

Geochemistry of the Lanthanide Elements

/ Fernando Bea

Department of Mineralogy and Petrology, University of Granada

1. Chemical properties

The Lanthanides, or Rare Earth Elements, are the following 15 elements: Lanthanum (La, Z = 57), Cerium (Ce, Z = 58), Praseodymium (Pr, Z = 59), Neodymium (Nd, Z = 60), Promethium (Pm, Z = 61), Samarium (Sm, Z = 62), Europium (Eu, Z = 63), Gadolinium (Gd, Z = 64), Terbium (Tb, Z = 65), Dysprosium (Dy, Z = 66), Holmium (Ho, Z = 67), Erbium (Er, Z = 68), Thulium (Tm, Z = 69), Ytterbium (Yb, Z = 70) and Lutetium (Lu, Z = 71). All but Promethium have naturally-occurring isotopes.

The Lanthanides have three valence electrons: two in the 6s orbital and one in the 5d orbital. Their electronic configuration changes as Z increases because the new electrons entering in the electron cloud are placed in the seven 4f orbitals. Lanthanum has no 4f electrons, Cerium has one, Praseodymium has two, etc., until Lutetium which has fourteen electrons that completely fill the 4f orbitals. The three valence electrons causes the REE³⁺ to be the most stable ions found in nature except for Europium, which is mostly as Eu²⁺, and Cerium which may be partially oxidized to Ce⁴⁺.

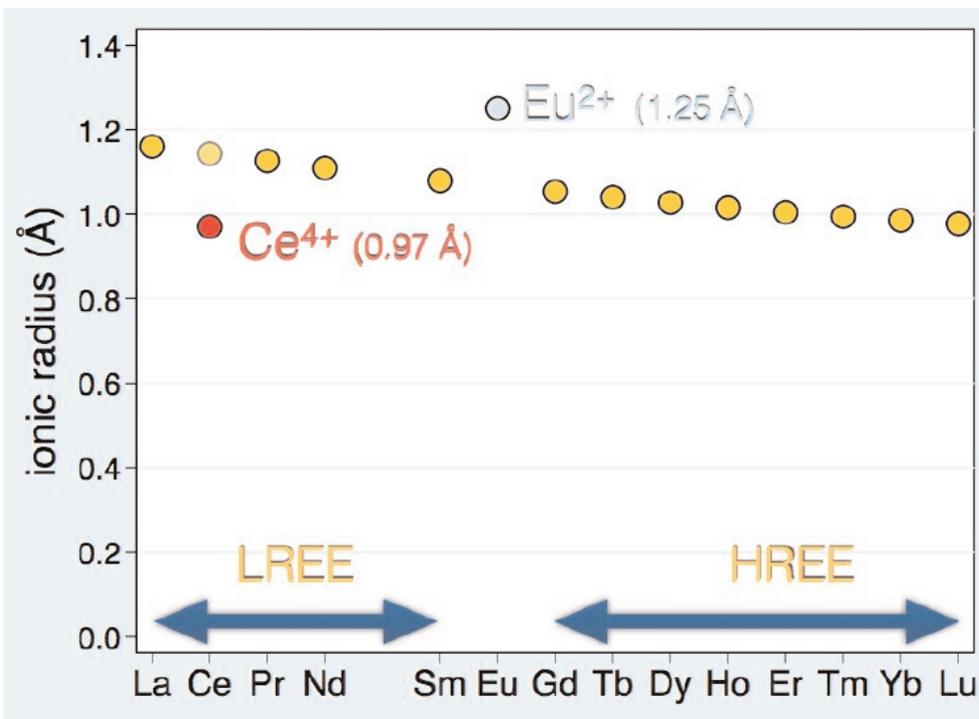


Fig. 1. . Ionic radii of the REE³⁺ ions, Eu²⁺ and Ce⁴⁺. The smooth decrease of the REE³⁺ ionic radius with increasing Z causes the Lanthanide contraction.

The entry of new electrons in the 4f orbitals, when the atoms have fully occupied the 6s orbital increases the electrostatic attraction between the N shell and the nucleus. This leads to a reduction of the REE³⁺ ionic radius with increasing Z, a phenomenon which is known as Lanthanide contraction. *Figure 1* shows the ionic radii (VI) of the most common REE ions.

