

FACT SHEET

RARE EARTH ELEMENTS ANALYSIS

The demand for rare earth elements has increased substantially owing to their unique physical, chemical and light-emitting properties. They are utilised in a range of new technologies and are increasing in importance due to the clean energy economy and the risk of supply disruption.

Overview

The name rare earth element is somewhat misleading, as they are neither rare nor from earth. Rare earth elements (REE) are relatively abundant in the earth's crust, however, are relatively evenly dispersed in the crust and rarely form concentrated ores. Rare earth elements are produced by supernova nucleosynthesis or by the s-process in asymptotic giant branch stars. Rare earths can be divided into light rare earth elements (LREE) which include La, Ce, Pr, Nd and Sm, and heavy rare earth elements (HREE) which include Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu plus Y.

World resources of LREE are hosted primarily in carbonatites, with the REE contained in bastnäsite and monazite. Bastnäsite deposits in China and the United States constitute the largest fraction of the world's rare earth economic resources. Monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand and the United States constitute the second largest segment. The latter are found in paleoplacer and recent placer deposits, sedimentary deposits, veins, pegmatites, carbonatites, and alkaline complexes. Alkali igneous intrusions in the Lovozero and Khibina Massifs in Russia are also highly enriched in REE, Nb and Ta.

A large portion of HREE is found in xenotime and monazite which occur in a wide variety of geologic environments. These include alkaline granites, hydrothermal deposits, laterites, placers, and vein-type deposits. A significant portion of HREE is associated with weathered clay deposits, yttrium-bearing



minerals in apatite-magnetite-bearing rocks, deposits of niobium-tantalum minerals, non-placer monazite-bearing deposits, sedimentary phosphate deposits, eudialyte-bearing deposits and some uranium ores. Undiscovered REE resources are thought to be very large relative to the expected demand¹. Rare earth elements are ranked as the highest mineral raw materials of critical concern, given uncertain future supplies and their importance to advanced industrial economies^{2,3}.

The demand for rare earth elements has increased substantially owing to their unique physical, chemical and light-emitting properties. They are exploited in a range of new technologies along with elements such as Y, Nb, Ta, Zr, Hf and Sc with which they are intimately associated in many deposits. Nd, Dy, Eu, Tb and Y are now considered "critical" rare earths in terms of their importance to the clean energy economy and the risk of supply disruption.

Techniques for Rare Earth Exploration

For many years chondrite normalised plots of the REE have been used in petrogenesis (Figure.1). A europium anomaly is generally an indication that a rock or the parent from which it was derived has fractionated plagioclase or a mineral into which Eu has partitioned. During magma crystallization in a reducing environment divalent Eu^{2+} preferentially incorporates into plagioclase substituting for Ca^{2+} . A plagioclase cumulate will have a positive Eu anomaly whereas the residual magma, from which it fractionated,

a negative anomaly. Large positive Eu anomalies occur in the most felsic rocks which also have a high Ba content and are severely depleted in HREE. A negative Eu anomaly is a signature of post-Archean sediments⁴. In addition to europium, one can observe cerium in two different states: soluble Ce^{3+} can be oxidised by atmospheric oxygen to less soluble Ce^{4+} . The presence of a Ce anomaly can be used to determine redox conditions in marine sediments like carbonates and phosphates⁵.

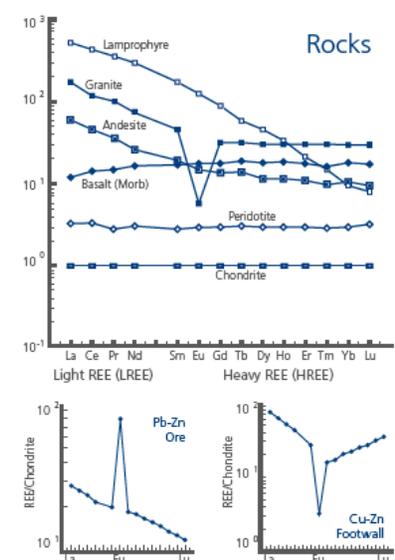


Figure 1. a) REE Chondrite plots of various rocks; b) chondrite plot of Pb-Zn ore with positive Eu anomaly, which is associated with Pb-Zn sulphides, New Brunswick, Canada (Graf⁶ et al, 1977); c) chondrite of Cu-Zn of footwall with negative Eu anomaly with enriched heavy REE ("birdwing profile") in rocks below the ore (Schade et al, 1989)⁷.



Most of REE deposits are restricted to areas underlain by Precambrian rocks, which have recognizable features and can be identified by aerial photography. However, this approach may not be suitable for complexes, which occur in clusters (Mt Weld, Australia) or linear belts (Araxá-Catalão, Brazil). Owing to the presence of U and Th in REE deposits, surface or airborne radiometric surveying can be used quite successfully. Placer deposits however, produce weak radiometric signatures so due care must be exercised. Geophysical methods can be used for buried mineralisation, but the effectiveness depends on the anomalous density as well as the magnetic susceptibility of the deposit and the associated rocks. Geochemical surveys using stream sediments, water and soil are used widely to identify REE host rocks. Biogeochemistry can be useful in identifying REE deposits below cover. Trenching and pitting by heavy equipment may also be useful for poorly exposed deposits.

Methods of Analysis

Whether you are using REE as indicators or exploring for REE deposits using soil, rock chips or drill core you need to choose an appropriate analytical method. There are numerous considerations that need to be taken into account when selecting the appropriate methodology for your samples. The HREE, Y, Zr, Hf, Nb and Ta are commonly hosted by refractory minerals that may not be completely digested by an acid digestion. For these samples, fusion using sodium peroxide of lithium borate fluxes provide a total dissolution of all rare earth containing minerals. Figure 2 shows the chondrite normalized plot for CRM's with good correlation between four-acid and fusion method whereas Figure 3 shows those certified reference materials where the recovery in the four-acid method is lower than the fusion. If lower detection limit analysis is required, Intertek can explore whether your samples are suitable for multi acid digestion.

