REE- MINERALS IN CARBONATITE, ALKALINE AND HYDROTHERMAL ROCKS, NORTHERN AND CENTRAL FINLAND

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Abstract

REE-rich minerals were identified and analyzed by electron microprobe from different targets located in the northern and central Finland. Both primary and hydrothermal minerals were found namely: phosphates (monazite-Ce), fluor-carbonates (bastnaesite-Ce), hydrated carbonates (ancylite-Ce), hydrated aluminium silicates, (allanite), oxides (fergusonite) and U-Pb rich minerals. Sokli Jammi- Kaulus carbonatite veins are enriched in LREE, P, F, Sr and Ba hosting in ancylite, bastnaesite, apatite and monazite.

Allanite-(Ce) and fergusonite (Y) are abundant in alkaline gneiss of the Katajakangas REE-occurrence. The Korsnäs Pb-REE deposit includes apatite with monazite inclusions, calcio-ancylite and bastnasite. The Mäkärä- Vaulo REE-prospect in arkosic gneisses is dominated by monazite, allanite and xenotime. Albitites at Enontekiö contain bastnaesite, monazite, allanite, xenotime and U-rich minerals includes davidite, masuyite and sayrite.

The Honkilehto Au-Co-S-mineralization at Kuusamo is characterized by U-rich minerals with bastnaesite and allanite. The results obtained provide vital insights into the mineralizing processes associated with REE-prospects in northern and central Finland.

Introduction

Economic REE deposits are not known in Finland. However, REEs were extracted in the 1960's century as a by-product in the fertilizer production from the apatite concentrates of the Kola Peninsula and the Korsnäs Pb mine in western Finland (1). In addition, small Nb- REE deposit, related with alkaline gneissic granite, from Otanmäki, Central Finland has been reported (2). During 2009-2012, the REE potential of Finland was studied by Geological Survey of Finland and potential source areas were identified according to the existing data and preliminary field studies (Fig. 1). The Fennoscandian Shield hosts several P-REE deposits in the Devonian Kola alkaline province in NW Russia and Finland (3, 4). The Sokli carbonatite complex (total area 20 km2) is part of the province (5, 6) and recent geochemical studies have confirmed that the area hosts high REE potential. This study has been focused on the fenite aureole and associated late-stage cross-cutting carbonatite dykes that seem to have the highest potential for REE mineralisation in the Sokli area (7). The REE-rich accessory minerals bastnaesite, monazite, allanite, fergusonite and xenotime play a key role in the storage and mobility of geochemically important trace elements (LREE, Y Th and U) and are relatively common accessory minerals in carbonatite veins and fenites.