The REEs have moderate electronegativity between 1.0 and 1.2 duly forming bond with an elevated ionic component. The trivalent ions have nearly identical chemical behavior thus being very difficult to separate one each other in the laboratory. Minerals, however, can fractionate them according to their ionic radii. In general, the feldspars have a marked preference for the lightest LREE³⁺ and Eu²⁺ whereas the ferro-magnesian minerals either prefer the HREE³⁺ (garnet, zircon) or are little selective (amphibole, clinopyroxene). Remarkably, the REE except Eu tend to form minerals of their own, phosphates, silicates, niobotantalates, carbonates, etc.

2. REE Abundances and the Masuda-Coryell Diagram

The REE are more abundant than other better known but more conspicuous elements such as Pb, Sn, Au, etc. (*Table 1*). Their relative proportions in the Silicate Earth (or Primitive Mantle) are identical to the proportions found in the carbonaceous chondrites (*Table 1*) which represent undifferentiated material similar to the one that formed the Earth. Geochemically, therefore, they are lithophile refractory elements.

Given that the chemical behavior of the REE is so similar, their abundance patterns in geological materials illustrate well the Oddo-Harkins Rule, i.e., the abundance of Z-odd elements is smaller than the abundance of neighboring Z-even elements. Dividing the concentration of each lanthanide in the Silicate Earth by that of the same element in the carbonaceous chondrites a constant ratio of 2.71 is obtained.

	C1-chondrites	Silicate Earth	N-MORB basalts	Continental Crust
La	0.237	0.648	3.895	18
Ce	0.613	1.675	12.001	42
Pr	0.0928	0.254	2.074	5
Nd	0.457	1.25	11.179	20
Sm	0.148	0.406	3.752	3.9
Eu	0.0563	0.154	1.335	1.2
Gd	0.199	0.544	5.077	3.6
Tb	0.0361	0.099	0.885	0.56
Dy	0.246	0.674	6.304	3.5
Ho	0.0546	0.149	1.342	0.76
Er	0.16	0.438	4.143	2.2
Tm	0.0247	0.068	0.621	0.3
Yb	0.161	0.441	3.9	2
Lu	0.0246	0.0675	0.589	0.33

Table 1. . REE abundances in some important geological materials. C1-chondrites and Silicate Earth from McDonough and Sun (1995). N-MORB from Hoffman (1988). Average Continental Crust from Rudnik and Fountain (1995).

Normalizing the REE concentration to the carbonaceous chondrites is thus a convenient way for eliminating the saw-tooth effect caused by the Oddo Harkins Rule (*Fig. 2A*). The chondrite-normalized concentrations are often displayed using a categorical graph called the Masuda-Coryell diagram after the two researchers who designed it. This diagram plots the logarithm of the rock/chondrite ratio (also called the normalized concentration) of each element in order

of increasing atomic number (Fig. 2B). The distance between two consecutive REE in the horizontal axis is sometimes made proportional to the difference of their REE³⁺ ionic radii. Nonetheless, this method makes little difference with respect to representing the REE at equal distances which additionally saves the embarrassing problem of representing the bivalent Europium ions. For proportionality sake, the diagram also includes, and leaves empty, the position of Promethium in the horizontal axis.

