

Exploration and Mining of Rare Earth Elements (REE) Using Tube-Based Thermo Scientific Portable XRF Analyzers



Introduction

Rare earth elements (REEs) are natural elements with an atomic number from 57 to 71. These elements are classified into two groups: light REEs (LREEs), representing lanthanum (La) to samarium (Sm), and heavy REE (HREE), representing europium (Eu) to lutetium (Lu). Scandium (Sc) and yttrium (Y) have similar chemical properties and tend to occur in the same ore deposits as REEs, particularly HREEs.

Although REEs are not as rare as precious metals, their mining and extraction technology is very costly. The exploration and mining of REEs has increased tremendously due to strong demand and short supply worldwide. These elements are used commonly in electronics (See Table 1).

Application

Although rare earth elements are relatively abundant in the earth's crust (see Table 2), they are rarely concentrated into mineable ore deposits. REEs are associated with alkaline rocks, carbonatite, pegmatite, and placer deposits (residual deposits formed from deep weathering) and are often discovered via geochemical exploration. They may also be absorbed in clay minerals. The ores of rare earth elements are mineralogically and chemically complex and commonly radioactive. REE mining is challenging because REEs are concentrated in more than one mineral, and each mineral requires a different costly extraction technology and mineral processing. Therefore, rare earth element deposits in which REEs are largely concentrated in a single mineral phase have a competitive advantage. To date, REE production has largely come from single-mineral-phase deposits, such

as Bayan Obo (bastnasite, $\text{Ce,La}(\text{CO}_3)\text{F}$), Mountain Pass (bastnasite), and heavy-mineral placers (monazite, $(\text{Ce,La,Nd,Th})\text{PO}_4$). As this case study shows, portable XRF is a very useful tool to qualitatively and quantitatively evaluate REE projects in real time in the field.

Portable XRF Analyzers in REE Exploration and Mining

Thermo Scientific portable XRF analyzers are available with your choice of excitation options, providing the optimal configuration for your analytical needs. Our current product offering includes three types of XRF analyzers for REE detection and

REE		Use
La	Lanthanum	Battery electrodes and camera lenses
Ce	Cerium	Polishing powder and fluid catalytic cracking catalyst for oil refineries
Pr	Praseodymium	Rare earth magnets and lasers
Nd	Neodymium	Ceramic capacitors
Sm	Samarium	Neutron capture
Eu	Europium	Lasers and mercury-vapor lamps
Gd	Gadolinium	Lasers, x-ray tubes, and computer memories
Tb	Terbium	Lasers and fluorescent lamps
Dy	Dysprosium	Rare earth magnets and lasers

Table 1. Examples of the use of REE

quantification: the Thermo Scientific Niton XL3t GOLDD+ (tube-based), Niton® XL3t Ultra (tube-based), and the Niton XLp 522K (isotope-based) analyzers. See Table 2 for the limits of detection.

The Niton XLp 522K analyzer can quickly analyze elements from titanium (Ti) to uranium (U). These analyzers cover a broader range of REEs than our tube-based analyzers, and offer direct analysis of the full suite of these elements: (La), (Ce), (Pr), and (Nd), (Sm), (Eu), (Gd), (Tb), and (Dy), as well as Y, U, and Th.

Our breakthrough Niton XL3t GOLDD+ and Niton XL3t Ultra tube-based analyzers provide an analytical range from magnesium (Mg) to U to fill most mining needs. With their 50kV miniaturized x-ray tube, it is now possible to excite most LREEs. Other elements associated with REE-bearing minerals such as U, Th, Y, and Sc may also be analyzed. By using the concentrations from these elements, especially Y and Sc, it is possible to infer concentrations of HREEs. With radioactive elements (U and Th), we suggest also using the Thermo Scientific RadEye gamma detector as an ancillary exploration tool.

Method

This investigation was carried out on phosphate samples from British Columbia, Canada. The samples were pulverized and cupped using polypropylene film and analyzed with a Thermo Scientific Niton XL3t GOLDD+ analyzer using Mining Analysis for 45 seconds on each filter (for a total analysis time of 3 minutes). In X-Y graphs (see Figure 1), the factory

REE		Earth Crust (ppm)
Y	Yttrium	33
La	Lanthanum	39
Ce	Cerium	66
Pr	Praseodymium	9
Nd	Neodymium	41
Sm	Samarium	7
Eu	Europium	2
Gd	Gadolinium	6
Tb	Terbium	1
Dy	Dysprosium	5

Table 2. Average REE concentration found in the earth's crust.

calibration and modified (using project-based Cal-Factor adjustments) XRF results are compared with lab (ICP-MS) assays of the same samples. Cal-Factors are matrix-based adjustments that are done using samples with matrices similar to unknown samples. This adjustment can be done directly in the instrument.

