

APPLICATION OF QUANTITATIVE AUTOMATED MINERALOGY IN REE IN EXPLORATION AND METALLURGY

Tassos Grammatikopoulos and Hugh de Souza¹

¹Address *SGS Canada Inc., 185 Concession Street, Lakefield, On. Canada, K0L 2H0*

Introduction

The term rare earth elements (REE) is used to describe the 15 metallic lanthanide elements, lanthanum through lutetium, plus the elements yttrium and scandium, which display similar physical and chemical properties (see IUPAC Nomenclature of Inorganic Chemistry, IR 3-6-2, 2004).

Economic and potentially economic REE deposits form two main groups. The first is a commonly occurring “light rare earth element” (LREE) rich group of deposits (La, Ce, Pr, Nd, Sm). The second is a less commonly occurring “heavy rare earth element” (HREE) rich group (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y). The LREE are hosted primarily by carbonatites and the HREE by highly alkaline to peralkaline ($Na + K > Al$) silicate igneous rocks. The LREE are produced mainly from bastnaesite, monazite, while HREE are produced almost exclusively from low-grade secondary ion adsorption clay deposits in which the REE are adsorbed onto surfaces of kaolinite and halloysite, the products of weathering of granites and sediments (Cornell, 1993, Chi and Tian 2009, Bao and Zhao 2008, Chakhmouradian and Wall 2012, Kynicky et al., 2012).

Most of REE deposits display a high degree of geological and mineralogical complexity that can have serious consequences for metallurgical processing if not well understood. Variable low temperature alteration processes redistribute the REEs in a range of minerals that can differ significantly between deposits. Hence, the proper characterization of the REE ores requires a multi disciplinary approach combining geology, mineralogy, geochemistry and mineral processing to define geological domains, and to develop and optimize metallurgical flowsheets to maximize grades and recoveries.

Quantitative automated mineralogy (QEMSCAN) is increasingly being applied to the study of ore deposits and mineral processing products. Information is derived from QEMSCAN, and other analytical techniques such as electron probe micro analysis (EPMA) and Laser Ablation ICP-MS, and is obtained from representative drill core and composite samples. Quantification parameters for REE minerals (REM) can lead to the identification of distinct zones (e.g., high HREE grades) and is

a critical first step in the domaining of an ore body, to characterize variability and its geometallurgical impact. Grain size, liberation and association of the REMs can determine the optimum liberation size of the minerals and affect grinding. Mineral speciation (e.g., monazite, xenotime, Zr-REE silicates) can dictate the recovery process (flotation, leaching). REM ratios can delineate mining blocks and help in the mine design.

Methodology

QEMSCAN Analysis

QEMSCAN (QS) uses an EVO 430 automated scanning electron microscope platform equipped with four light-element high count rate energy-dispersive X-ray spectrometers and iDiscover software capable of processing the data and images. QS is operated with a 25 kV accelerating voltage and a 5nA beam current. The QS measures, and the iDiscover software processes, data from every pixel across a sample with a pixel size defined based on the scope of the analysis. The data can be processed off line. The software assigns each pixel a mineral name based on 1,000 counts of energy dispersive X-ray spectral data and backscatter electron intensities. Additional information on the nature of samples and analytical techniques can be found in Grammatikopoulos et al. (2013).

Results

The mass % and the chemistry of the REM in the deposits vary widely. Table 1 shows some common REE minerals and their formulas to illustrate the chemical complexity. Zircon, titanite and apatite, and others are not primary REE-bearing minerals but are important REE-Y-Nb carriers in some deposits. The complexity of the REE deposits varies widely. Figure 1 shows backscattered electron (BSE) images to illustrate the occurrence of REM from different deposits. They show complexly intergrown REM.

Geochemical analyses alone cannot be used to calculate the normative mineralogy of the deposits because the REM usually occur as solid solution series.. However, they are useful because they can indicate trends of mineralization and aid interpretations when the mineralogy is known. Figure 2 illustrates a plot of Ce vs. La, Y and Dy clearly indicating (a) two different trends of mineralization and (b) differentiating between zones of light and heavy REE.