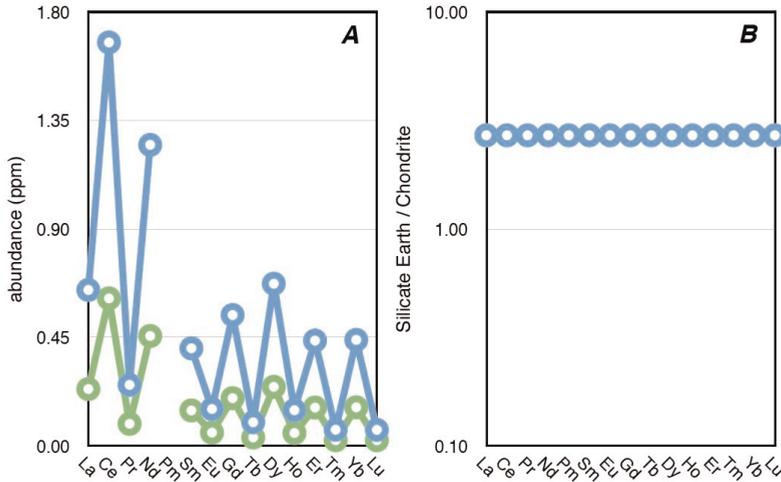


Fig. 2. **A)** Absolute REE abundances in C1-chondrites (green) and Silicate Earth (blue). Note the saw-tooth profile due to the Oddo-Harkins Rule. **B)** Normalizing to the chondrites smooths the graph which is now horizontal at a constant 2.7 x chondrite.

3. Relevant features of the Masuda-Coryell diagram

Rocks plotted in the Masuda-Coryell diagram produce smooth graphs that can be read in petrogenetic terms (Fig. 3). Caution must be exerted, however, because despite their apparent simplicity these diagrams not always can be univocally interpreted, especially in rocks derived from sources with REE-patterns that depart markedly from being horizontal, as is the case of most crustal protoliths. For example, the LREE depletion in Fig. 3A is due to the fact that its source (upper mantle) is heavily depleted in these elements, and not to the more compatible behavior of the LREE with respect to HREE as it might be superficially believed.

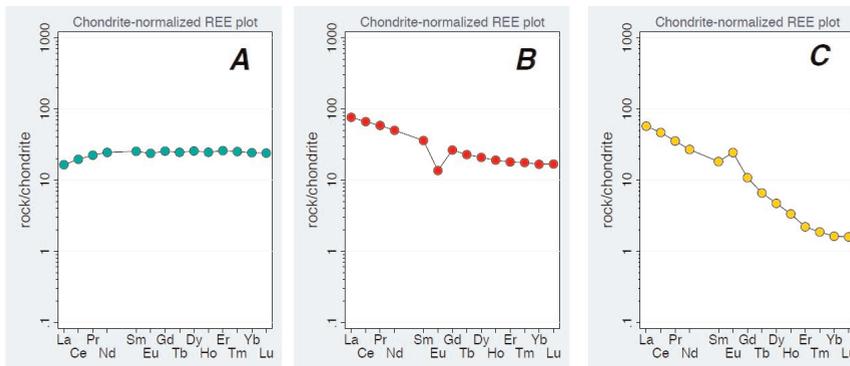


Fig. 3. Three examples of chondrite-normalized diagrams. **A)** N-MORB basalt showing a depletion of the LREE with respect to the HREE; the depletion increases with decreasing Z. **B)** Monazite-bearing peraluminous granite with LREE > HREE and a marked negative Eu anomaly. **C)** An Archean trondhemitic (plagiogranite) with LREE >> HREE and a marked Eu positive anomaly.

The most relevant features in the Masuda-Coryell diagram are the following:

1. Overall quantity and slope. The slope is generally referred as the ratio La_N/Lu_N (or La_N/Yb_N if Lu was not determined).
2. Eu anomaly. Given its distinct valence and radius, Eu^{2+} often behaves de-coupled of the rest of REE ions. This is reflected in the chondrite-normalized diagrams because Eu plots in a position notably different to that resulting from interpolation between Sm and Gd. The Eu anomaly is numerically expressed as the ratio Eu_N/Eu^* where Eu^* is $\sqrt{(Sm_N \times Gd_N)}$. If this value is > 1 we say the anomaly is positive (Fig. 3C). If the ratio is < 1 we say the anomaly is negative (Figs 3B).
3. Ce anomaly. It happens when Ce is partially oxidized to Ce^{4+} . It may also be positive or negative and is numerically expressed as the ratio Ce_N/Ce^* where Ce^* is $\sqrt{(La_N \times Pr_N)}$.
4. Nd anomaly. It is always negative. It is related to extreme monazite fractionation.

