



# Quantification of trace REE-minerals using automated mineralogy

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**Abstract.** The exploration for rare earth element deposits is currently experiencing a boom period due to their importance as a component within modern materials and technology devices. This study focuses on using automated mineralogy (QEMSCAN<sup>®</sup>) to aid in identifying the primary REE-bearing mineralogy, as these minerals are only present in trace amounts and are difficult to quantify using other technologies. The data show that it was possible to quantify such minerals (e.g. monazite and allanite) to as low as 0.05 wt. %. This information is crucial for the final choice of the exploitation technologies. In addition, other important variables such as mineral grain sizes, mineral liberation, REE department, and mineral associations, as well as textural observations, can be ascertained. Such information will aid in defining the most suitable mineral processing procedures for extracting the rare earth elements.

**Keywords:** rare earth elements, REE deposits, Ion-adsorption, QEMSCAN<sup>®</sup>, Chile

## Introduction

The rare earth elements (REE's) are a group of 17 chemically similar metallic elements, including the 15 lanthanides as well as scandium and yttrium. Because of this chemical similarity the various REE's can very easily substitute for each other and often occur together within various minerals. Within the Earth's crust they are estimated to have an overall abundance of 9.2 ppm (Rudnick et al., 2003). The REE's do not occur naturally as metallic elements, but do occur in a wide range of mineral types, for example halides, carbonates, oxides, phosphates and silicates, which often have the most abundant REE element as a suffix (British Geological Survey, 2011).

REE mineral deposits occur in a wide range of igneous, sedimentary and metamorphic rocks and are generally classified into two types: primary deposits associated with igneous and hydrothermal processes, and secondary deposits concentrated by sedimentary process and weathering (British Geological Survey, 2011). A detailed summary of REE deposits and their classifications is

provided by Orris and Grauch (2002), Grauch and Mariano (2008), and Hellman and Duncan (2014).

REE's have been increasingly exploited from the mid-20th century as technological advancement requires their beneficial properties. Consequently, the market demand and prices for REE's are strong and robust, especially given that world production is almost monopolistically controlled by China. Current REE reserves, whilst unreliable, indicate that China controls almost 50% of known deposits by volume. Significantly, REE production in China has steadily increased from the 1990's, and is currently 97% of total world production as at 2010 (British Geological Survey, 2011; Castor and Hedrick, 2006). Chile has several prospective REE occurrences and opportunities exist to exploit the high prices and monopolistic market supply. The automated mineralogical analysis (QEMSCAN<sup>®</sup>) of a suite of samples representing different protolith lithologies from one such REE-deposit was used to quantify the primary REE-ore mineralogy

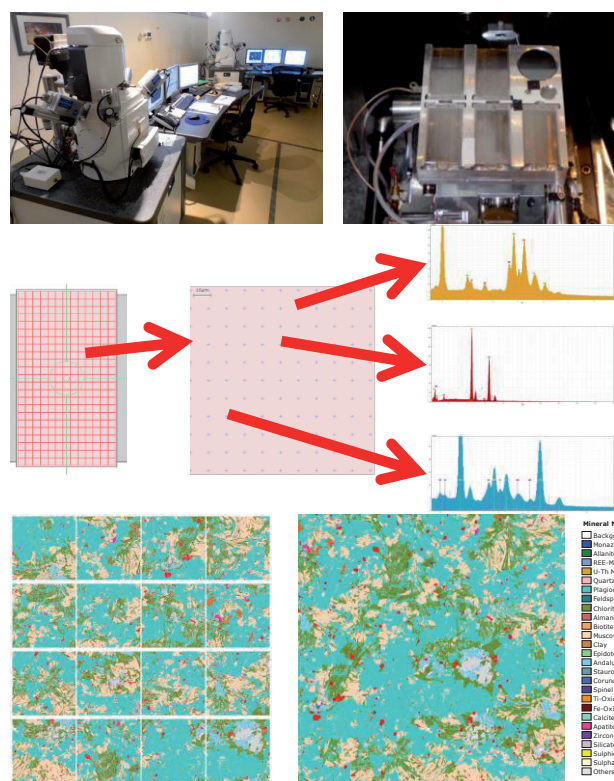
## Sample Description

The samples were supplied by Biolantanidos from a REE project located in the eighth region in Chile. This study reports the QEMSCAN<sup>®</sup> analysis of 5 samples: 4 from a Garnet Granite (GG) and 1 from a Biotite Granite (GB).