The study of drill core samples aims to characterize the different rock types, distribution of REM, alteration, and overall textural features of the rocks associated with the mineralization. The digital images, generated from the QS analysis, provide unperturbed textural features of the samples on a mesoscopic level (mm-cm in scale). REM are typically very fine-grained in the rocks examined (<10 μm to rarely 1 mm in size). Figure 2 illustrates representative pseudo colour images of two different drill core samples. The samples are chosen to illustrate the contrasting

mineral assemblages and styles of mineralization of the gangue minerals and REE styles of mineralization *in situ*. Figure 2a shows strong allanite mineralization and patchy to brecciated textures, whereas 2b shows disseminated and locally segregated monazite.

Table 1. Common REE minerals and formulas

| Mineral | Formula |
|-------------|--|
| Y-allanite | $(Ca, Y)_2(Al, Fe, REE)_3Si_3O_{12}(OH)$ |
| Monazite | $(LREE, Y, Th)PO_4$ |
| Bastnaesite | $REE(CO_3)F$ |
| Synchysite | $Ca(Ce, REE)(CO_3)_2F$ |
| Fergusonite | $(REE, Y)NbO_4$ |
| Eudialyte | $Na_4Ca_{1.5}Ce_{0.5}Fe^{2+}_{0.6}Mn^{2+}_{0.3}Y_{0.1}ZrSi_8O_{22}(OH)_{1.5}Cl_{0.5}$ |
| Xenotime | $(Y, Yb, HREE)(PO_4)$ |
| Mosandrite | $Na_2Ca_3Ce_{1.5}Y_{0.5}Ti_{0.6}Nb_{0.3}Zr_{0.1}(Si_2O_7)_2O_{1.5}F_{3.5}$ |
| Chevkinite | $Ce_{1.7}La_{1.4}Ca_{0.8}Th_{0.1}Fe^{2+}_{1.8}Mg_{0.2}Ti_{2.5}Fe^{3+}_{0.5}Si_4O_{22}$ |
| Zircon | $Zr_{0.9}Hf_{0.05}REE_{0.05}SiO_4$ |
| Columbite | $(Fe, Mn, Mg)(Nb, Ta)_2O_6$ |
| Apatite | $(Ca, REE, Sr)_5(PO_4)_3(OH, F, Cl)$ |
| Titanite | $Ca_{0.95}REE_{0.05}Ti_{0.75}Al_{0.2}Fe^{3+}_{0.05}SiO_{4.9}F_{0.1}$ |

Assay rejects can be used to determine the mineralogy of the ore. Figure 4 illustrates the ore variability defined across drill holes and along depth. The mineralogical results do not reflect an isolated single sample, but a continuum of larger samples that correspond to the samples used for the geochemical analysis. Variability analyses aim to quantify the mineralogy of intervals in order to define potential HREE and LREE zones. By comparing the geochemical analysis and mineral distributions of the zones of enriched LREE and HREE, a mineralogical differentiation is demonstrated (e.g., Nechalacho). The data can be used to map the deposit and define mineralization trends (Figure 5).

Composite samples, prepared from a number of drill cores, represent or aim to define domains within deposits. They are analyzed to provide the liberation and association attributes of the REM and define the initial target grind sizes. For liberation and association analysis, particle liberation is defined based on 2D particle area percent. Particles are classified as pure (100% surface area), free ($\geq 95\%$) and liberated ($\geq 80\%$).