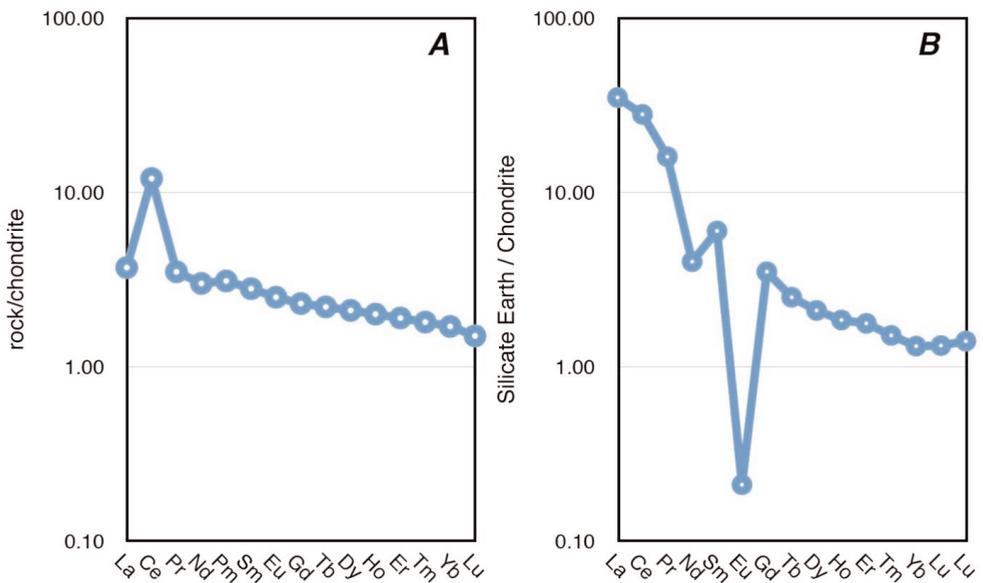


Fig. 4. Examples of minor anomalies in chondrite-normalized diagrams. **A)** Altered basalt showing a positive Ce anomaly. It may also be negative. **B)** Fractionated granite showing a Nd anomaly. The Nd anomaly is always negative

4. The tetrad effect

Chemists working on the extraction of REE organic compounds from aqueous solutions observed that dissolution with a flat chondrite-normalized REE plot produced an extract with a pattern divided in four convex segments: (1) La-Ce-Pr-Nd (2) Pm-Sm-Eu-Gd (3) Gd-Tb-Dy-Ho (4) Er-Tm-Yb-Lu. If the segments are upwards-convex, the effect is called **m-type**. If they are downwards-convex, the effect is called **w-type**, both being complementary.

The tetrad effect has been applied to igneous rocks for explaining Nd, Gd and Ho anomalies, but it seems to be an artifact due to poorly-corrected isobaric interferences in mass spectrometry REE analyses, especially in ICP-MS.

5. REE Residence

A key point for understanding the geochemistry of the REEs and interpret it properly is to know which minerals contain them and in which quantities and ratios.

a) Major Minerals

Among common petrographic minerals only amphibole, clinopyroxene, the feldspars and garnet contain detectable amounts of REE. Neither olivine, nor orthopyroxene, muscovite, and biotite have measurable REE concentrations. Reported analyses of these minerals with elevated REE contents are concentrate analyses contaminated with REE accessories. Other minerals such as epidote, cordierite and tourmaline may have modest concentrations of them.

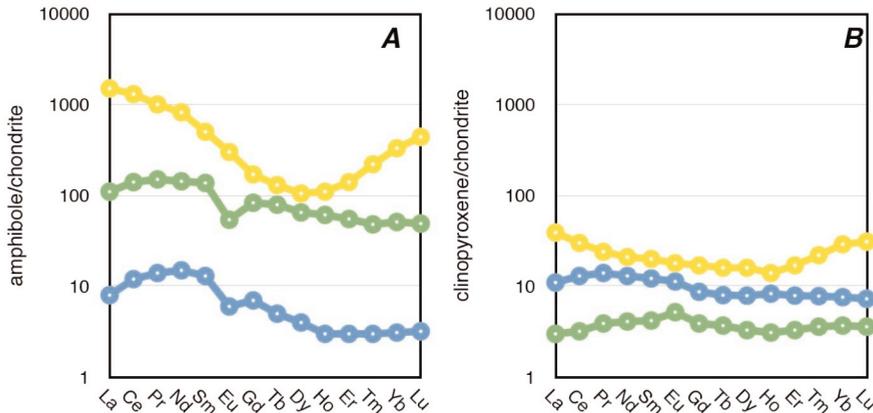


Fig. 5. Chondrite-normalized REE patterns of amphibole (A) and clinopyroxene (B). In either case the blue and green lines represent the minimum and maximum values expectable in calcic varieties. The yellow line represents alkaline varieties.

