid complex, Arabian Shield. Geochemical constraints on the origin of peralkaline and related granites. *J. Geol. Soc. London* 143, 287-295.
- Hauck, S.A. (1990): Petrogenesis and tectonic setting of middle Proterozoic iron oxide-rich ore deposits—An ore deposit model for Olympic Dam-type mineralization. *U.S. Geol. Surv. Bull.* 1932, 4-39.
- Hedrick, J.B. (1998): Rare earths: U.S. Geological Survey Minerals Yearbook 1997. [[http://minerals.usgs.gov/minerals/pubs/commodity/rare\\_earths/740498.pdf](http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/740498.pdf)]
- Hein, J.R., Koschinsky, A., Halbach, P., Manheim, F.T., Bau, M., Kang, J.-K., Roberts, L. (2000): Cobalt-rich ferromanganese crusts in the Pacific. In: *Handbook of Marine Mineral Deposits* In S. Cronan, (ed.). CRC Press, Boca Raton, Florida, 239-279.
- Hein, J.R., Conrad, T.A., Staudigel, H. (2010): Seamount mineral deposits - a source of rare metals for high-technology industries. *Oceanography* 23: 184-189.
- Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A. (2013): Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. *Ore Geol. Rev.* 51, 1-14.
- Hill, C., Forti, P. (1997): *Cave minerals of the world.* Huntsville, Alabama, National Speleological Society, 463 p.
- Hitzman, H.D. (2000): Iron oxide Cu-Au deposits. What, where, when, and why?. In T.M. Porter (ed.): *Hydrothermal Iron Oxide Copper-Gold and Related Deposits: A Global Perspective, Volume 1: Adelaide*, Australian Mineral Foundation, 201–218.
- Hitzman, M.W., Oreskes, N., Einaudi, M.T. (1992): Geological characteristics and tectonic setting of Proterozoic iron oxide (Cu-U-Au-REE) deposits. *Precambrian Research* 58, 241-287.
- Hoernle, K., Tilton, G., Le Bas, M.J., Duggen, S., Garbe-Schönberg, D. (2002): Geochemistry of oceanic carbonatites compared with continental carbonatites: mantle recycling of oceanic crustal carbonate. *Contrib. Mineral. Petrol.* 142, 520-542.
- Hogarth, D.D., Chao, G.Y., Plant, A.G., Steacy, H.R. (1974): Caysichite, a new silico-carbonate of yttrium and calcium. *Can. Mineral.* 12, 293-298.
- Holtstam, D., Andersson, U.B. (2007): The REE minerals of the Bastnäs-type deposits, south-central Sweden. *Can. Mineral.* 45, 1073-1114.
- Holtstam, D., Grins, J., Nysten, P. (2004): Haleniusite-(La) from the Bastnäs deposit, Västmanland, Sweden: a new REE oxyfluoride mineral species. *Can. Mineral.* 42, 1097-1103.
- Horbe, A., Costa, M. (1999): Geochemical evolution of a lateritic Sn-Zr-Th-Nb-Y-REE bearing ore body derived from apogranite: the case of Pitinga,

- Amazonas-Brazil. *J. Geochem. Explor.* 66, 339-351.
- Hornig-Kjarsgaard, I. (1998): Rare earth elements in sövitic carbonatites and their mineral phases. *J. Petrol.* 39, 2105-2121.
- Horvart, L., Gault, R.A. (1990): The mineralogy of Mount Saint Hilaire, Québec. *Mineral. Record* 21,4, 283-310.
- Hower, J.C., Ruppert, L.F., Eble, C.F. (1999): Lanthanum, yttrium, and zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky: *Int. J. Coal Geol.* 39, 141-153.
- Hower, J.C., Groppo, J.G., Henke, K.R., Hood, M.M., Eble, C.F., Honaker, R.Q., Zhang, W., Qian, D. (2015): Notes on the potential for the concentration of Rare Earth Elements and Yttrium in coal combustion fly ash.
- Hunt, J.A., Baker, T., Thorkelson, D.J. (2007): A Review of Iron Oxide Copper-Gold Deposits, with Focus on the Wernecke Breccias, Yukon, Canada, as an Example of a Non-Magmatic End Member and Implications for IOCG Genesis and Classification. *Explor. Mining Geol.* 16, 209-232.
- Jackson, W.D., Christiansen, G. (1993): International strategic minerals inventory summary report- Rare-earth oxides. U.S. Geological Survey Circular 930-N, 68 p.
- Janeczek, J., Ewing, R. (1996): Phosphatian co-finite with rare earth elements and Ce-rich françoisite-(Nd) from sandstone beneath a natural fission reactor at Bangombé, Gabon. *Mineral. Mag.* 60, 665-669.
- Johan, Z., Johan, V. (1994): REE oxyfluorides from the Cinovec granitic cupola, Czech Republic. *C.R. Acad. Sci. Paris, Sér. II*, 318, 1333-1340.
- Kampunzu, A., Mohr, P. (1991): Magmatic evolution and petrogenesis in the East African Rift system. In A. B. Kampunzu and R.T. Lubala (eds.), *Magmatism in Extensional Settings, the Phanerozoic African Plate*. Springer-Verlag, Berlin, 85-136.
- Kato, Y., Fujinaga, K., Nakamura, K., Takaya, Y., Kitamura, K., Ohta, J., Toda, R., Nakashima, T., Iwamori, H. (2011): Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements. *Nature Geosciences* 4, 535-539.
- Kerr, I.D. (1998): Mineralogy, chemistry and hydrothermal evolution of the Pea Ridge iron-oxide-rare earth element deposit, Missouri, United States of America. Unpubl. Ph.D. thesis, Univ. Windsor, Electronic Theses and Dissertations. Paper 2735. 113 p. <http://scholar.uwindsor.ca/cgi/viewcontent.cgi?article=3734&context=etd>.
- Khater, A.E.M. (2004): Polonium-210 budget in cigarettes. *J. Envir. Radioactivity* 71, 33-41.
- Khomyakov, A.P., Sørensen, H. (2001): Zoning in steenstrupine-(Ce) from the Ilimaussaq alkaline complex, South Greenland: a review and discussion. *Geol. Greenland Surv. Bull.* 190, 109-118.
- Kirnarskii, Iu.M. (1997): Carbonatitas. In J.C. Melgarejo (ed.): *Atlas de asociaciones minerales en lámina delgada*. Ed. UB, 66-78.
- Kjellman, J., \_ern\_, P., Smeds, S.A. (1999): Diversified NYF pegmatite populations of the Swedish Proterozoic: outline of a comparative study. *Can. Mineral.* 37, 832-833.
- Klinkhammer, G., Elderfield, H., Hudson, A. (1983): Rare earth elements in seawater near hydrothermal vents. *Nature*, 305: 185-188.
- Klyucharev, D.S., Volkova, N.M., Comyn, M.F. (2013): The problems associated with using non-conventional rare-earth minerals. *J. Geochem. Explor.* 133, 138-148.
- Kogarko, L.N. (1990): Ore-forming potential of alkaline magmas. *Lithos* 26, 167-175.
- Kogarko, L.N., Kononova, V.A., Orlova, M.P., Woolley, A.R. (1995): *Alkaline Rocks and Carbonatites of the World. Part 2: Former USSR*. London, Chapman and Hall, 226 p.
- Kogarko, L.N., Kononova, V.A., Vartiainen, H. (1995): Kola and Karelia. in *Alkaline Rocks and Carbonatites of the World., Part H: Former USSR*, Chapman & Hall, 10-45.
- Kogarko, L.N., Williams, C.T., Woolley, A.R. (2002): Chemical evolution and petrogenetic