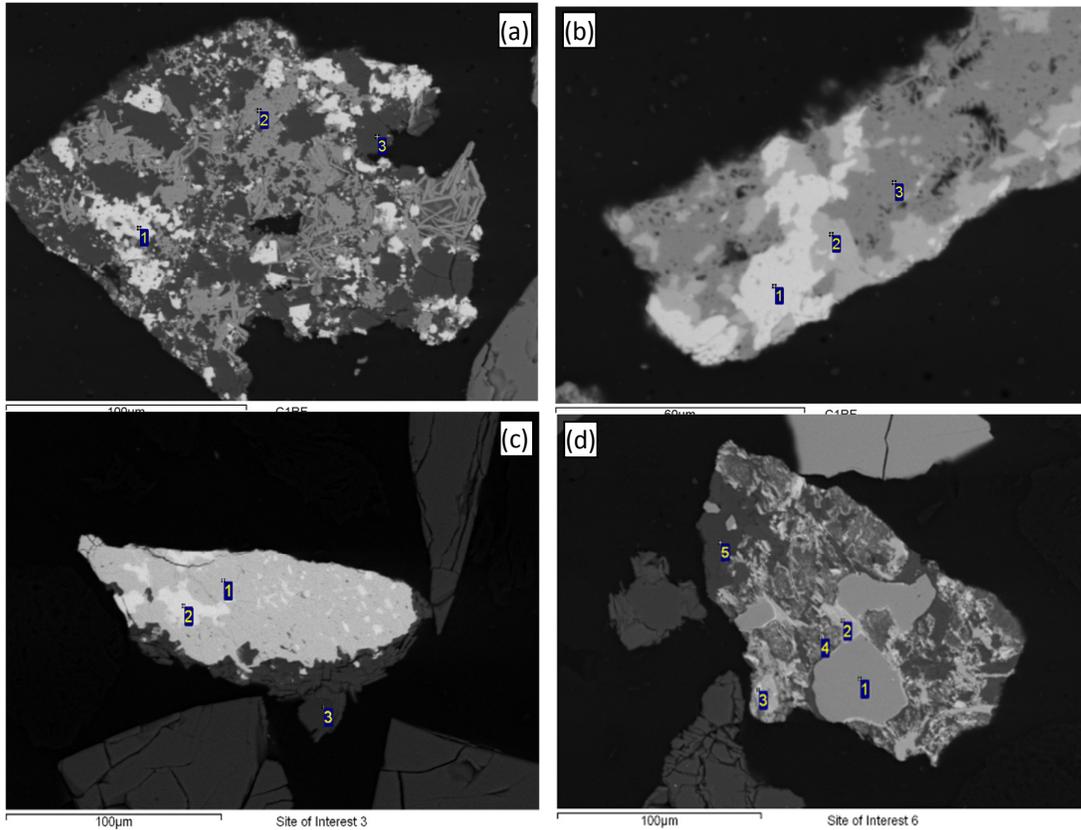


Figure 1. Backscattered electron images of REE minerals

(a) Bastnaesite (n-1) among Fe-oxides (n-2) and quartz (n-3); (b) monazite (n-1), xenotime (n-2) and Fe-oxides (n-3); (c) monazite locked in thorite; (d) and pyrite (n-1), synchysite (n-2), brannerite (n-3), allanite (n-4), quartz (n-5).