## Analytical Methodology

Representative probe sections were made for each sample and carbon coated prior to automated mineralogical analysis at CISEM (Centro de Investigación y Servicios Mineralógicos), Universidad Católica del Norte (UCN), Antofagasta, Chile. The analyses were made using a QEMSCAN<sup>®</sup> model E430, which is based on a ZEISS EVO 50 Scanning Electron Microscope (SEM) combined with Bruker Series 4 x-ray energy dispersive spectrometer (EDS) detectors. Routine analysis is performed with a spot size of less than 1 µm at an operating voltage of 25 kV and a beam current of 5 nA. The standard 1000 counts per point were acquired and this yields a detection limit of approximately 2 wt% per element for each mineral classification point. Measurements were performed using

iMeasure v5.3.2 and data reduction using iDiscover v5.3.2. The samples were analysed in Fieldscan mode at a field size of 1500  $\mu\text{m}$  (approximate magnification of 50x) or 2500  $\mu\text{m}$  (approximate magnification of 30x). The back scattered electron levels were calibrated from 0-255 where Quartz = 42, Copper = 130, and Gold = 232. Mineral analysis can be completed using a variety of different operating modes; in this study the samples were mineralogically and compositionally mapped using the fieldscan operating mode (see Figure 1). In this operating mode, the electron beam is rastered across the sample at a predefined stepping interval and at each analysis point an X-ray spectrum is measured. In addition, these QEMSCAN<sup>®</sup> analyses were complemented by petrographic optical microscopic descriptions and ICP-AES trace analysis to determine whole rock REE concentrations.



**Figure 1.** Schematic diagram outlining how the QEMSCAN<sup>®</sup> fieldscan measurement mode systematically measures the entire area of the sample. Top row: Image of QS31 and QS45 housed at CISEM; carbon-coated polished sections in block holder awaiting analysis. Middle row: polished section is separated into predefined fields; each field overlaid with a pre-defined grid of pixels; an x-ray spectrum and backscatter value are acquired for every pixel and classified by the SIP database to enable the assignment of mineralogy and chemical composition. Bottom row: a false colour map is created for each field where each colour represent a specific mineral or chemical grouping; the fields are combined to generate a single mosaic of the analysed area that can be investigated with the iDiscover software.

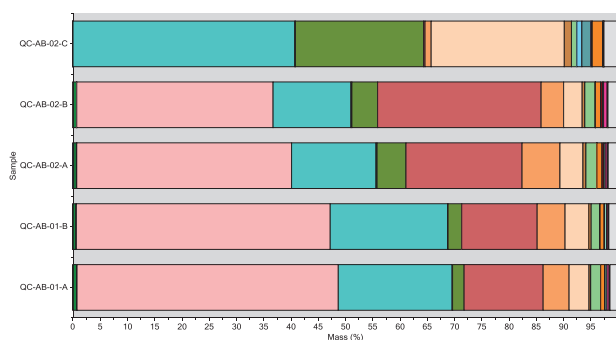
## Results

The modal mineralogy and mineralogical maps for the 5 polished sections are given in Figures 2 and 3, respectively. The similarity between the four sections from the same Garnet Granite lithologic unit is apparent (Figure 1). These 4 samples are dominated by quartz (36 – 48%), andesine plagioclase (14 – 22%), almandine garnet (14 – 30 %) with minor concentrations of biotite (4 – 6%), muscovite (3 – 4%), chlorite (2 – 5%), epidote (1 – 2%) ilmenite (0.7 – 1.0 %), apatite (0.3 – 0.6%) and zircon (0.1%). The REE-ore minerals are minor, but relatively consistent modal percentages, of monazite (0.1 – 0.2%), and allanite (0.5 – 0.6%).