Amphibole is the REE-richer major mineral. It shows a moderate enrichment in LREE, especially Sm-Nd, over the HREE and no or a small Eu anomaly (Fig. 5). Al-alkaline amphiboles are often enriched in the heaviest REE. Clinopyroxene has similar pattern to amphibole but at a lower concentration (Fig. 5).

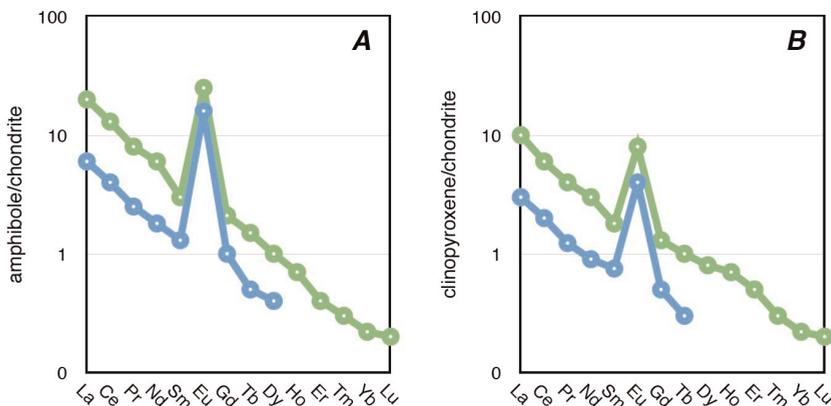


Fig. 6. Chondrite-normalized REE patterns of feldspars (A) and plagioclases (B). In either case the blue and green lines represent the minimum and maximum expectable values.

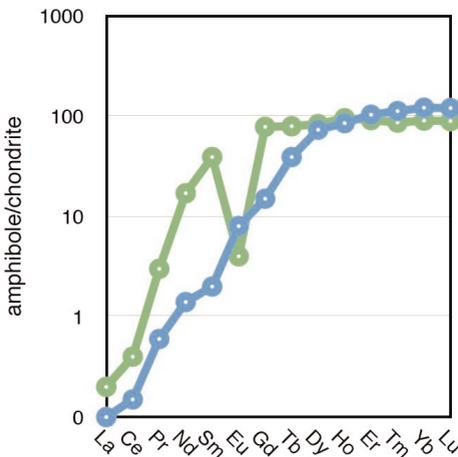


Fig. 7. Chondrite-normalized REE patterns of low-pressure (blue) and high-pressure (green) garnets. The Gd/Dy ratio may be used as a geobarometer (Bea et al., 1997).

The feldspars are enriched in the lightest REE and Sr, thus showing a marked decrease from La onwards and a strong Eu positive anomaly (Fig. 6). The HREE are often below detection limits of the LA-ICP-MS systems. Generally speaking, K-feldspar is enriched in REE with respect to coexisting plagioclase.

Garnet is selectively enriched in HREE (Fig. 7). The concentration of Gd to Dy increases with increasing pressure so that the Gd/Dy ratio can be used as a geobarometer in monazite-saturated metapelitic rocks.

b) Accessory Minerals

A significant part of the REE budget in common rocks resides in accessory minerals. This effect is not severe in mafic and ultramafic rocks but acquires increasing importance as the rock becomes more felsic. The most important REE-rich accessories are:

1. Phosphates, such as monazite, xenotime and, to a lesser extent, apatite
2. Silicates, such as allanite, titanite, zircon, bristolite, huttonite-thorite, etc.
3. Niobotantalates, such as pyrochlore, samarskite, aeschinite, fergusonite, etc.
4. Carbonates, such as parisite and bastnaesite.