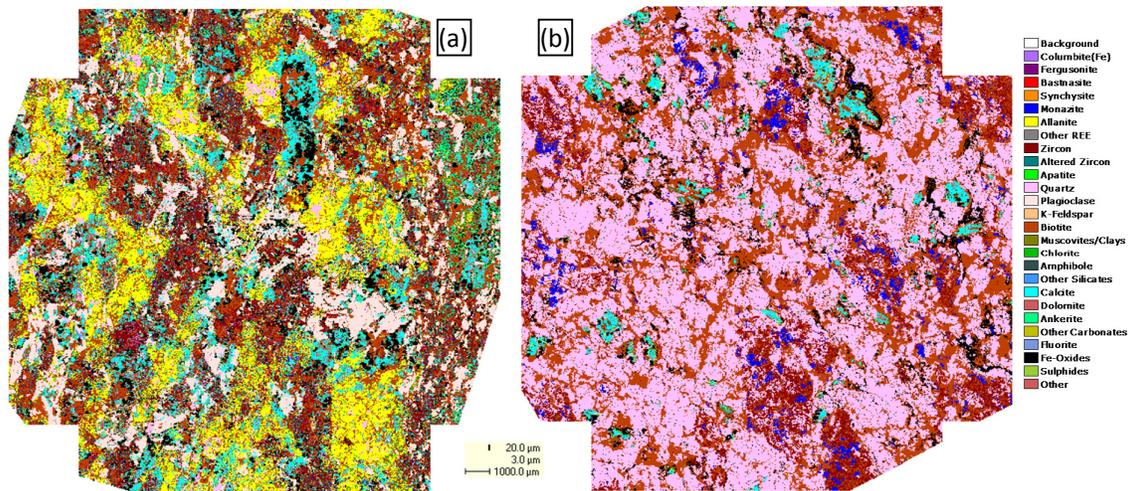


Figure 2. Pseudo coloured mineralogical images from QEMSCAN

Non-liberated grains are classified according to association characteristics, where binary association groups refer to particle area percent $\geq 95\%$ of the two minerals or mineral groups. Figure 6 shows an example of liberation of monazite from a carbonatite deposit. Liberation calculated for the head sample is $\sim 41\%$ (pure, free and liberated combined). Liberation values generally increase with decreasing size from 1% to 7% to 35% to 60%.