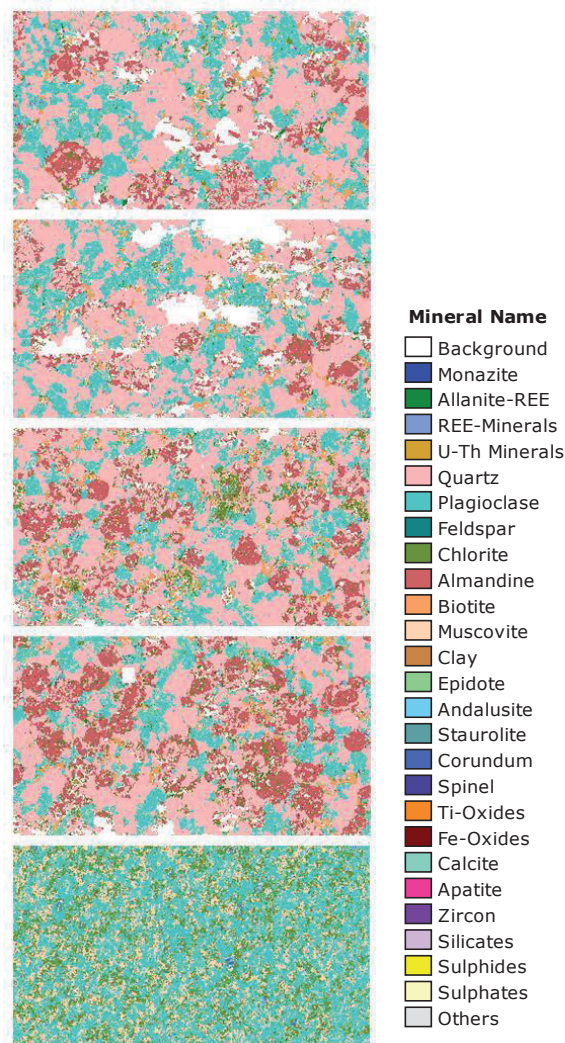
In contrast, the solitary sample from the Diorite lithologic unit is dominated by andesine plagioclase (41%), chlorite (24%), and muscovite (24%), with minor concentrations of ilmenite (2%), staurolite (2%), biotite (1%), epidote (1%), and andalusite (1%). In addition, there are trace levels of apatite (0.09%), zircon (0.04%). The REE-mineralogy yield low concentrations of monazite (0.05%); no allanite or other REE-bearing minerals were observed.

Whilst the modal concentration of REE-bearing minerals is low, they are clearly discernable at higher resolution scanning. For example, Figures 4 and 5 are detailed mineralogical and elemental maps highlighting the presence of these minerals in sample QC-AB-01 and QC-AB-02a, respectively. In addition, both allanite and monazite have a BSE signal significantly stronger (brighter) than the host rock silicates and oxides (Figures 4b and 5b) making them easily distinguishable in the BSE images. Elemental maps confirm the presence of Ce and Nd in both monazite and allanite minerals (Figures 4c,d and 5c,d). In addition, high count single point EDS spectra of numerous monazite and allanite-REE grains confirm that the dominate rare earth element is Ce, but that there is also appreciable La and Nd (Figure 6). This is consistent with the elevated whole rock REE concentrations for these samples, especially Ce, La, and Nd (Table 1, column 1 and 2).