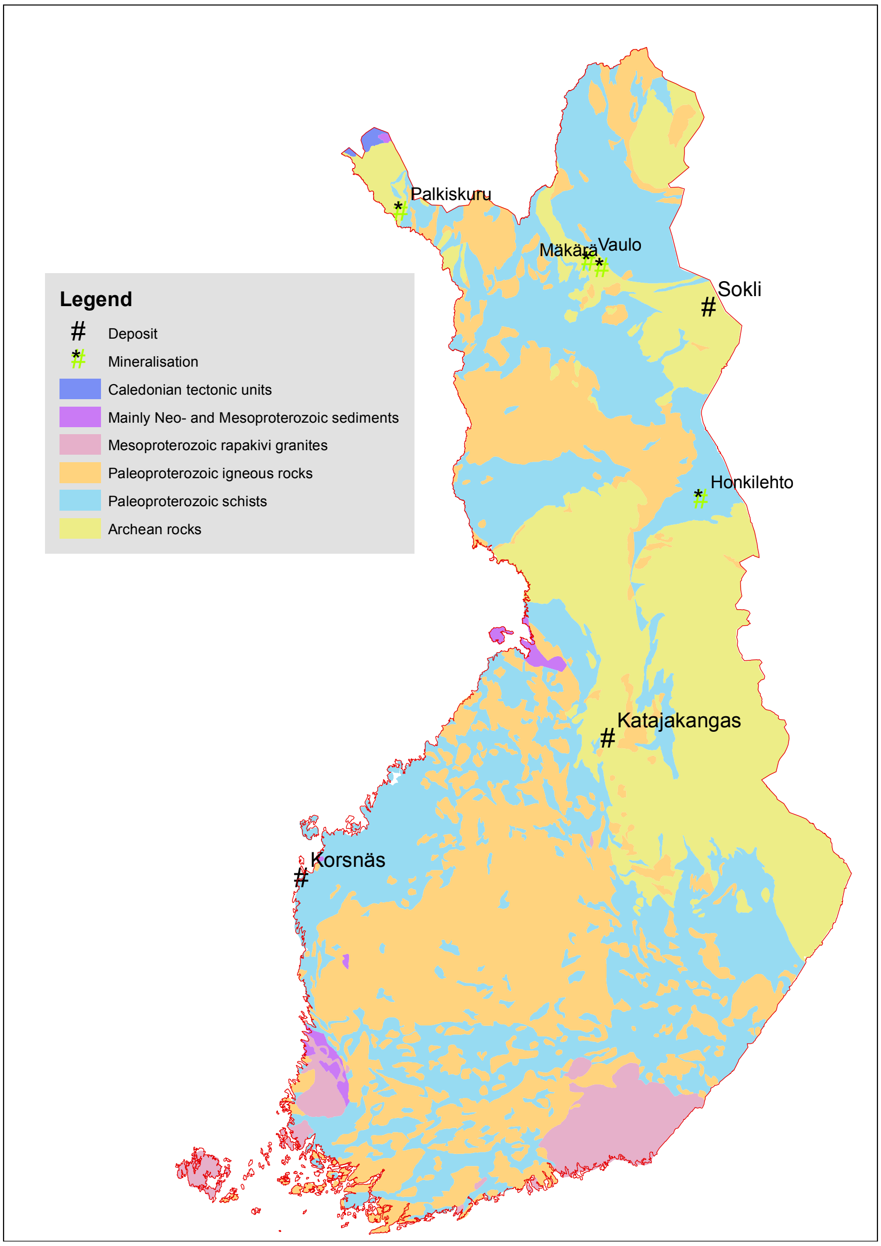

Figure 1: Location map of the studied areas.

In this study, backscattered electron (BSE) imaging and electron microscope analysis (EDS) are used to document various mineralogical characteristics and paragenesis of various types of REE minerals from different localities in Finland. The principal REE-minerals in studied rocks are phosphates (monazite-Ce), carbonates (bastnaesite-Ce), hydrated carbonates (ancylite-Ce), hydrate aluminum silicates (allanite), and oxides (fergusonite). Other REEs such as britholite, thorite, carbocernaite and columbite have been reported from some of the studied samples.

The research was circled around three objectives: (1) to study the REE, Y, Th and U composition of the major minerals; (2) to learn the nature, abundance, composition, grain-size distribution, textural relationships and associations of REE, Y, Th, U-rich accessories; (3) to determine the relative contributions of accessory minerals to REE, Y, Th and U.

Samples and analytic methods

The samples were collected from drill cores and outcrops of 6 different targets (Table 1). More than 50 polished thin sections were prepared from representative specimens of REE-mineral assemblages and examined under a polarizing microscope. The mineral compositions were analyzed by scanning electron microscope (SEM) JEOL JSM 5900 LV, at the Research laboratory of the Geological Survey of Finland (GTK), Espoo. Mineral chemistry was investigated by standard electron microprobe techniques on polished sections, using CAMECASX100/LKP at the Research laboratory, GTK, Espoo. The accelerating voltage was 15keV with beam current of 20nA. In order to detect fluorine in the analysis, spot size was kept 5 µm, whereas 1 µm was used where fluorine was not desirable.

Mineralogy and mineral chemistry

More than twenty REE-bearing minerals have been identified in the studied samples from different target areas in Central and North Finland. The mineralogy and paragenesis of accessory REE-rich minerals and the associated minerals are summarized in Table (1). Representative EPMA analyses of the REE-bearing minerals are presented in Table (2). It is obvious Ce predominates over both La and all other REE in most of the studied samples.

Jammi and Kaulus carbonatite veins in Sokli complex

The Sokli carbonatite (ca. 360-380 Ma) in northeastern Finland is part of the Kola alkaline province and hosts an unexploited phosphate deposit enriched in Nb, Ta, Zr, REE and U (4,8). The carbonatite intrusion consists of a magmatic carbonatite core, which is surrounded by a metacarbonatite and a wide fenite aureole, altogether about 9 km in diameter. The late-stage carbonatite vein dykes in the central fracture zone and in the fenite zone have a high potential for REE mineralisation (8, 9). The REE minerals that occur in Jammi and Kaulus carbonatite veins are almost entirely LREE ancylite-(Ce), calcioancylite-(Ce), monazite, allanite and bastnaesite (Ce). Ancylite-(Ce) is the most common in carbonatite veins and occurs as coarse grained phenocrysts with an average diameter of 300 µm. Calcioancylite (Ce) is commonly associated with barite, strontianite and pyrite (Fig. 2a).

Table 1: The main REE-minerals in studied samples.

Locality	Rock type	REE-mineral phases
Sokli Jammi and Kaulus	Carbonatite veins	F-apatite, Sr-apatite, monazite, bastnaesite, ancylite, strontianite, baryte
Katajakangas	Alkaline-gneiss	Allanite, monazite, ancylite, bastnäsite, parasite, fergusonite, euxenite columbite-tantalite and pyrochlore
Korsnäs	Carbonatite	Apatite, monazite, carbocernaite, calcio-ancylite, bastnaesite, and barytocalcite.
Mäkärä	Arkosic gneiss	Monazite, allanite and xenotime
Enontekiö Palkiskuru	Albite-carbonate rock	Bastnaesite, monazite, allanite, xenotime, davidite, masuyite and /or sayrite.
Honkilehto	Carbonate-mica schist	Bastnaesite, allanite, davidite, U-Pb minerals, U-Si minerals

Monazite (Ce) occurs most commonly in the form of microcrystalline, sporadic, isolated equidimensional crystals and associated mainly with apatite. The crystal habit of bastnaesite and allanite in the studied carbonatites appears to be acicular or needle-shaped forming either in radial accumulations or intricate cross-cutting grids within a variety of minerals such as albite and dolomite(Fig.2b). Apatite in late carbonatite veins contains significant amounts of REE2O3, which indicates that the rare earth elements could be a by-product in the future phosphate production at Sokli.