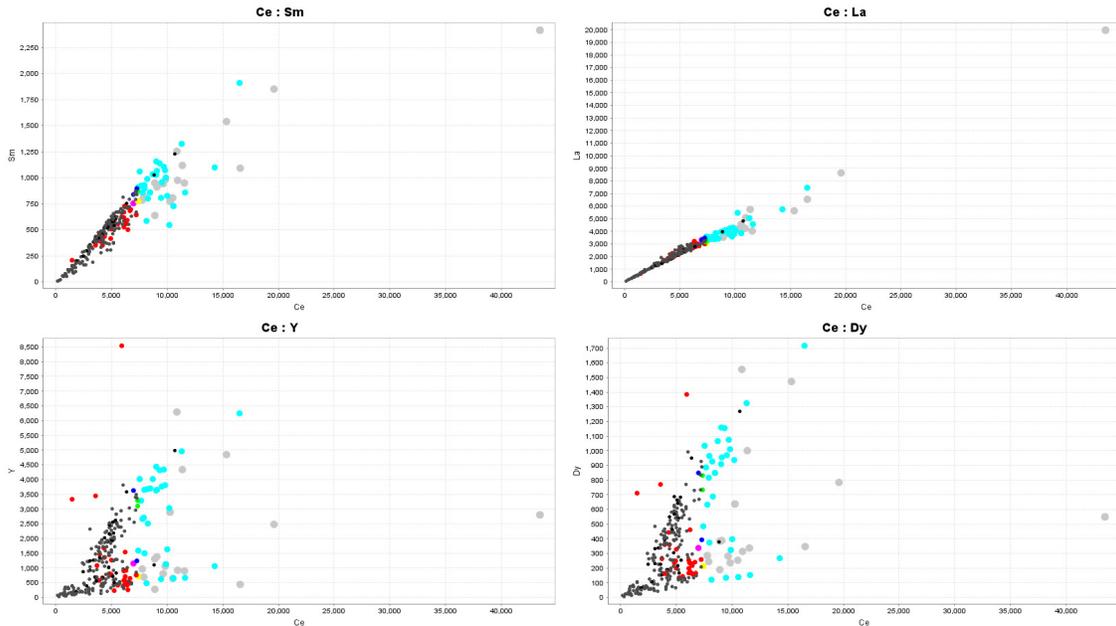


Figure 3. Ce vs Sm, Y and Dy

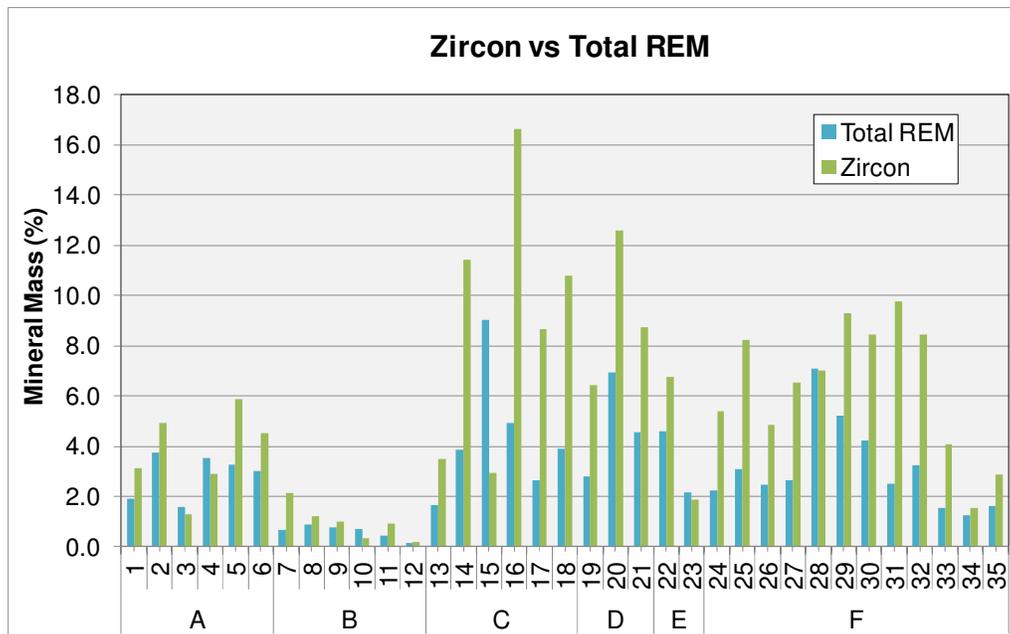


Figure 4. Mineral variability across different zones

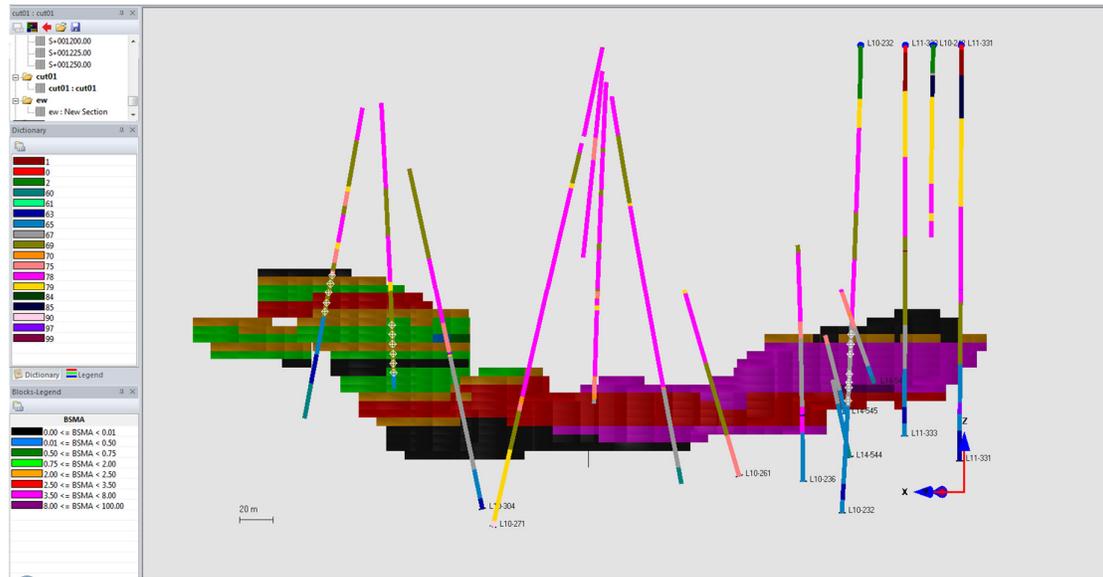


Figure 5. Cross section of a deposit using mineral variability

REM display wide-ranging solid solution compositions that vary among and across deposits. In addition, commonly occurring silicate minerals e.g., apatite, zircon and titanite can carry significant REE in their matrices. The distribution of the REE is critical because it provides insights to the main LREE and HREE carriers. It enables mass balance calculations to predict potential concentrates and tailings losses. Figure 7 illustrates an example of the elemental department calculated for a composite sample. Titanite and apatite which are considered refractory carry significant amounts of Ce and Y (<6%).