- implications of loparite in the layered, agpaitic Lovozero complex, Kola Peninsula, Russia. *Mineralogy and Petrology*, 74, 1-24.
- Koschinsky, A., Halbach, P. (1995): Sequential leaching of marine ferromanganese precipitates: genetic implications. *Geochim. Cosmochim. Acta* 59: 5113-5132.
- Koschinsky, A., Hein, J.R. (2003): Acquisition of elements from seawater by ferromanganese crusts: Solid phase associations and seawater speciation. *Marine Geol.* 198: 331-351.
- Koschinsky, A., Hein, J., Schmidt, K., Alexander, B., Bau, M. (2010): Rare and Valuable Metals for High-Tech Applications Found in Marine Ferromanganese Nodules and Crusts: Relationships To Genetic End members. Toward the Sustainable Development of Marine Minerals: Geological, Technological, and Economic Aspects UMI 2010 · Gelendzhik, Russia.
- Kovalenko, V.I., Tsaryava, G.M., Goreglyad, A.V., Yarmolyuk, V.V., Troitsky, V.A., Hervig, R.L., Farmer, G.L. (1995): The peralkaline granite-related Khaldzan-Buregtey rare metal (Zr, Nb, REE) deposit, western Mongolia. *Econ. Geol.* 90, 530-547.
- Kralec, K. (2011): Rare Earth Elements prospects and occurrences in Utah. *Bull. Utah Geol. Surv.* 47 pp.
- Kravchenko, S.M., Pokrovskiy, B.G. (1995): The Tomtor alkaline ultrabasic massif and related REE-Nb deposits, northern Siberia. *Econ. Geol.* 90, 676-689.
- Kravchenko, S.M., Czamanske, G., Fedorenko, V.A. (2003): Geochemistry of carbonatites of the Tomtor massif. *Geochem. Internat.* 41, 545-558.
- Kraynov, S.R., Mer'kov, A.N., Petrova, N.G., Baturinskaya, I.V., Zharikova, V.M. (1969): Highly alkaline (pH>12) fluosilicate waters in the deeper zones of the Lovozero massif, *Geochem. Int.* 6, 635-640.
- Kruger, N. (2015): A "rare" opportunity. *Newsletter Nevada Geol. Surv.* 6-8.
- Kumral, M., Çoban, H., Caran, S. (2007): Th-, U- and LREE-bearing grossular, chromian ferriallanite-(Ce) and chromian cerite-(Ce) in skarn xenoliths ejected from the Gölcük maar crater, Isparta, Anatolia, Turkey. *Can. Mineral.* 45, 1115-1129.
- Kwak, T.A.P., Abeyasinghe, P.B. (1987): Rare earth and uranium minerals present as daughter crystals in fluid inclusions, Mary Kathleen U-REE skarn, Queensland, Australia. *Mineral. Mag.* 51, 665-670.
- Kynicky, J., Smith, M.P., Xu, C. (2012): Diversity of rare earth deposits; the key example of China. *Elements* 8, 361-367.
- Kyser, K., Cuney, M. (2009): Chapter 8: Unconformity-related uranium deposits. In M. Cuney, M. y K. Kyser (eds.), *Recent and Not-So-Recent Developments in Uranium Deposits and Implications for Exploration*. Mineral. Assoc. Canada, Short Course Series, 161-219.
- Laskou, M., Andreou, G. (2003): Rare earth elements distribution and REE-minerals from the Parnassos-Ghiona bauxite deposits, Greece. In d. Eliopoulos, et al. (Ed.), *Mineral Exploration and Sustainable Development*, 7th Biennial SGA Meeting, Athens. Mill Press, Rotterdam, 89-92.
- Lauf, R.J. (1997): Secondary sulfate minerals from Alum Cave Bluff: microscopy and microanalysis. *Metals & Ceramic Division, Oak Ridge National Laboratory, ORNL/TM-1347*. 43p.
- Lefebvre, J.-J., Gasparini, C. (1980): Florencite, an occurrence in the Zairian Copperbelt. *Can. Mineral.* 18, 301-311.
- Lehbib, S. (2015): Estudio geológico y metalogénico del precámbrico del Sáhara Occidental. Tesis doctoral inédita. Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals de la Universitat de Barcelona. Pendiente de presentación.
- Lehbib, S., Arribas, A., Melgarejo, J.C., Martin, R.F. (2011): Rare-element minerals of the alkaline suites of the Western Sahara. *Peralk-carb*, Thübingen.
- Lentz, D.R. (1998): Late-tectonic U-Th-Mo-REE-skarn and carbonatitic vein-dyke systems in the southwestern Grenville Province: a pegmatite-related pneumatolytic model linked to marble melting (limestone syntexis). In D.R. Lentz (ed.). *Mineralized Intrusion-Related Skarn Systems*. Mineral. Assoc. Can., Short Course 26, 519-657.

- Li, Zaihui, Din, Jun, Xu, Jinsha, Liao, Chaogui, Yin, Fuguang, L., Tao, Cheng, Li, Li, Junmin (2013): Discovery of the REE minerals in the Wulong-Nanchuan bauxite deposits Chongqing, China: Insights on conditions of formation and processes. *J. Geochem. Explor.* 133, 88-102.
- Li, Xiaochun, Zhao, Xinfu, Zhou, Mei-Fu, Chen, Wei Terry, Chu, Zhuyin (2015): Fluid Inclusion and Isotopic Constraints on the Origin of the Paleoproterozoic Yinachang Fe-Cu-(REE) Deposit, Southwest China. *Econ. Geol.* 110, 1339-1369.
- Linnen, R.L., Van Lichtervelde, M., \_ern\_, P. (2012): Granitic pegmatites as sources of strategic metals. *Elements* 8, 275-280.
- Linnen, R.L., Samson, I.M., Williams-Jones, A.E., Chakhmouradian, A.R. (2014): Geochemistry of the rare-earth element, Nb, Ta, Hf, and Zr deposits. In H. Holland and K. Turekian (eds.): *Treatise on Geochemistry, Second Edition*, Elsevier. Vol. 13, 543-568.
- London, D. (2008): Pegmatites. *Can. Mineral. Spec. Publ.* 10, 347 pp.
- Long, K.R., Van Gosen, B.S., Foley, N.K., Cordier, D. (2010): The principal rare earth elements deposits of the United States. A summary of domestic deposits and a global perspective. *U.S. Geol. Surv. Sci. Invest. Rep.* 2010-5220.
- Lottermoser, B.G. (1995): Rare earth element mineralogy of the Olympic Dam Cu-U-Au-Ag deposit, Roxby Downs, South Australia: implications for ore genesis. *Neues Jahrb. Mineral., Monatsh.*, 371-384.
- Lottermoser, B.G. (1987): Churchite from the Mt Weld carbonatite laterite, Western Australia. *Mineral. Mag.* 51, 468-469.
- Lottermoser, B.G. (1990): Rare-earth element mineralisation within the Mt. Weld carbonatite laterite, Western Australia. *Lithos* 24, 151-167.
- Lumpkin, G.R. (1998): Rare-element mineralogy and internal evolution of the Rutherford #2 pegmatite, Amelia County, Virginia: A classic locality revisited. *Can. Mineral.* 36, 339-353.
- Maksimovic, Z., Pantó, G. (1985): Hydroxyl-bas-  
tnaesite-(Nd), a new mineral from Montenegro, Yugoslavia. *Mineral. Mag.* 49, 717-720.
- Maksimovic, Z.J., Pantó, Gy (1996): Authigenic rare-earth minerals in karst bauxites and karstic nickel deposits. In A.P. Jones, F. Wall, C.T. Williams (Eds.): *Rare Earth Minerals: Chemistry, Origin and Ore deposits. Mineral. Soc. Series* 7, 257-279.
- Malcherek, T., Mihailova, B., Schlüter, J., Husdal, T. (2012): Atelisite-(Y), a new rare earth defect silicate of the KDP structure type. *Eur. J. Mineral.* 24, 1053-1060.
- Mameli, P., Mongelli, G., Oggiano, G., Dinelli, E. (2007): Geological, geochemical and mineralogical features of some bauxite deposits from Nurra (Western Sardinia, Italy): insights on conditions of formation and parental affinity. *Intern. J. Earth Sci.* 96, 887-902.
- Manfredi, T.R., Neto, A.C.B., Pereira, V.P., Barbanson, L., Schuck, C. (2013): The parisite-(Ce) mineralization associated with the Fazenda Varela carbonatite (Correia Pinto, SC). *Pesquisas em Geociências* 40, 295-307.
- Mangas, J., Pérez-Torrado, F.J., Reguilón, R.M., Martín-Izard, A. (1997): Rare earth minerals in carbonatites of Basal Complex of Fuerteventura (Canary Islands, Spain). In H. Papunen (ed.): *Mineral Deposits, Research and Exploration. Where do they meet?* Balkema, Rotterdam, 475-478.
- Manning, D.A.C., Hill, P.I. (1990): The petrogenetic and metallogenetic significance of topaz granite from the Southwest England orefield. In H.J. Stein, Hannah, J.L. (eds.): *Ore-bearing granite systems; petrogenesis and mineralizing processes.* *Geol. Soc. Am. Spec. Paper* 246, 89-102.
- Maravic, H.V., Morteani, G. (1980): Petrology and geochemistry of the carbonatite and syenite complex of Lueshe, NE Zaire. *Lithos* 13, 159-170.
- Mariano, A.N. (1989a): Nature of economic mineralization in carbonatites and related rocks. In K. Bell (Ed.): *Carbonatites-Genesis and Evolution.* Unwin Hyman, London, 149-176.
- Mariano, A.N. (1989b): Economic geology of rare-earth elements. In: B.R. Lipin y G.A. McKay (eds): *Geochemistry and mineralogy of rare earth ele-*