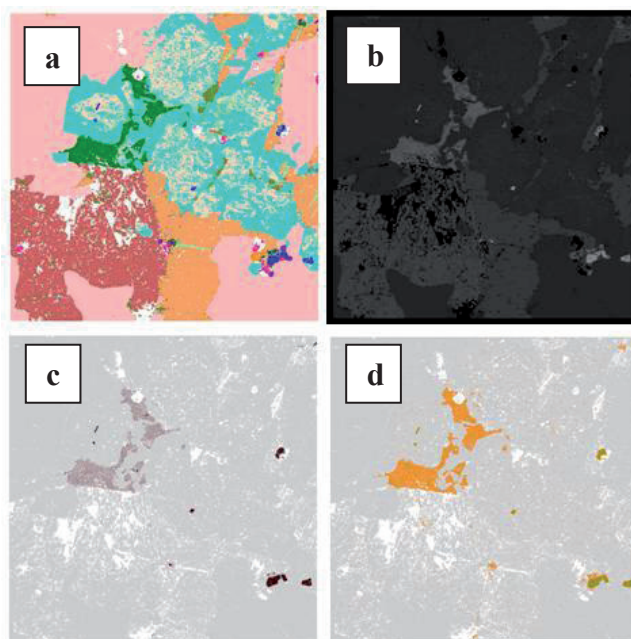
The sample for the dioritic lithology contains no allanite-REE, but does however contain monazite. The lower concentrations of REE-bearing minerals is consistent with the lower whole rock REE concentrations (Table 1, column 3). Furthermore, it is apparent that the monazite grains in this sample are significantly smaller (generally < 10  $\mu\text{m}$ ) compared to the monazites from the garnet granite unit.



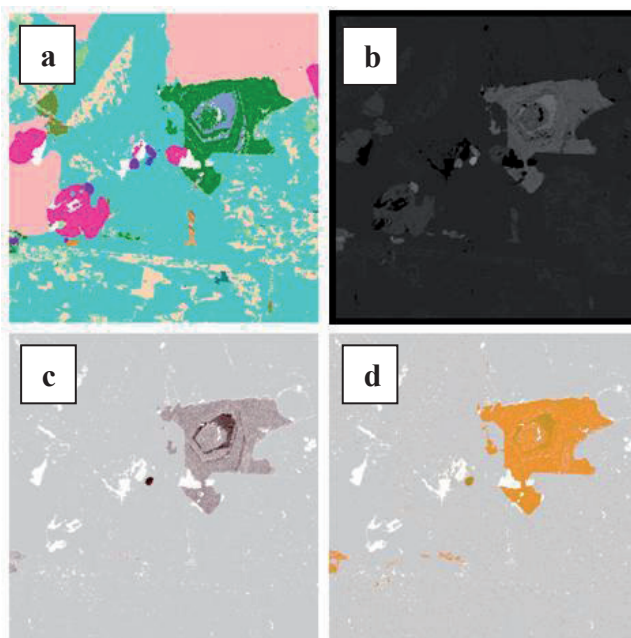
**Figure 2.** Modal mineralogy of five samples highlighting the variability between the two different geological units. Mineral legend as per Figure 3.



**Figure 3.** QEMSCAN<sup>®</sup> mineral maps of five samples representing two different lithologic units. Field of view: 3.5\*2.0 cm for each sample. From top to bottom: Samples QC-AB-01a, QC-AB-01b, QC-AB-02a, QC-AB-02b, QC-AB-02c. See text for a description.



**Figure 4.** Sample QC-AB-01b: (a) QEMSCAN<sup>®</sup> mineral map (legend as per Figure 3), (b) BSE Image (c) QEMSCAN<sup>®</sup> Ce elemental map, and (d) QEMSCAN<sup>®</sup> Nd elemental map. Field of view: 2500 µm.



**Figure 5.** Sample QC-AB-02b: (a) QEMSCAN<sup>®</sup> mineral map (legend as per Figure 3), (b) BSE Image (c) QEMSCAN<sup>®</sup> Ce elemental map, and (d) QEMSCAN<sup>®</sup> Nd elemental map. Field of view: 1000 µm. See text for a description.

## Discussion and Conclusion

The preliminary results of the automated mineralogy analysis of 5 probe sections could identify trace amounts of two primary REE-bearing minerals, namely allanite and monazite, to concentrations as low as 0.05 wt%. For the

samples analysed, allanite is the main REE mineral. Future analysis of the results will include other variables such as determining grain size distributions of REE-bearing minerals, mineral liberation analysis, as well as their mineral associations. This information will be important in identifying the most appropriate mineral processing procedures to maximise REE recuperation. The analysis of other samples representative of the other geological units will enable a more detailed deposit characterization of the rare earth elements at this locality.