Discussion

REE deposits typically are the product of both magmatic and hydrothermal processes and therefore the distribution of the REM is complex. Thus, the textural analysis indicates contrasting rock types and styles of mineralization and unlocks the in situ texture of the REM that are useful for exploration purposes. Quantification of the REM, coupled with geological and geochemical data, can help delineate HREE and LREE zones, map the orebody, and assist in selection of samples for metallurgical test work. The REE distribution among the main carriers is critical for metallurgical test work. The liberation and association of the REM is also critical for selecting the proper beneficiation method (i.e., flotation, gravity).

Domains of HREE and LREE are useful to define because certain minerals cannot be properly recovered. Thus, they can be avoided during mining if possible. Furthermore, metallurgical balances using only REE (e.g., Ce, Y) are not adequate to understand the high or low recovery of certain minerals. Mineral balances are necessary in order to optimize the process. The data can then be used to

populate the geological and mining models in order to at least optimize the REE recovery.

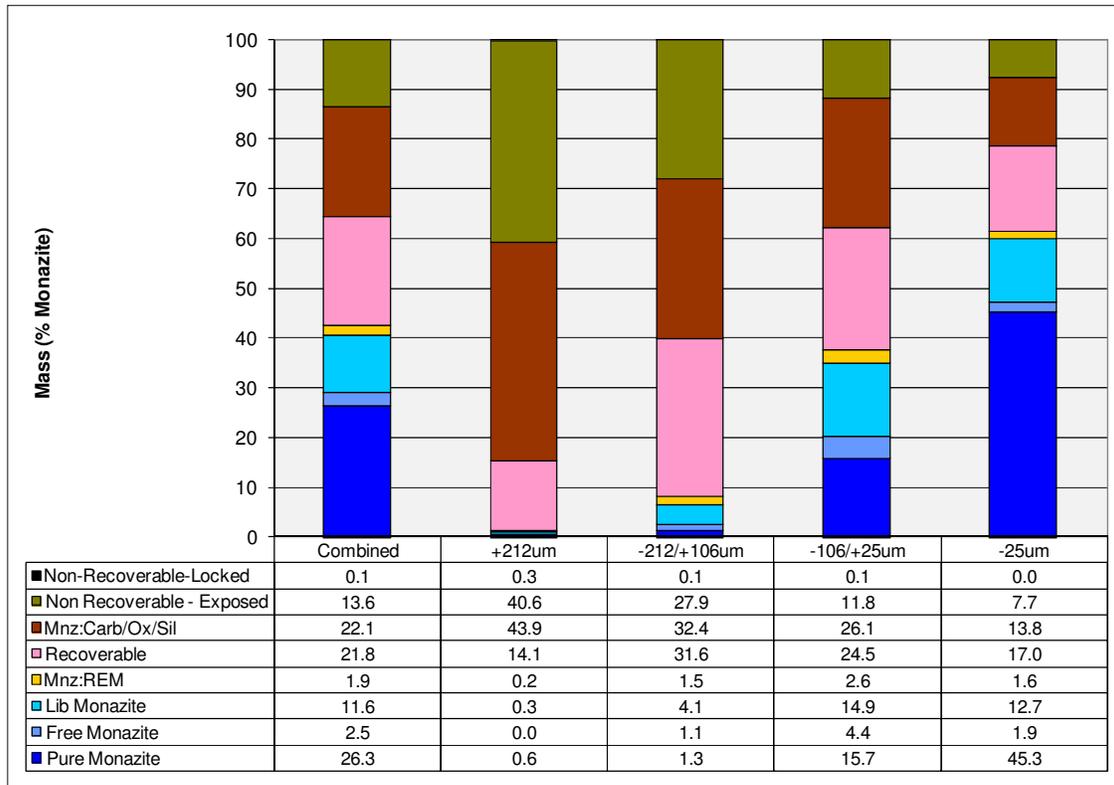


Figure 6. Recoverability as a function of liberation and exposure of monazite

Conclusions

A synthesis of quantitative data from automated mineralogical analysis, mineral chemistry, and geological information can properly delineate the ore, predict REE grades and recoveries, and assist with the classification of mineral resources and economic potential. This is part of evaluating the economic potential of the REE deposits. The quantification and improved understanding of inherent mineralogical parameters in exploration, and metallurgy using automated and quantitative mineralogy constitutes an integral part of the geometallurgical framework.