- ments. *MSA Rev. Mineral.* 21, 309-337.
- Marmont, S. (1990): *Unconformity-type uranium deposits*. In R.G. Roberts y P.A. Sheenan (eds). *Ore deposit models*. *Geoscience Canada Reprint Series 3*, 103-115.
- Martin, R.F., De Vito, C. (2005): *The pattern of enrichment in felsic pegmatites ultimately depend on tectonic setting*. *Can. Mineral.* 43, 2027-2048.
- Martins, T., Chakhmouradian, A.R., Medici, L. (2014): *Perovskite alteration in kimberlites and carbonatites: the role of kassite, CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub>*. *Phys. Chem. Minerals*, 41, 473-484.
- Mathew, M., Takagi, S., Waerstad, K.R., Frazier, A.W. (1981): *The crystal structure of synthetic chukhrovite, Ca<sub>4</sub>AlSi(SO<sub>4</sub>)F<sub>13</sub>•12H<sub>2</sub>O*. *Amer. Mineral.* 66, 392-397.
- McKay, D. (1962): *Goyazite and florencite from two african carbonatites*. *Mineral. Mag.* 33, 281-297.
- McLemore, V.T. (2010): *Geology and mineral deposits of the Galinas Mountains, Lincoln and Torance Counties, New Mexico: Preliminary report*. New Mexico Bureau of Geology and Mineral Resources. New Mexico Institute of Mining and Technology. Open File Report OF-532, 92 p.
- McPhie, J., Kamenetsky, V., Allen, Sh., Ehrig, K., Agangi, A., Bath, A. (2011): *The fluorine link between a supergiant ore deposit and a silicic large igneous province*. *Geology* 39, 1003-1006.
- Meinert, L.D., Dipple, G.M., Nicolescu, S. (2005): *World skarn deposits*. *Econ. Geol.* 100th Anniv. Vol., 299-336.
- Meintzer, R., Mitchell, R.S. (1988): *The epigene alteration of allanite*. *Can. Mineral.* 26, 945-955.
- Melgarejo, J.C. (1992): *Estudio geológico y metalogenético del Paleozoico del sector sur de las Cordilleras Costeras Catalanas*. *Col. Monografías ITGE* 103, 605 p.
- Melgarejo, J.C., Alfonso, P. (1997): *Depósitos estratiformes de hierro y de manganeso*. In J.C. Melgarejo (Ed.), *Atlas de asociaciones minerales en lámina delgada*. Edicions UB, Barcelona, 309-322.
- Melgarejo, J.C., Fontan, F., Alfonso, P., Camprubí, A., Costa, F., Salvany, M.C., Sáez, G., Arcas, A. (1997): *Asociaciones minerales de rocas fosfáticas sedimentarias y sus derivados meteóricos y metamórficos*. In J.C. Melgarejo (Ed.), *Atlas de asociaciones minerales en lámina delgada*. Edicions UB, Barcelona, 129-152.
- Melgarejo, J.C., Prol-Ledesma, R.M. (1999): *Th and REE deposits in the Oaxaca Complex in southern Mexico*. In C.J. Stanley et al. (eds): *Mineral Deposits: Processes to Processing*. Balkema, Rotterdam, The Netherlands (389-392).
- Melgarejo, J.C., Costanzo, A., Bambi, A.C.J.M., Gonçalves, A.O., Neto, A.B. (2012): *Subsolidus processes as a key factor on the distribution of Nb species in plutonic carbonatites: the Tchivira case, Angola*. *Lithos* 152, 187-201.
- Metz, M.C., Brookins, D. G., Rosenberg, P.E., Zartman, R.E. (1985): *Geology and geochemistry of the Snowbird deposit, Mineral County, Montana*. *Econ. Geol.* 80, 394-409.
- Migdisov, A.A., Williams-Jones, A.E. (2002): *A spectrophotometric study of neodymium (III) complexation in chloride solutions*. *Geochim. Cosmochim. Acta* 66, 4311-4323.
- Migdisov, A.A., Williams-Jones, A.E. (2006): *A spectrophotometric study of erbium (III) speciation in chloride solutions at elevated temperatures*. *Chem. Geol.* 234, 17-27.
- Migdisov, A.A., Reukov, V.V., Williams-Jones, A.E. (2006): *A spectrophotometric study of neodymium (III) complexation in sulfate solutions at elevated temperatures*. *Geochim. Cosmochim. Acta* 70, 983-992.
- Migdisov, A.A., Williams-Jones, A.E. (2007): *An experimental study of the solubility and speciation of neodymium (III) fluoride in F-bearing aqueous solutions*. *Geochim. Cosmochim. Acta* 71, 3056-3069.
- Migdisov, A.A., Williams-Jones, A.E. (2008): *A spectrophotometric study of Nd(III), Sm(III) and Er(III) complexation in sulfate-bearing solutions at elevated temperatures*. *Geochim. Cosmochim. Acta* 72, 5291-5303.
- Migdisov, A.A., Williams-Jones, A.E., Wagner, T.