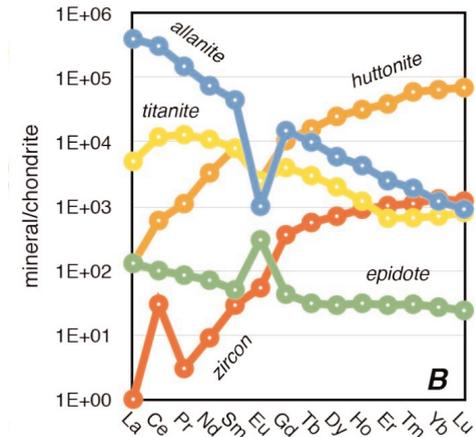
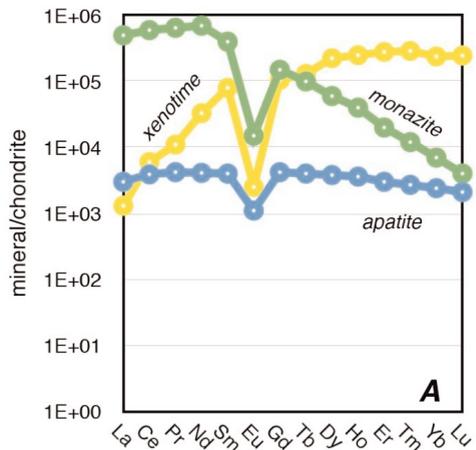


Fig. 8. Chondrite-normalized REE patterns of accessory phosphates (A) and silicates (B). From Bea (1996a) and unpublished data.

Figure 8 shows typical chondrite-normalized diagrams for the most common accessories. The nature of the accessories assemblage depends on the rock aluminosity.

Peraluminous rocks all most often contain monazite and huttonite whereas metaluminous rocks use to contain allanite and thorite, locally accompanied by parisite and other REE silicates. Peralkaline rocks may contain any REE minerals, but niobotantalates and carbonates usually carry most of the budget. Zircon is ubiquitous.