Results

Figure 1 shows that there is a high correlation between portable XRF and lab data for P, Y, La, and Pr, particularly for set of data obtained after using Cal-Factor. High correlation in Y suggests that the samples are likely enriched in HREE as well.

Limits of Detection in ppm (mg/kg) — 45s per filter —					
Elements		Niton XL3t Ultra		Niton XL3t GOLDD+	Niton XL3p 522K
		Natural Sample	SiO ₂ Matrix	SiO ₂ Matrix	SiO ₂ Matrix
Y	Yttrium	4	1.5	5	11
La	Lanthanum	43	34	50	25
Ce	Cerium	47	40	60	40
Pr	Praseodymium	57	46	65	30
Nd	Neodymium	93	75	90	30
Sm	Samarium	NA	NA	NA	40
Eu	Europium	NA	NA	NA	40
Gd	Gadolinium	NA	NA	NA	60
Tb	Terbium	NA	NA	NA	40
Dy	Dysprosium	NA	NA	NA	80

Element list shown is not exhaustive. For limits of detection for elements not shown, please contact your local Thermo Scientific portable XRF analyzer representative.

Notes: All measurements are made without the aid of helium (He). NA = Not Analyzed.

Table 3: REE limits of detection for the Niton XL3t GOLDD+ (tube-based), Niton XL3t Ultra (tube-based), and the Niton XLp 522K (isotope-based) analyzers.

Conclusion

Geochemical exploration is the main method of REE exploration. Ores of rare earth elements are mineralogically and chemically complex and commonly radioactive. Currently, REEs are extracted from two mined minerals (bastnasite and monazite).

Depending on the REE project type, Niton XL3t GOLDD+, Niton XL3t Ultra, and Niton XLp 522K analyzers are all useful instruments that can provide real-time, on-site assays of REE and other elements in any type of geological samples. Using Cal-Factors and adjusting data based on project samples improves the assay data. The recent improvement in our Cal-Factors is called Type Standardization. This allows users to do this adjustment directly in the instrument.



Bastnasite (crystal)

Photo courtesy of iRocks.com

To discuss your particular applications and performance requirements, or to schedule an on-site demonstration, please contact your local Thermo Scientific portable analyzer representative or contact us directly by email at niton@thermofisher.com, or visit our website at www.thermoscientific.com/niton.

We would like to thank Dr. George Simandl for his technical and geological support.