- (2009) An experimental study of the solubility and speciation of the Rare Earth Elements (III) in fluoride- and chloride-bearing aqueous solutions at temperatures up to 300°C. *Geochim. Cosmochim. Acta* 73, 7087-7109.
- Migdisov, A.A., Williams-Jones, A.E. (2014): Hydrothermal transport and deposition of the rare earth elements by fluorine-bearing aqueous liquids. *Mineralium Deposita* 49, 987-997.
- Milton, C., Ingram, B., Clark, J.R., Dwornik, E.J. (1965): Mckelveyite, a new hydrous sodium barium rare-earth uranium carbonate mineral from the Green River Formation, Wyoming. *Amer. Mineral.* 50, 593-612.
- Minuzzi, O.R.R., Ferron, J.M.T.M., Neto, A.C.B., Pereira, V.P. (2003): Primeira Notícia da Descoberta de Waimirita e Atroarita, Dois Novos Minerais na Mina de Pitinga, AM, Brasil. *Pesquisas em Geociências* 30, 99-101.
- Mitchell, R.H. (1996): Classification of undersaturated and related alkaline rocks. In R.H. Mitchell (ed.): *Undersaturated alkaline rocks: mineralogy, petrogenesis and economic potential*. MAC Short Course 24, Winnipeg, Manitoba, 1-22.
- Mitchell, R.H. (2005): Carbonatites and carbonatites and carbonatites. *Can. Mineral.* 43, 2049-2068.
- Mitchell, R.H., Chakhmouradian, A.R. (1996): Compositional variation of loparite from the Lovozero alkaline complex, Russia. *Can. Mineral.* 34, 977-990.
- Mitchell, R.H., Chakhmouradian, A.R. (1998): Th-rich loparite from the Khibina alkaline complex, Kola Peninsula: isomorphism and paragenesis. *Mineral. Mag.* 62, 341-353.
- Mitchell, R.H., Chakhmouradian, A.R. 1999): Sr-bearing perovskite and loparite from lamproite and agpaite nepheline enite pegmatites. *Can. Mineral.* 37, 99-112.
- Modreski, P.J. (1979): Rare Earth Elements in agardite and in other minerals from the Red Cloud district. Abstracts 1st Annual New Mexico Mineral Symposium. November 29-30, Socorro, NM, 10.
- Möller, P. (1989b): REE(Y), Nb, and Ta enrichment in pegmatites and carbonatite-alkalic rock complexes. In P. Möller, P. \_ern\_, F. Saupé (eds): *Lanthanides, Tantalum and Niobium*. Springer-Verlag, Berlin, 104-144.
- Mongelli, G. (1997): Ce-anomalies in the textural components of Upper Cretaceous karst bauxites from the Apulian carbonate platform (southern Italy). *Chem. Geol.* 140, 69-79.
- Mordberg, L.E. (1993): Patterns of distribution and behaviour of trace elements in bauxites. *Chem. Geol.* 107, 241-244.
- Mordberg, L.E. (1999): Geochemical evolution of a Devonian diaspore-crandallite-svanbergite-bearing weathering profile in the Middle Timan, Russia. *J. Geochem. Explor.* 66, 353-361.
- Mordberg, L.E., Stanley, C.J., Germann, K. (2000): Rare earth element anomalies in crandallite group minerals from the Schugorsk bauxite deposit, Timan, Russia. *Eur. J. Mineral.* 12, 1229-1243.
- Morteani, G., Preinfalk, C. (1996): REE distribution and REE carriers in laterites formed on the alkaline complexes of Araxá and Catalão, Brazil. In A.P. Jones, F. Wall, C.T. Williams (Eds.): *Rare Earth Minerals: Chemistry, Origin and Ore deposits*. Mineral. Soc. Series 7, 227-255.
- Mortimer, H., Staatz, Van E., Saw, A.D., Walber, J.S. (1972): Occurrence and distribution of Rare Earths in the Lemhi Pass Thorium veins, Idaho and Montana. *Econ. Geol.* 67, 72-82.
- Moxham, R.M., Walker G.W., Baumgardner, L.H. (1958): Geologic and airborne radioactivity studies in the Rock Corral area, San Bernardino County, California. *U.S. Geol. Surv. Bull.* 1021-C, 109-125.
- Nadeau, O., Cayer, A., Pelletier, M., Stevenson, R., Jébrak, M. (2015): The Paleoproterozoic Montviel carbonatite-hosted REE -Nb deposit, Abitibi, Canada: Geology, mineralogy, geochemistry and genesis. *Ore Geol. Rev.* 67, 314-335.
- Nagasawa, H. (1970): Rare earth concentrations in zircons and apatites and their host dacites and granites. *Earth Planet. Sci. Letters* 9, 359-364.
- Nagy, G., Draganits, E., Demény, A., Pantó, G., Árkai,

- P. (2002): Genesis and transformation of monazite, florencite and rhabdophane during medium grade metamorphism: examples from the Sopron Hills, Eastern Alps. *Chemical Geology* 191, 25-46.
- Nasraoui, M., Toulkeridis, Th., Clauer, N., Bilal, E. (2000): Differentiated hydrothermal and meteoric alterations of the Lueshe carbonatite complex (Democratic Republic of Congo) identified by a REE study combined with a sequential acid-leaching experiment. *Chem. Geol.* 165, 109-132.
- Neary, C.R., Highley, D.E. (1984): The economic importance of the rare earth elements. In P. Henderson (ed.), *Rare Earth Element Geochemistry*. Amsterdam, Elsevier, 423-466.
- Neto, A.C.B., Pereira, V.P., Ronchi, L.H., de Lima, E.F., Frantz, J.C. (2009): The world-class Sn, Nb, Ta, F (Y, REE, Li) deposit and the massive cryolite associated with the albite-enriched facies of the Madeira A-type granite, Pitinga mine district, Amazonas State, Brazil. *Can. Mineral.* 47, 1329-1357.
- Neumann, H. (1961): The scandium content of some Norwegian minerals and the formation of thortveitite, a reconnaissance study. *Norsk Geol. Tidss.* 41, 197-210.
- Ngwenya, B.T. (1994): Hydrothermal rare earth mineralisation in carbonatites of the Tundulu complex, Malawi: processes at the fluid-rock interface. *Geochim. Cosmochim. Acta* 58, 2061-2072.
- Ni, Y., Hughes, J.M., Mariano, A.N. (1995): Crystal chemistry of the monazite and xenotime structures. *Am. Mineral.* 80, 21-26.
- Nilssen, B. (1971): Yttrialite from Ivedal, Iveland, South Norway. *Norsk. Geol. Tidss.* 51, 1-8.
- Nilssen, B. (1973): Gadolinite from Hundholmen, Tysfjord, North Norway. *Norsk. Geol. Tidss.* 55, 343-348.
- Nuelle, L.M., Day, W.C., Sidder, G.B., Seeger, C.M. (1992): Geology and mineral paragenesis of the Pea Ridge iron ore mine, Washington County, Missouri. Origin of the rare-earth-element- and gold-bearing breccia pipes: U.S. Geological Survey Bulletin 1989A, 11 p.
- Olmi, F., Sabelli, C., Brizzi, G. (1988): Agardite-(Y), gysinite-(Nd) and other rare minerals from Sardinia. *Mineral. Record* 19, 305-310.
- Olson, J.C., Shawe, D.R., Pray, L.C., Sharp, W.N. (1954): Rare-Earth Mineral Deposits of the Mountain Pass District, San Bernardino County California. *Geol. Surv. Prof. Paper* 261, 1-91.
- Olson, J.C., Marvin, R.F., Park, R.L., Mehnert, H.H. (1977): Age and tectonic setting of lower paleozoic alkalic and mafic rocks, carbonatites, and thorium veins in south-central Colorado: U.S. Geol. Surv. J. Res. 5, 673-687.
- Oreskes, N., Einaudi, M.T. (2006): Origin of rare earth element-enriched hematite breccias at the Olympic Dam Cu-U-Au-Ag deposit, Roxby Downs, South Australia. *Econ. Geol.* 85, 1-28.
- Orozco, G., Rizo, R. (1998): Depósitos de zeolitas naturales de Cuba. In J. proenza y J.C. Melgarejo (eds.): *Introducción a la geología y metalogenia de Cuba*. *Acta Geol. Hispan.* 33, 335-349.
- Orris, G.J., Grauch, R.I. (2002): *Rare Earth Element Mines, Deposits, and Occurrences*. USGS.Open-File Rep. 02-189. Reston, VA.
- Owen, R.M., Olivarez, A.M. (1988): Geochemistry of rare earth elements in Pacific hydrothermal sediments. *Marine Chem.* 25, 183-196.
- Pan, Y., Stauffer, M.R. (2000): Cerium anomaly and Th/U fractionation in the 1.85 Ga Flin Flon Paleosol: clues from REE- and U-rich accessory minerals and implications for paleoatmospheric reconstruction. *Am. Mineral.* 85, 898-911.
- Papangelakis, V.G., Moldoveanu, G. (2014): Recovery of rare-earth elements from clay minerals. ERES2014: 1st European Rare Earth Resources Conference. Milos, 191-202.
- Pardillo Vaquer, F. (1947): La caliborita de Sallent. *Estudios Geológicos* 7, 41-55.
- Peacor, D.R., Rouse, R.C., Essene, E.J. (1999): Coskrenite-(Ce),  $(Ce,Nd,La)_2(SO_4)_2(C_2O_4) \cdot 8H_2O$ , a new rare-earth oxalate mineral from Alum Cave Bluff, Tennessee: characterization and crystal structure. *Can. Mineral.*, 37, 1453-1462.
- Pekov, I.V., Chukanov, N.V., Rønso, J.G., Sørensen,