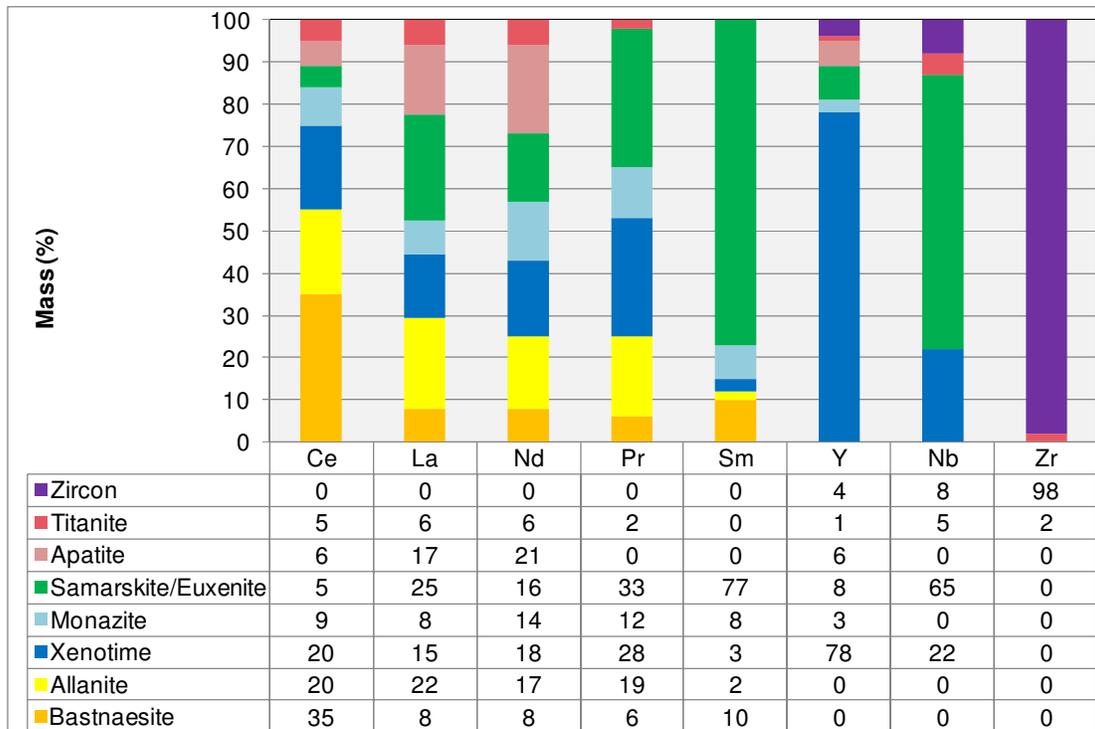


Figure 7. REE distribution

References

- CORNELL, D.H. 1993. Rare earths from supernova to superconductor. *Pure Applied Chemistry*, 85, 2453-2464.
- CHI, R & TIAN, J. 2009. *Weathered Crust Elution- Deposited Rare Earth Ores*, Nova Science Pub Inc, 2009, 288 pp.
- BAO, Z. & ZHAO, Z. 2008. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in South China. *Ore Geology Reviews*, 33, 519-535.
- CHAKHMOURADIAN, A.R. & WALL, F. 2012. Rare Earth Elements: Minerals, Mines, Magnets (and More). *Elements*, 8, 333-340.
- GRAMMATIKOPOULOS, T., MERCER, W. & GUNNING, C. 2013. Mineralogical characterization using the QEMSCAN of the Nechalacho heavy rare earth metal deposit, Northwest Territories, Canada. *Canadian Metallurgical Quarterly*, 52, 265-277.
- KYNICKY, J., SMITH, M. & XU, C. 2012. Diversity of Rare Earth Deposits: A Key Example of China. *Elements*, 8, 361-367.