**Table 1.** Concentration of rare earth elements (ppm).

REE (ppm)	QC-AB-01	QC-AB-02-A	QC-AB-02-B
<b>La</b>	466.5	410.7	81.8
<b>Ce</b>	991.7	868.7	183.4
<b>Pr</b>	105.7	94.8	20.1
<b>Nd</b>	438.4	401.7	80.9
<b>Sm</b>	63.4	58.7	13.5
<b>Eu</b>	2.16	2.16	3.06
<b>Gd</b>	66.4	61.3	10.8
<b>Tb</b>	9.92	10	1.04
<b>Dy</b>	70.4	77.1	4.93
<b>Ho</b>	16.2	17.6	0.81
<b>Er</b>	47.5	54.2	1.93
<b>Tm</b>	7.29	7.85	0.3
<b>Yb</b>	51.8	63.3	1.8
<b>Lu</b>	7.61	9.09	0.33

### Acknowledgements

The authors wish to acknowledge the support of SGS Minerals S.A., Santiago, Chile, who provided sample preparation and trace element data, and CISEM (Centro de Investigación y Servicios Mineralógicos), Universidad Católica del Norte, Antofagasta, Chile who provided QEMSCAN® analytical time.

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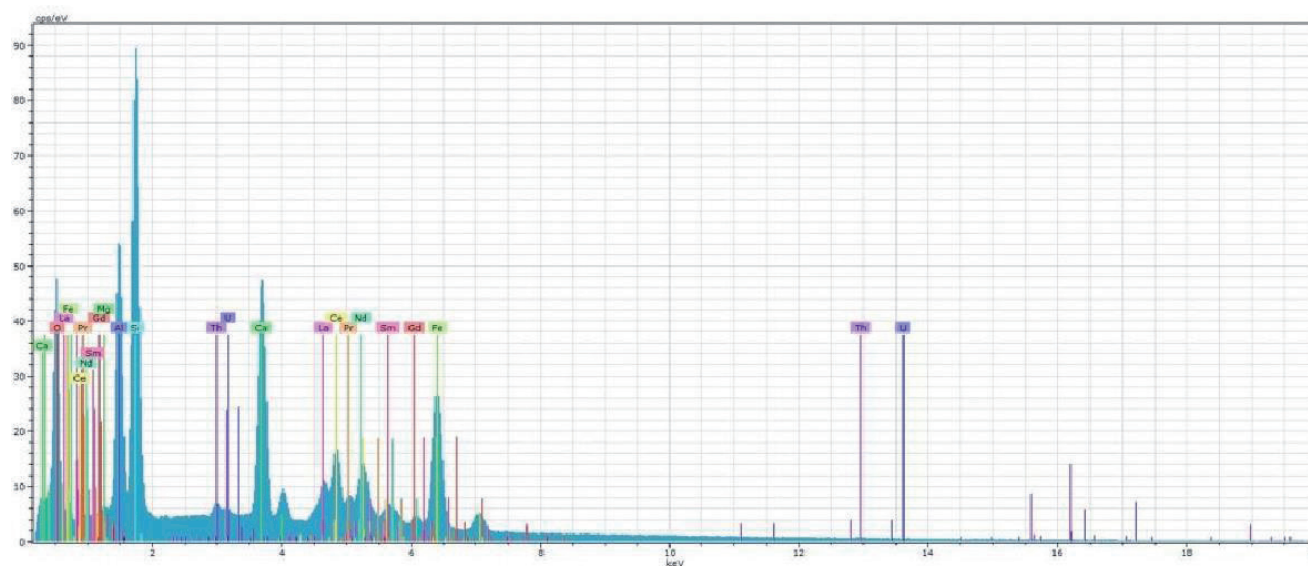
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**Figure 6.** High count single point EDS spectrum of allanite, indicating the presence of the various REE elements. It should also be noted that the allanite also contains low-levels of Th and U.