- H. (1997a): *Erikite - a pseudomorph after vitusite*. *Neues Jahrb. Mineral. Monatsh.*, 97-112.
- Pekov, I.V., Petersen, O.V., Voloshin, A.V. (1997b): *Calcio-ancylite-(Ce) from Ilímaussaq and Narssârssuk, Greenland, Kola peninsula and Polar Urals, Russia; ancylite-(Ce)-calcioancylite-(Ce) an isomorphous series*. *Neues Jahrb. Mineral. Abh.* 171, 309-322.
- Pekov, I.V., Zubkova, N.V., Husdal, T.A., Kononkova, N.N., Agakhanov, A.A., Zadov, A.E., Puscharovsky, D.Yu. (2012): *Carlgieseckeite - (Nd),  $\text{NaNdCa}_3(\text{PO}_4)_3\text{F}$ , a new belovite-group mineral species from the Ilímaussaq alkaline complex, South Greenland*. *Can. Mineral.* 50, 571-580.
- Pell, J. (1996): *Mineral deposits associated with carbonatites and related alkaline igneous rocks*. In R.H. Mitchell (ed.): *Undersaturated alkaline rocks: mineralogy, petrogenesis and economic potential*. MAC Short Course 24, Winnipeg, Manitoba, 271-312.
- Perhac, R.M. (1970): *Geology and mineral deposits of the Gallinas Mountains, Lincoln and Torrance Counties, New Mexico: New Mexico Bureau of Mines and Mineral Resources Bulletin 95, 51 p., 2 plates*.
- Perhac, R.M., Heinrich, E.W. (1964): *Fluorite-bastnaesite deposits of the Gallinas Mountains, New Mexico and bastnaesite paragenesis*: *Econ. Geol.* 59, 226-239.
- Perring, C.S., Pollard, P.J., Dong, G., Nunn, A.J., Blake, K.L. (2000): *The Lightning Creek Sill Complex, Cloncurry district, Northwest Queensland: a source of fluids for Fe Oxide Cu-Au mineralization and sodic-calcic alteration*. *Econ. Geol.* 95, 1067-1089.
- Peterson, R.C., MacFarlane, D.B. (1993): *The rare-earth-element chemistry of allanite from the Grenville Province*. *Can. Mineral.* 31, 159-166.
- Petrov, S.V. (2004): *Economic deposits associated with the alkaline and ultrabasic complexes of the Kola Peninsula*. In F. Wall, A.N. Zaitsev (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. *Mineral. Soc. Series 10*. Mineral. Soc., London, 469-490.
- Pilipiuk, A.N., Ivanikov, V.V., Bulakh, A.G. (2001): *Unusual rocks and mineralisation in a new carbonatite complex at Kandaguba, Kola Peninsula, Russia*. *Lithos* 56, 333-347.
- Pinckston, D.R., Smith, D.G.W. (1995): *Mineralogy of the Lake zone, Thor Lake rare-metals deposit, N.W.T., Canada*. *Can. J. Earth Sci.* 32, 516-532.
- Piret, P., Deliens, M. (1982): *Nouvelles données sur la schuilingite, carbonate hydraté de terres rares, de plomb et de cuivre*. *Bull. Minéral.*, 105, 225-228.
- Piret, P., Deliens, M., Piret-Meunier, J. (1988): *La françoisite-(Nd), nouveau phosphate d'uranyle et de terres rares; propriétés et structure cristalline*. *Bull. Minéral.* 111, 443-444.
- Poitrasson, F., Oelkers, E., Schott, J., Montel, J.-M. (2004): *Experimental determination of synthetic  $\text{NdPO}_4$  monazite end-member solubility in water from 21 °C to 300 °C: implications for rare earth element mobility in crustal fluids*. *Geochim Cosmochim Acta* 68, 2207-2221.
- Price, J.G., Rubin, J.N., Henry, C.D., Pinkston, Th.L., Tweedy, S.W., Koppelaar, D.W. (1990): *Rare-metal enriched peraluminous rhyolites in a continental arc, Sierra Blanca area, Trans-Pecos Texas, chemical modification by vapor-phase crystallization*. In H.J. Stein, Hannah, J.L. (eds.): *Ore-bearing granite systems; petrogenesis and mineralizing processes*. *Geol. Soc. Am. Spec. Paper* 246, 103-120.
- Prol-Ledesma, R.M., Martin, R.F., Melgarejo, J.C. (2012): *The El Muerto "NYF" granitic pegmatite, Oaxaca, Mexico, and its striking enrichment in allanite-(Ce) and monazite-(Ce)*. *Can. Mineral.* 50, 1055-1076.
- Pujol, N., Andreazini Sabaté, A., Schamuells, S., Amores Casals, S., Villanova-de-Benavent, C., Torró, L., Melgarejo, J.C., Manteca, J.I. (2013): *Primary and secondary deposits from the Crisoleja area (Pb-Zn-Ag-Sn), La Unión, Murcia, Spain*. In E. Jonsson et al. (ed). *Mineral deposit research for a high tech world 3, Proceedings of the 12th Biennial SGA Meeting, 12-15 August 2013, Elanders Sverige AB Uppsala, Sweden*, 1307-1310.
- Rapp, R.P., Watson, E.B. (1986): *Monazite solubility and dissolution kinetics: implications for the*

- thorium and light rare-earth earth chemistry of felsic magmas. *Contrib. Mineral. Petrol.* 94, 304-316.
- Rasmussen, B. (1996): Early diagenetic REE phosphate minerals (florencite, gorceixite, crandallite and xenotime) in marine sandstones: a major sink for oceanic phosphorus. *Amer. J. Sci.* 296, 601-632.
- Raup, O.B., Gude, A.J., Dwornik, E.J., Cuttitta, F., Rose, H.J.Jr. (1968): Braitschite, a new hydrous calcium rare-earth borate mineral from the Paradox basin, Grand County, Utah. *Amer. Mineral.* 53, 1081-1095.
- Richards, J.P., Mumin A.H. (2013): Magmatic-hydrothermal processes within an evolving Earth. Iron oxide copper-gold and porphyry Cu±Mo±Au deposits. *Geology* 41, 767-770.
- Rieger, A.A., Marschik, R., Díaz, M., Hözl, S., Chiaradia, M., Akker, B., Spangenberg, J.E. (2010): The Hypogene Iron Oxide Copper-Gold Mineralization in the Mantoverde District, Northern Chile. *Econ. Geol.* 105, 1271-1299.
- Roeder, P.L., MacArthur, D., Ma Xin-pei, Palmer, G.R., Mariano, A.N. (1987): Cathodoluminescence and microprobe study of rare-earth elements in apatite. *Am. Mineral.* 72, 801-811.
- Rogers, M.G. (2011): Saskatchewan descriptive mineral deposit models. Saskatchewan Ministry of Energy and Resources. Open file report 2011-57. URL <http://er.gov.sk.ca/OF2011-57>. 112 p.
- Rolland, Y., Cox, S., Boullier, A.M., Pennacchioni, G., Mancktelow, N. (2003): Rare earth and trace element mobility in mid-crustal shear zones: insights from the Mont Blanc Massif (Western Alps). *Earth Planet. Sci. Lett.* 214, 203-219.
- Rønsbo, J.G., Khomyakov, A.P., Semenov, E.I., Voronkov, A.A., Garanin, V.K (1979) Vitusite, a new phosphate of sodium and rare earths from the Lovozero alkaline massif, Kola and Ilímaussaq alkaline intrusion, South Greenland. *Neues Jahrb. Mineral. Abh.* 137, 42-53.
- Rosenblum, S., Mosier, E.L. (1983): Mineralogy and occurrence of Europium-rich dark monazite. *U.S. Geol. Surv. Prof. Paper* 1181, 72 pp.
- Ross Heath, G. (1981): Iron-manganese nodules of the Deep Sea. *Econ. Geol.* 75 anniversary vol., 736-765.
- Ruberti, E., Enrich, G.E.R., Gomes, C.B., Comin-Chiaramonti (2008): Hydrothermal REE fluorcarbonate mineralization at Barra do Itapirapuã, a multiple stockwork carbonatite, southern Brazil. *Can. Mineral.* 46, 901-914.
- Rubin, J.N., Henry, C.D., Price, J.G. (1993): The mobility of zirconium and other "immobile" elements during hydrothermal alteration. *Chem. Geol.* 110, 29-47.
- Ruzicka, V. (1995): Unconformity-type uranium deposits. In R.V. Kirkham, W.D. Sinclair, R.I. Thorpe, J.M. Duke (eds.), *Mineral Deposit Modeling*, Geol. Assoc. Canada Spec. Paper 40, 125-150.
- Saebø, P.Ch. (1961): On lanthanite in Norway. *Norsk Geol. Tidss.* 41, 312-317.
- Sahama, T.G., Knorring, O. von, Lehtinen, M. (1970): Cerotungstite, a cerian analogue to ytrotungstite, from Uganda. *Bull. Geol. Soc. Finland*, 42, 223-228.
- Salvi S, Williams-Jones AE (2005) Alkaline granite-syenite deposits. In: Linnen RL, Samson IM (eds) *Rare Element Geochemistry and Mineral Deposits*. Geological Association of Canada Short Course Notes 17, pp 315-341.
- Salvi, S., Fontan, F., Monchoux, P., Williams-Jones, A.E., Moine, B. (2000): Hydrothermal mobilization of high field strength elements in alkaline igneous systems: evidence from the Tamazeght Complex (Morocco). *Econ. Geol.* 95, 559-576.
- Salvi, S., Williams-Jones, A.E. (1990): The role of hydrothermal processes in the granite-hosted Zr, Y, EE deposit at Strange Lake, Québec-Labrador: Evidence from fluid inclusions. *Geochim. Cosmochim. Acta* 54, 2403-2418.
- Salvi, S., Williams-Jones, A.E. (1996): The role of hydrothermal processes in concentrating high-field strength elements in the Strange Lake peralkaline complex, northeastern Canada. *Geochim. Cosmochim. Acta* 60, 1917-1932.
- Samson, I.M., Wood, S.A. (2004): The rare earth elements: Behavior in hydrothermal fluids and con-