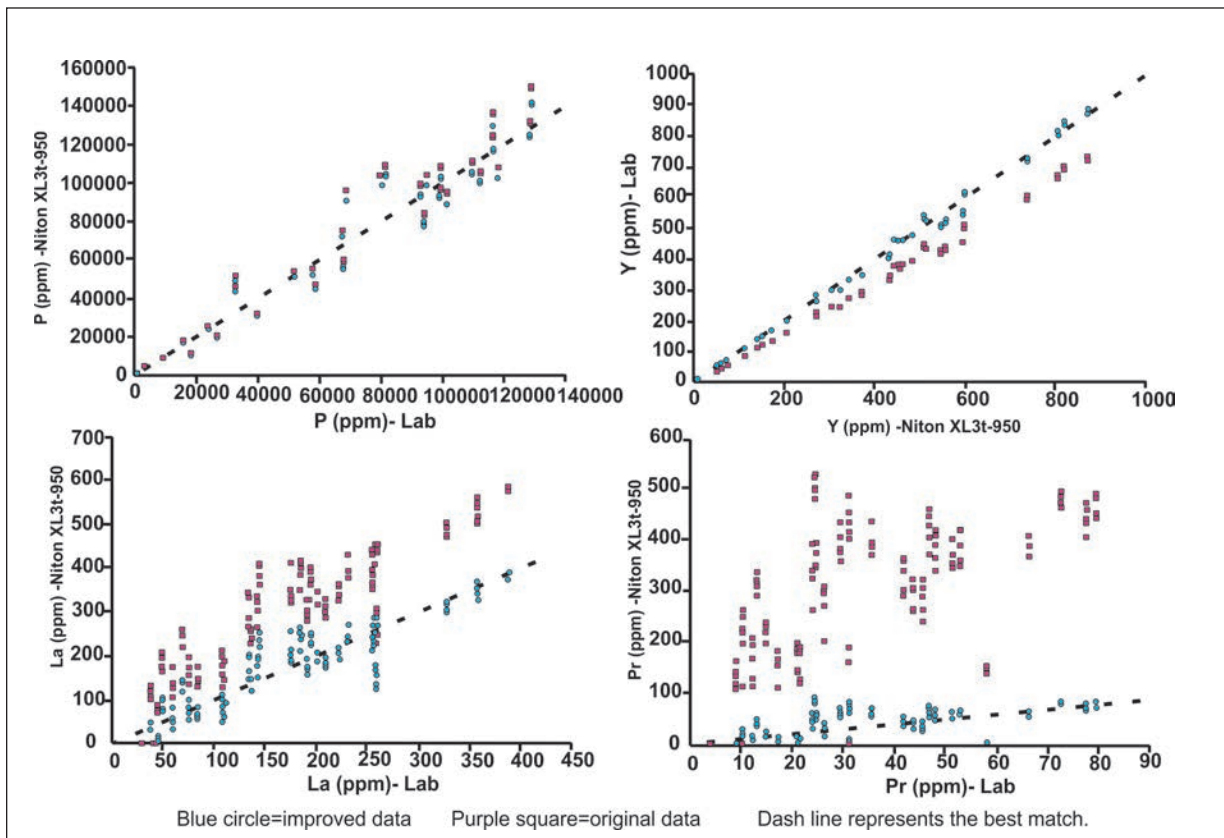


Figure 1. Correlation diagrams for P, Y, La, and Pr analyzed using the Niton XL3t GOLDD+ analyzer.

In addition to the offices listed below, Thermo Fisher Scientific maintains a network of sales and service organizations throughout the world.

Key to Energy Values

Thermo Scientific X-RAY ENERGY REFERENCE

H Hydrogen 1																	He Helium 2															
Li Lithium 3	Be Beryllium 4																	B Boron 5	C Carbon 6	N Nitrogen 7	O Oxygen 8	F Fluorine 9	Ne Neon 10									
Na Sodium 11	Mg Magnesium 12																	Al Aluminum 13	Si Silicon 14	P Phosphorus 15	S Sulfur 16	Cl Chlorine 17	Ar Argon 18									
K Potassium 19	Ca Calcium 20	Sc Scandium 21	Ti Titanium 22	V Vanadium 23	Cr Chromium 24	Mn Manganese 25	Fe Iron 26	Co Cobalt 27	Ni Nickel 28	Cu Copper 29	Zn Zinc 30	Ga Gallium 31	Ge Germanium 32	As Arsenic 33	Se Selenium 34	Br Bromine 35	Kr Krypton 36															
Rb Rubidium 37	Sr Strontium 38	Y Yttrium 39	Zr Zirconium 40	Nb Niobium 41	Mo Molybdenum 42	Tc Technetium 43	Ru Ruthenium 44	Rh Rhodium 45	Pd Palladium 46	Ag Silver 47	Cd Cadmium 48	In Indium 49	Sn Tin 50	Sb Antimony 51	Te Tellurium 52	I Iodine 53	Xe Xenon 54															
Cs Cesium 55	Ba Barium 56																	Hf Hafnium 72	Ta Tantalum 73	W Tungsten 74	Re Rhenium 75	Os Osmium 76	Ir Iridium 77	Pt Platinum 78	Au Gold 79	Hg Mercury 80	Tl Thallium 81	Pb Lead 82	Bi Bismuth 83	Po Polonium 84	At Astatine 85	Rn Radon 86
Fr Francium 87	Ra Radium 88																															
		57-71																														
		88-103		La Lanthanum 57	Ce Cerium 58	Pr Praseodymium 59	Nd Neodymium 60	Pm Promethium 61	Sm Samarium 62	Eu Europium 63	Gd Gadolinium 64	Tb Terbium 65	Dy Dysprosium 66	Ho Holmium 67	Er Erbium 68	Tm Thulium 69	Yb Ytterbium 70	Lu Lutetium 71														
				Ac Actinium 89	Th Thorium 90	Pa Protactinium 91	U Uranium 92	Np Neptunium 93	Pu Plutonium 94	Am Americium 95	Cm Curium 96	Bk Berkelium 97	Cf Californium 98	Es Einsteinium 99	Fm Fermium 100	Md Mendelevium 101	No Nobelium 102	Lr Lawrencium 103														

Requires GOLDD technology for metal alloys

Requires GOLDD technology for mining & minerals mode

☐ Rare Earth Elements (REE) measurable with either the Niton XL3t or the Niton XLP 522K

☐ Heavy Rare Earth Elements (HREE): Requires Niton XLP analyzer

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Thermo Scientific Niton XRF analyzers are the ideal choice for measuring both light and heavy rare earth elements as well as providing reliable results for a comprehensive range of key element groups for mineral exploration.