Instrumentation selection is also important for the quantification of rare earth elements. ICP-OES and ICP-MS can be used for the quantification after the appropriate digestion technique but special consideration needs to be taken into account to remove the associated interferences, especially on ICP-MS where there are numerous overlapping isotopes of rare earth elements with the same mass to charge ratio. Intertek offers an ICP-MS-QQQ package allowing for the interference free quantification of your samples. Intertek can also offer an XRF

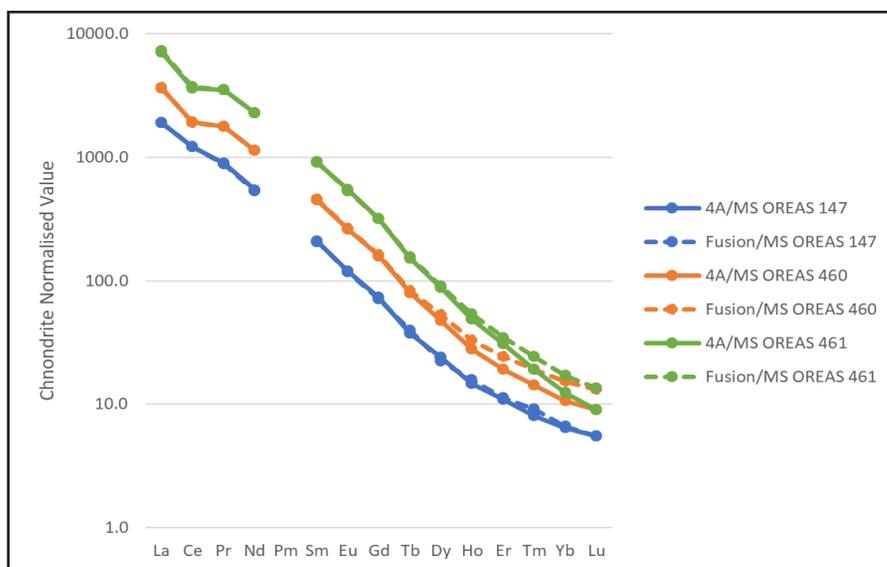


Figure 2: Chondrite normalised plot for certified reference materials with similar recoveries in four-acid and fusion techniques.

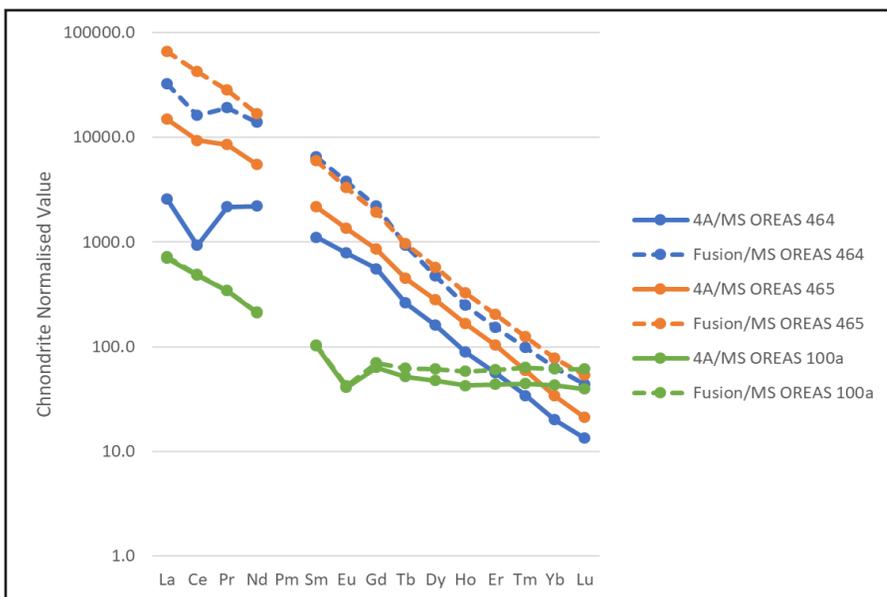


Figure 3: Chondrite normalised plot for certified reference materials with lower recoveries from the four acid method when compared with the fusion methods.

analysis for your rare earth concentrate samples with ICP-MS-QQQ to quantify the impurities.

7 Schade, J., Cornell, D.H., Theart, H.F.J. 1989. Rare earth element and isotopic evidence for the genesis of the Prieska massive sulfide deposit, South Africa. *Economic Geology* 84, 49-63.

- 1 U.S. Geological Survey, Mineral Commodity Summaries, 2009.
- 2 REE handbook, PROEDGE wire, <http://www.reehandbook.com>
- 3 U.S. Geological Survey, Mineral Commodity Summaries, 2010.
- 4 Rudnick, L.R. 1991. Restites, Eu anomalies, and the lower continental crust. *Geochemica et Cosmochimica*, 56, 963-970.
- 5 Shields, G. et al. 1998. Stratigraphic trends in cerium anomaly in authigenic marine carbonates and phosphates: diagenetic alteration or seawater signals. *Goldschmidt conference Toulouse*.
- 6 Graf, J.L. 1977. Rare earth elements as hydrothermal tracers during the formation of massive sulphide deposits in volcanic rocks. *Economic Geology*, v.72, no. 4, p. 527-548.

FOR MORE INFORMATION

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