- centration in hydrothermal mineral deposits, exclusive of alkaline settings. In R.L. Linnen y I.M. Samson (eds.): *Rare-Element Geochemistry and Ore Deposits*. Geol. Assoc. Canada, Short C. Notes 17, 269-297.
- Samson, I.M., Wood, S.A., Finucane, K. (2004): *Fluid Inclusion Characteristics and Genesis of the Fluorite-Parisite Mineralization in the Snowbird Deposit, Montana*. *Econ. Geol.* 99, 1727-1744.
- Sanmartí Rodríguez, L., Gaya Manós, A., Molina Treviño, C., Amores Casals, S., Villanova-de-Benavent, C., Torró i Abat, L., Melgarejo, J.C., Manteca, J.I. (2013): *The mineral association in the Emilia and Brunita Pb-Zn-Ag-(Sn) deposits, La Unión, Murcia, Spain*. In Jonsson, E. et al. (ed). *Mineral deposit research for a high tech world 3, Proceedings of the 12th Biennial SGA Meeting, 12-15 August 2013, Elanders Sverige AB Uppsala, Sweden*, 1311-1314.
- Schreiner, R.A. (1993): *Mineral investigation of the rare-earth-element-bearing deposits, Red Cloud Mining district, Gallinas Mountains, Lincoln County, New Mexico: U.S. Bureau of Mines, MLA 99-93, 189 p.*
- Schroter, T. (1989): *The Abu Tartur phosphorite deposit, Western Desert, Egypt*. In A.J.G. Notholt, R.P. Sheldon, D.F. Davidson (eds.), *Phosphate deposits of the world, Vol. 2, Phosphate rock resources: Cambridge, Cambridge University Press, 194-199.*
- Seredin, V.V. (1996): *Rare earth element-bearing coals from the Russian Far East deposits*. *Intern. J. Coal Geol.* 30, 101-129.
- Service, R.F. (2010): *Nations move to head off shortages of rare earths*. *Science* 327, 1596-1597.
- Sarp, H., Bertrand, J. (1985): *Gysinite, Pb(Nd,La)(CO<sub>3</sub>)<sub>2</sub>(OH)·H<sub>2</sub>O, a new lead, rare-earth carbonate from Shinkolobwe, Shaba, Zaïre and its relationship to ancylite*. *Am. Mineral.* 70, 1314-1317.
- Sheard, E.R., Williams-Jones, A.E., Heiligmann, M., Pederson, C., Trueman, D.L. (2012): *Controls on the concentration of zirconium, niobium, and the rare earth elements in the Thor Lake rare metal deposit, Northwest Territories, Canada*. *Econ. Geol.* 107, 81-104.
- Sidder, G.B., Day, W.C., Nuelle, L.M., Seeger, C.M., Kisvarsanyi, E.B. (1993): *Mineralogic and fluid-inclusion studies of the Pea Ridge iron-rare-earth-element deposit, southeast Missouri: U.S. Geological Survey Bulletin 2039, 205-216.*
- Sijaric, G., Farré-de-Pablo, J., Jou-Claus, S., Portell-Ramírez, L., Soler-Capdevila, J., Bermanec, V., Melgarejo, J.C. (2012): *Sulfuros complejos asociados al depósito evaporítico de Tuzla (Bosnia Oriental)*. *Macla* 16, 254-255.
- Simmons, W.B., Webber, K.L. (2008): *Pegmatite genesis: state of the art*. *Eur. J. Mineral.* 20, 421-438.
- Simmons, W.B., Hanson, S.L., Falster, A.U., Webber, K.L. (2012): *A comparison of the mineralogical and geochemical character and geological setting of Proterozoic REE-rich granitic pegmatites of the North-Central and Southwestern US*. *Can. Mineral.* 50, 1695-1712.
- Sinclair, W.D., Jambor, J.L., Birkett, T.C. (1992): *Rare earths and the potential for rare-earth deposits in Canada*. *Explor. Mining Geol.* 1, 265-281.
- Sinisi, R. (2015): *Trace and rare earth elements fractionation in volcanic- and sediment-hosted Mn ores: a study case of Sardinia (western Italy)*. *Geophysical Research Abstracts Vol. 17, EGU2015-13099, EGU General Assembly.*
- Sjöqvist, A.S.L., Cornell, D.H., Andersen, T., Erambert, M., Ek, M., Leijd, M. (2013): *Three Compositional Varieties of Rare-Earth Element Ore: Eudialyte-Group Minerals from the Norra Kärr Alkaline Complex, Southern Sweden*. *Minerals* 3, 94-120.
- \_koda, R., Novák, M. (2007): *Y,REE,Nb,Ta,Ti-oxide (AB<sub>2</sub>O<sub>6</sub>) minerals from REL-REE euxenite-subtype pegmatites of the T<sub>eb</sub> Pluton, Czech Republic; substitutions and fractionation trends* *Lithos* 95, 43-57.
- Slack, J.F. (2012): *Strata-Bound Fe-Co-Cu-Au-Bi-Y-REE Deposits of the Idaho Cobalt Belt: Multistage Hydrothermal Mineralization in a Magmatic-Related Iron Oxide Copper-Gold System*. *Econ. Geol.* 107, 1089-1113.
- Smeds, S.A. (1990): *Regional trends in mineral assemblages of Swedish Proterozoic granitic*