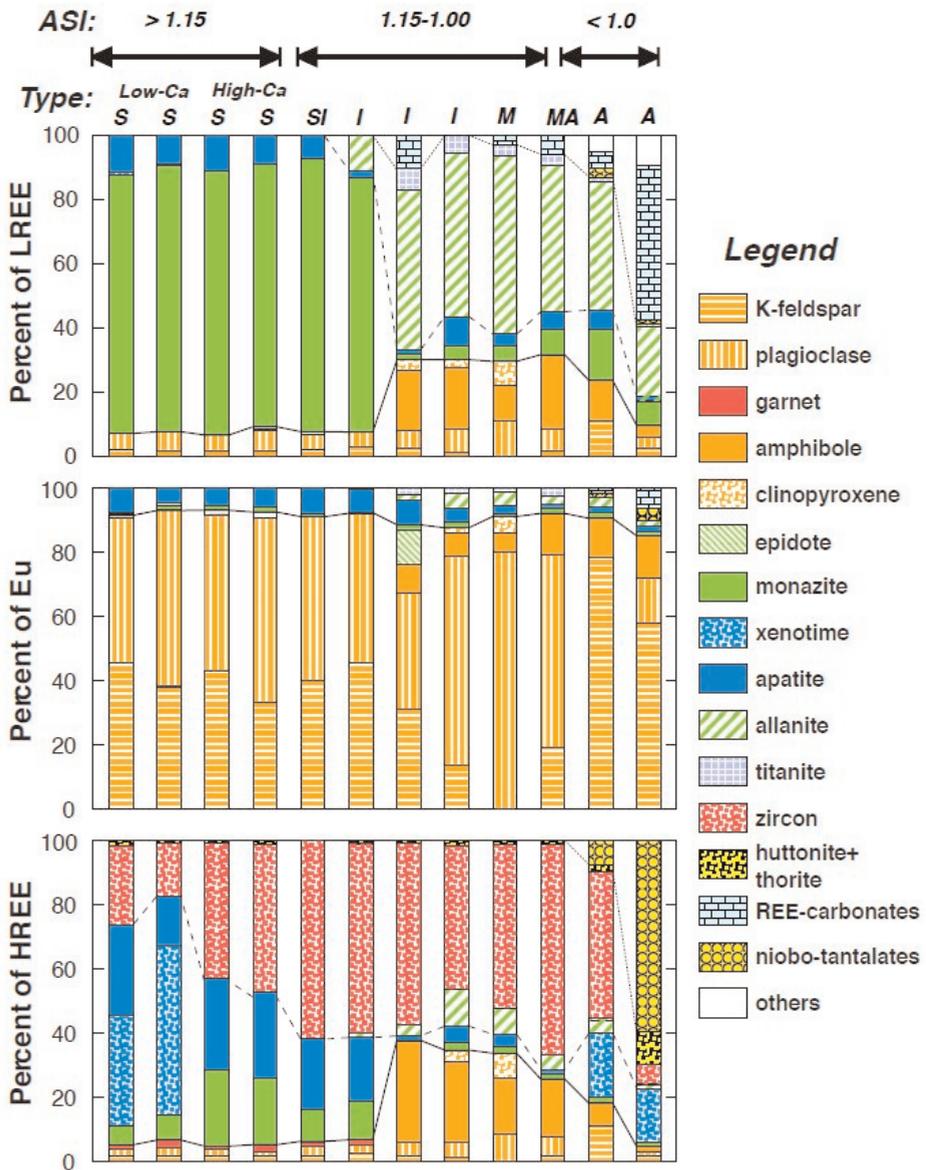


Fig. 9. Relative percentage of REE carried out by major vs. accessory phases in the whole spectrum of granite rocks. Note that only Eu is mostly controlled by major minerals whereas LREE and HREE are mostly controlled by accessories. From Bea (1996a).

Considering rocks mineralogy, it follows that the REE residence in mafic rocks is mostly controlled by major minerals, i.e., clinopyroxene, amphibole and plagioclase; when present, garnet, apatite, zircon, perovskite, and titanite may also play a significant role. In felsic rocks, on the other hand, the REE except Eu mostly dwell in accessory minerals (Fig. 9), up to 90-95 % in peraluminous and peralkaline rocks, and about 70 % in metaluminous, amphibole-bearing rocks.

The residence in accessory phases causes non-henrian behavior in the REEs, and affects markedly the REE partitioning during fractionation processes. The accessories solubility and solution kinetics as well as partial shielding by major minerals (Bea, 1996b) causes unpredictable partition coefficients and lends trace element fractionation equations inapplicable.

6. Final Remarks

The Rare Earth Elements geochemistry is a powerful petrogenetic tool which wisely used may result in great interpretations. The rule of thumb is to consider that the REEs:

- In mantle-derived rocks and magmas, the REEs give information about the behavior of major phases during partial melting and crystallization.
- In crustal mafic-to-intermediate systems the REEs also give information about the behavior of major phases, but the role of apatite, titanite, epidote and allanite must also be considered
- In crustal felsic and metapelitic systems, the REEs give information mostly about the behavior of accessory phases and the interplay between these and the major minerals.

7. References

Bea, F. (1996a). Residence of REE, Y, Th and U in granites and crustal protoliths; Implications for the chemistry of crustal melts. *Journal of Petrology*, 37(3), 521-552.

Bea, F. (1996b). Controls on the Trace Element Composition of Crustal Melts. *Transaction of the Royal Society of Edinburg: Earth Sciences*, 87(133-41), 33-42.

Bea, F., Montero, P., Garuti, G., & Zacharini, F. (1997). Pressure-dependence of rare earth element distribution in amphibolite- and granulite-grade garnets. A LA-ICP-MS study. *Geostandards Newsletters*, 21(2), 253-270.

Henderson, P.(1984). *Rare Earth Element Geochemistry*. Elsevier, 520 p.

Hofmann, A. W. (1988). Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth and Planetary Science Letters*, 90, 297-314.

Jones, A.P.; Wall, F. & Williams C.T. (1996). *Rare Earth Minerals: Chemistry, origin and ore deposits*. Chapman & Hill, 372 p.

McDonough, W. F., & Sun, S. S. (1995). The composition of the Earth. *Chemical Geology*, 120(3-4), 223-253.

Rudnick, R. L., & Fountain, D. M. (1995). Nature and Composition of the Continental-Crust . A Lower Crustal Perspective. *Reviews of Geophysics*, 33(3), 267-309.