- pegmatites and their geological significance. *Geol. För. Stock. Förh.* 112, 227-242.
- Smith, M.P., Henderson, P., Campbell, L. (2000): Fractionation of the REE during hydrothermal processes: Constraints from the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China. *Geochim. Cosmochim. Acta* 64, 3141-3160.
- Smith, M.P., Henderson, P., Jeffries, T. (2002): The formation and alteration of allanite in skarn from the Beinn an Dubhaich granite aureole, Skye. *Eur. J. Mineral.* 14, 471-486.
- Smith, M.P., Henderson, P., Jeffries, T.E.R., Long, J., Williams, C.T. (2004): The rare earth elements and uranium in garnets from the Beinn an Dubhaich aureole, Skye, Scotland, UK: constraints on processes in a dynamic hydrothermal system. *J. Petrol.* 45, 457-484.
- Sørensen, H. (1970): Internal structures and geological setting of the three agpaitic intrusions: Khibiny and Lovozero of the Kola Peninsula and Ilímaussaq, South Greenland. *Can. Mineral.* 10, 299-334.
- Sørensen, H. (Ed.) (1974): *The alkaline rocks.* John Wiley & Sons, London. 622 p.
- Sørensen, H. (1992): Agpaitic nepheline syenites: a potential source of rare elements. *Appl. Geochem.* 7, 417-427.
- Sørensen, H. (2001): Brief introduction to the geology of the Ilímaussaq alkaline complex, South Greenland, and its exploration history. *Geol. Greenland Surv. Bull.* 190, 7-23.
- Sørensen, H., Larsen, L.M. (2001): The hyperagpaitic stage in the evolution of the Ilímaussaq complex, South Greenland. *Geol. Greenland Surv. Bull.* 190, 83-94.
- Sørensen, H., Bohse, H., Bailey, J.C. (2006): The origin and mode of emplacement of lujavrites in the Ilímaussaq alkaline complex, South Greenland. *Lithos*, 91, 286-300
- Soler, J., Farré, J., Portell, L., Jou, S., Corrales, O., Amores, S., Villanova, C., Torró, L., Melgarejo, J.C., Manteca, J.I. (2013): The San José and Gloria Pb-Zn-Ag-Sn deposits, La Unión, Murcia: An approach to the mineral sequence. In Jonsson, E. et al. (ed). *Mineral deposit research for a high tech world 3, Proceedings of the 12th Biennial SGA Meeting, 12-15 August 2013, Elanders Sverige AB Uppsala, Sweden*, 1315-1318.
- Staat, M.H. (1972): *Geology and description of the thorium-bearing veins, Lemhi Pass quadrangle, Idaho and Montana: U.S. Geological Survey Bulletin* 1351, 94 p.
- Staat, M.H. (1974): *Thorium veins in the United States: Econ. Geol.* 69, 494-507.
- Staat, M.H. (1979): *Geology and mineral resources of the Lemhi Pass thorium district, Idaho and Montana: U.S. Geol. Surv. Prof. Paper* 1049-A, 90 p.
- Staat, M.H. (1983): *Geology and description of thorium and rare-earth deposits in the southern Bear Lodge Mountains, northern Wyoming: U.S. Geol. Surv. Prof. Paper* 1049-D, 52 p.
- Staat, M.H. (1985): *Geology and description of the thorium and rare-earth veins in the Laughlin Peak area, Colfax County, New Mexico: U.S. Geol. Surv. Prof. Paper* 1049-E, 32 p.
- Staat, M.H. (1992): *Descriptive model of thorium-rare-earth veins. In J.D. Bliss (ed.): Developments in mineral deposit modeling: U.S. Geol. Surv., Bull.* 2004, 13-15.
- Sverdrup, T.L., Bryn, K.O., Saebø, P. C. (1959): Bastnäsit, a new mineral for Norway. *Norsk Geol. Tidss.* 39, 238-247.
- Tallarico, F.H.B., Figueiredo, B.R., Groves, D.I., Kositcin, N., McNaughton, N.J., Fletcher, I.R., Rego J.L. (2005): *Geology and SHRIMP U-Pb Geochronology of the Igarapé Bahia deposit, Carajas Copper-Gold Belt, Brazil: an Archean (2.57 Ga) example of Iron-Oxide Cu-Au-(U-REE) Mineralization. Econ. Geol.* 100, 7-28.
- Taylor, R.P., Pollard, P. J. (1996): Rare earth element mineralization in peralkaline systems: the T-zone REE-Y-Be deposit, Thor Lake, Northwest Territories, Canada. In Jones, A.P., Wall, F., Williams, C.T. (eds.), *Rare Earth minerals-chemistry, origin and ore deposits. Mineral. Soc. Ser.* 7, 167-192.

- Torres, B., Artiaga, D., Torró, L., Tauler, E., Melgarejo, J.C. (2013): The Poopó Sn-Ag-Zn-Pb vein deposit, Bolivia: structure and mineralogy. In E.Jonsson et al. (ed). *Mineral deposit research for a high tech world 3, Proceedings of the 12th Biennial SGA Meeting, 12-15 August 2013, Elanders Sverige AB Uppsala, Sweden, 1327-1330.*
- Torró, L., Villanova, C., Castillo, M., Campeny, M., Gonçalves, A.O., Melgarejo, J.C. (2012): Niobium and rare earth minerals from the Virulundo carbonatite, Namibe, Angola. *Mineral. Mag.* 76, 393-409.
- Trueman, N.A. (1965): The phosphate, volcanic and carbonate rocks of Christmas Island (Indian Ocean). *J. Geol. Soc. Aust.* 12: 261-283.
- Uher, P., Broska, I. (1995): Pegmatites in two suites of Variscan orogenic granitic rocks (Western Carpathians, Slovakia). *Mineral. Petrol.* 55, 27-36.
- Van Wambeke, L. (1977): The Karonge rare earth deposits, Republic of Burundi: new mineralogical-geochemical data and origin of the mineralization. *Mineral. Deposita* 12, 373-380.
- Verplanck, P.L., Van Gosen, B.S., Seal, R.R., McCafferty, A.E. (2014): A deposit model for carbonatite and peralkaline intrusion-related rare earth element deposits: U.S. Geol. Surv. Sci. Invest. Rep. 2010-5070-J, 58 p, <http://dx.doi.org/10.3133/sir20105070J>.
- Villanova de Benavent, C., Galí, S., Melgarejo, J.C., Gonçalves, A.O. (2011): Fe-Ti(V) oxide mineralogy and thermo-oxybarometry from the Kunene anorthosite complex deposits (SW Angola). *Antofagasta, Chile, Proc. 11th biennial meeting SGA.*
- Vaquero, C. (1979): Descubrimiento, por primera vez en España, de una monacita de facies aberrantes portadora de Europio. *Bol. Geol. Min.* 90, 374-379.
- Vlasov, K.A., Kuz'menko, M.Z., Es'kova, E.M. (1966): The Lovozero Alkaline Massif. Oliver & Boyd, Edinburgh and London.
- Vlasov, K.A. (1966): Geochemistry and mineralogy of rare elements and genetic types of their deposits. Jerusalem, Israel Program for Scientific Translations vol 1, 688 p., vol. 2, 945 p., vol. 3, 916 p.
- Vorma, A., Ojanperä, P., Hoffrén, V., Siivola, J., Löfgren, A. (1966): On the rare earth minerals from Pyörönmaa pegmatite in Kangasala, SW Finland. *Bull. Com. Géol. Finlande* 222, 241-274.
- Walenta, K. (1979): Chukhrovit-(Ce) and Rhabdophan-(Ce) aus der Grube Clara bei Oberwolfach im mittlern Schwarzwald. *Chem. Erde* 38, 331-339.
- Wall, F., Mariano, A.N. (1996): Rare earth minerals in carbonatites: a discussion centred on the Kangankunde Carbonatite, Malawi. In: *Rare Earth Minerals: Chemistry, Origin and Ore Deposits.* (A.P. Jones, F. Wall and C.T. Williams, eds.). Mineralogical Society Series, 7. Chapman and Hall, London, 193-225.
- Wall, F., Niku-Paavola, V.N., Storey, C., Mueller, A., Jeffries, T. (2008): Xenotime-(Y) from carbonatite dykes at Lofdal, Namibia; unusually low LREE/HREE ratio in carbonatite, and the first dating of xenotime-(Y) overgrowths on zircon. *Can. Mineral.* 46, 861-877.
- Wallwork, K., Kolitsch, U., Pring, A., Nasdala, L. (2002): Decrespignyite-(Y), a new copper yttrium rare earth carbonate chloride hydrate from Paratoo, South Australia. *Mineral. Mag.*, 66, 181-188.
- Wang, D., Yang, J., Yan, S. (2001): A special orogenic-type rare earth element deposit in Maoniuping, Sichuan, China: geology and geochemistry. *Resour. Geol.* 51,177-188.
- Wang J.W., Tatsumoto, M., Li, X.B., Premo, W.R., Chao, E.C.T. (1994): A precise  $^{232}\text{Th}$ - $^{208}\text{Pb}$  chronology of fine-grained monazite: Age of the Bayan Obo REE-Fe-Nb ore deposit, China: *Geochim. Cosmochim. Acta* 58, 3155-3169.
- Wang, Q.F., Deng, J., Liu, X.F., Zhang, Q.Z., Sun, S., Jiang, C.Z., Zhou, F. (2010): Discovery of the REE minerals and its geological significance in the Quyang bauxite deposit, West Guangxi, China. *J. Asian Earth Sci.* 39, 701-712.
- Wang, W., Pranolo, Y., Cheng, C.Y. (2011): Metallurgical processes for scandium recovery from various resources: A review.

*Hydrometallurgy* 108, 100-108.

Wendlandt, R.F., Harrison, W.J. (1979): Rare earth partitioning between immiscible carbonate and silicate liquids and CO<sub>2</sub> vapor: results and implications for the formation of light rare earth-enriched rocks, *Contrib. Miner. Petrol.* 69, 409-419.

Whalen, J.B., Currie, K.L., Chappell, B.W. (1987): A-type granites: geochemical characteristics, discrimination and petrogenesis: *Contrib. Mineral. Petrol.* 95, 40-418.

Whitten, C.W., Yancey, R.J. (1990): Characterization of the Rare-Earth Mineralogy at the Pea Ridge Deposit, Missouri. *Rep. Invest. Bur. Mines, US Dept. Interior* 9331, 1-9.

Williams, P.J., Barton, M.D., Fontboté, L., de Haller, A., Johnson, D.A., Mark, G., Marschik, R., Oliver, N.H.S. (2005): Iron-oxide-copper-gold deposits. *Geology, space-time distribution, and possible modes of origin: Econ. Geol.* 100th Anniversary Volume, 371-406.

Williams-Jones, A.E., Samson, I.M., Olivo, G.R. (2000): The genesis of hydrothermal fluorite-REE deposits in the Gallinas Mountains, New Mexico. *Econ. Geol.* 95, 327-342.

Williams-Jones, A.E., Migdisov, A.A., Samson, I.M. (2012): Hydrothermal mobilization of the rare earth elements—a tale of “ceria” and “yttria”. *Elements* 8, 355-360.

Wise, M.A., Cerny, P., Falster, A.U. (1998): Scandium substitution in columbite-group minerals and ixiolite. *Can. Mineral.* 36, 673-680.

Wood, S.A. (1990a): The aqueous geochemistry of the rare-earth elements and yttrium 2. Theoretical predictions of speciation in hydrothermal solutions to 350°C at saturation water vapor pressure. *Chem. Geol.* 88, 99-125.

Wood, S.A. (1990b): The aqueous geochemistry of the rare-earth elements and yttrium 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chem Geol.* 82, 159-186.

Wood, S.A., Williams-Jones, A. (1994): The aqueous geochemistry of the rare earth ele-

ments and yttrium 4. Monazite solubility and REE mobility in exhalative massive sulfide-depositing environments. *Chem. Geol.* 7, 47-60.

Wood, S.A., Palmer, D., Wesolowski, D., Bénézech, P. (2002): The aqueous geochemistry of the rare earth elements and yttrium. Part XI. The solubility of Nd(OH)<sub>3</sub> and hydrolysis of Nd<sup>3+</sup> from 30 to 290 C at saturated water vapor pressure with in-situ pHm measurement. In: Hellmann R, Wood SA (eds) *Water-Rock Interact. Ore Depos. Environ. Geochemistry* ATribut. to David A. Crerar, 229-256.

Woodward, L.A., Fulp, M.S. (1991): Gold mineralization associated with alkali trachyte breccias in the Gallinas mining district, Lincoln County, New Mexico: *New Mexico Geological Society, Guidebook* 42, 323-325.

Woolley, A.R., Kempe, D.R.C. (1989): Carbonatites: nomenclature, average chemical compositions, and element distribution. In K. Bell (ed.): *Carbonatites: Genesis and Evolution.* Unwin Hyman Inc., Winchester, Massachusetts, 1-14.

Woolley, A.R., Church, A.A. (2005): Extrusive carbonatites: A brief review. *Lithos* 85, 1-14.

Woolley, A.R., Kjarsgaard, B.A. (2008): Paragenetic types of carbonatite as indicated by the diversity and relative abundances of associated silicate rocks: evidence from a global database. *Can. Mineral.* 46, 741-752.

Wu, C., Yuan, Z., Bai, G. (1996): Rare earth deposits in China. In A.P. Jones, F. Wall, C.T. Williams (eds.), *Rare earth minerals-chemistry, origin and ore deposits.* *Mineral. Soc. Series* 7, 281-310.

Wu, Ch. (2008): Bayan Obo Controversy: Carbonatites versus Iron Oxide-Cu-Au-(REE-U). *Resource Geol.* 58, 348-354.

Yang, X., Yang, X., Chen, Sh., Chen, T., Zhang, P., Tao, K., Le Bas, M.J., Wilson, R.N., Branson, R., Campbell, L.S., Williams, T.C., Henderson, P. (1999): New occurrence of Ba-REE fluorocarbonate minerals at Bayan Obo, Inner Mongolia, North China, and their mineralogical features. *Science Bull.* 44, 1419-1423.

- Yang X.M., Yang, X.Y., Zheng, Y.F., Le Bas, M.J. (2003): A rare earth element-rich carbonatite dyke at Bayan Obo, Inner Mongolia, North China: *Mineral. Petrol.* 78, 93-110.
- Yang, X.Y., Sun, W.D., Zhang, Y.X., Zheng, Y.F. (2009): Geochemical constraints on the genesis of the Bayan Obo Fe-Nb-REE deposit in Inner Mongolia, China: *Geochim. Cosmochim. Acta* 73, 1417-1435.
- Yang, K.F., Fan, H.R., Santosh, M., Hu, F.F., Wang, K-Y (2011): Mesoproterozoic carbonatitic magmatism in the Bayan Obo deposit, Inner Mongolia, North China: Constraints for the mechanism of super accumulation of rare earth elements. *Ore Geol. Rev.* 40, 12-131.
- Young, E.J., Sims, P.K. (1961): Petrography and origin of xenotime and monazite concentrations, Central City district, Colorado: *U.S. Geol. Surv. Bull.* 1032-F, 273-299.
- Yurimoto, H., Duke, E.F., Shearer, C.K. (1990): Are discontinuous chondrite-normalized REE patterns in granitic pegmatite systems the results of monazite fractionation?. *Geochim. Cosmochim. Acta* 54, 2141-2145.
- Zaitsev, A.N., Wall, F., Le Bas, M.J. (1998): REE-Sr-Ba minerals from the Khibina carbonatites, Kola Peninsula, Russia: their mineralogy, paragenesis and evolution. *Mineral. Mag.* 62, 225-250.
- Zaitsev, A.N., Williams, C.T., Jeffries, T.E., Strekopytov, S., Moutte, J., Ivashchenkova, O.V., Spratt, J., Petrov, S.V., Wall, F., Seltmann, R., Borozdin, A.P. (2014): Rare earth elements in phoscorites and carbonatites of the Devonian Kola Alkaline Province, Russia: examples from Kovdor, Khibina, Vuoriyarvi and Turiy Mys complexes, *Ore Geol. Rev.* 61, 204-225.
- Zaitsev, A.N., Sitnikova, M.A., Subbotin, V.V., Fernández-Suárez, J., Jeffries, T.E. (2004): Sallanlatvi complex - a rare example of magnesite and siderite carbonatites. In F. Wall, A.N.
- Zaitsev (Eds.), *phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province. Mineral. Soc. Series, 10. Mineral. Soc., London, 201-245.*
- Zhang, Z.Q., Tang, S.H., Yuan, Z.X., Bai, G., Wang, J.H. (2001): The Sm-Nd and Rb-Sr isotopic systems of the dolomites in the Bayan Obo ore deposit, Inner Mongolia, China: *Acta Petrol. Sinica* 17, 637-642.
- Zheng, L., Gujjan, L., Chen-Lin, Ch., Cuicui, Q., Ying, Z. (2007): Geochemistry of rare earth elements in Permian coals from the Huaibei Coalfield, China. *J. Asian Earth Sci.* 31, 167-176.