Katajakangas

The Katajakangas Nb-REE deposit is located within alkaline gneissic granite at Otanmäki, central Finland. The Nb-REE mineralisation consists of a few metres wide, narrow lenses or layers in sheared quartz-feldspar gneiss with riebeckite and alkaline pyroxene. These narrow mineralised zones contain high concentrations of Nb, Zr, Y, Th and lanthanides, with an estimated Nb-YREE resource of 0.46 Mt with 2.4% RE2O3, 0.31% Y2O3 and 0.76% Nb205. The Zr and Th contents in the occurrence range from 0.7% to 1.5% and 0.1% to 0.2%, respectively (10). Drill core samples have relatively high HREE contents compared with samples from carbonatites (7).

New mineralogical data, which is obtained in this study, indicate that REE are present in allanite, monazite, ancylite (Ce), bastnäsite (Ce), parasite (Ce), whereas, Y is present in, fergusonite (Y), euxenite (Y) and yttroclumbite. Nb is present in columbite and fergusonite, whereas, U-Th occurs in uranpyrochlore (betafite) and in yttrilite (Y, TH). Electron microprobe (EMPA) data indicates that ferugsonite-(Y) host Nb and forms irregulargrains that vary in size from 100μm to more than 400 μm. Fergusonite is not chemically homogeneous, many crystals display growth zoning with bright domains, (Fig. 2c). The bright domains show 2.5% U and high contents of Y (23%) and Nb (38%) as fergusonite (Y) mineral phase (Table 2). Allanite occurs as subhedral to anhedral crystals and exhibits oscillatory zoning (Fig. 2c). Zoning profiles of allanite (Ce) show increase in Ce2O3, La2O3 and Nd2O3, whereas decrease in CaO, FeO and Al2O3 from core to rim (Table 2). Allanite crystals also show acicular crystals and aggregates of radiating individual crystals (Fig. 2d).

Table 2: Electron microprobe analyses of REE-rich minerals from studied areas.

Mineral chemistery	Allanite Katajakangas	Ancylite Kaulus	Bastnäsite Mäkärä	Cerite Tana Belt	Davidite Enontekiö	Euxenite Honkilehto	Fergusonite Katajakangas	Monazite Jammi
SiO_2	24.1			6.5		5.8	2.1	
Al_2O_3	7.5			1.7				
FeO	6.6			1.1	17	1	1.5	
TiO_2					46.2	1.3		
MgO	2.9							
CaO	10.4	1.8				4.2	3.2	5.1
P_2O_5		2.5	0.3	1.1				22.3
SrO		21.9						4
BaO		0.5						
PbO					1.5			
Cr_2O_3					11.3			
V_2O_3					3.1			
Nb_2O_5						37.6	39.6	
Ta_2O_5						1	0.2	
ThO2	3.1		0.7	0.1			2	6.1
UO_2					5.6	4.6	2	
Y_2O_3			0.7		1.5	19.5	23.9	
La_2O_3	13.6	14.4	16.5		3.1			15.5
Ce_2O_3	24.9	30.6	35.1	76.8	2.8			33
Nd_2O_3	9	8.6	10.5	1.4				13.5
Pr_2O_3		2.5						
Gd_2O_3			0.7					
SmO			0.8					
F		0.6	6.2	1.4			0.9	
Total	99.12	74.4	77.0	91	92.1	93	91	99.5

Korsnäs Pb-REE deposit

The area is dominated by metasedimentary rocks such as mica gneiss calc-silicate gneiss and marble, which are recently interpreted as magmatic carbonatite, composing of coarse grained calcite, feldspar, diopside, REE-bearing apatite, monazite, barite, britholite and ancylite. Two groups of sample from the Korsnäs are represented. The first group is calcite-marble or carbonatite characterized by enrichment in volatile-bearing REE-carbonates, ancylite-(Ce) and bastnäsite-(Ce), with traces of monazite. Analyses of multigrain calico-ancylite grains are rich in LREE as Ce (~45%), La (~25%) and Nd (~12%). whereas bastnäsite contains 21–75 wt% REE2O3, 1.3-7.5 F and 20-77% CaO.

Back-scattered electron (BSE) imaging of multiple grains of calcio-ancylite revealed the presence of Ca-ancylit grains disseminated through calcite (Fig. 3a). Ancylite varies considerably in form. Most crystals are subhedral, some are euhedral and in few cases form fine aggregates along bastnaesite. The second group of samples marked by abundant crystals of apatite with exsolution-induced domains of monazite grains, and the monazite contains 49 wt% REE2O3, P2O5 28 wt% and CaO 16 wt%. Back-scattered electron (BSE) imaging of studied samples show that monazite and britholite inclusions occur both randomly and in large clusters of monazite grains included within apatite grains (Fig. 3b).

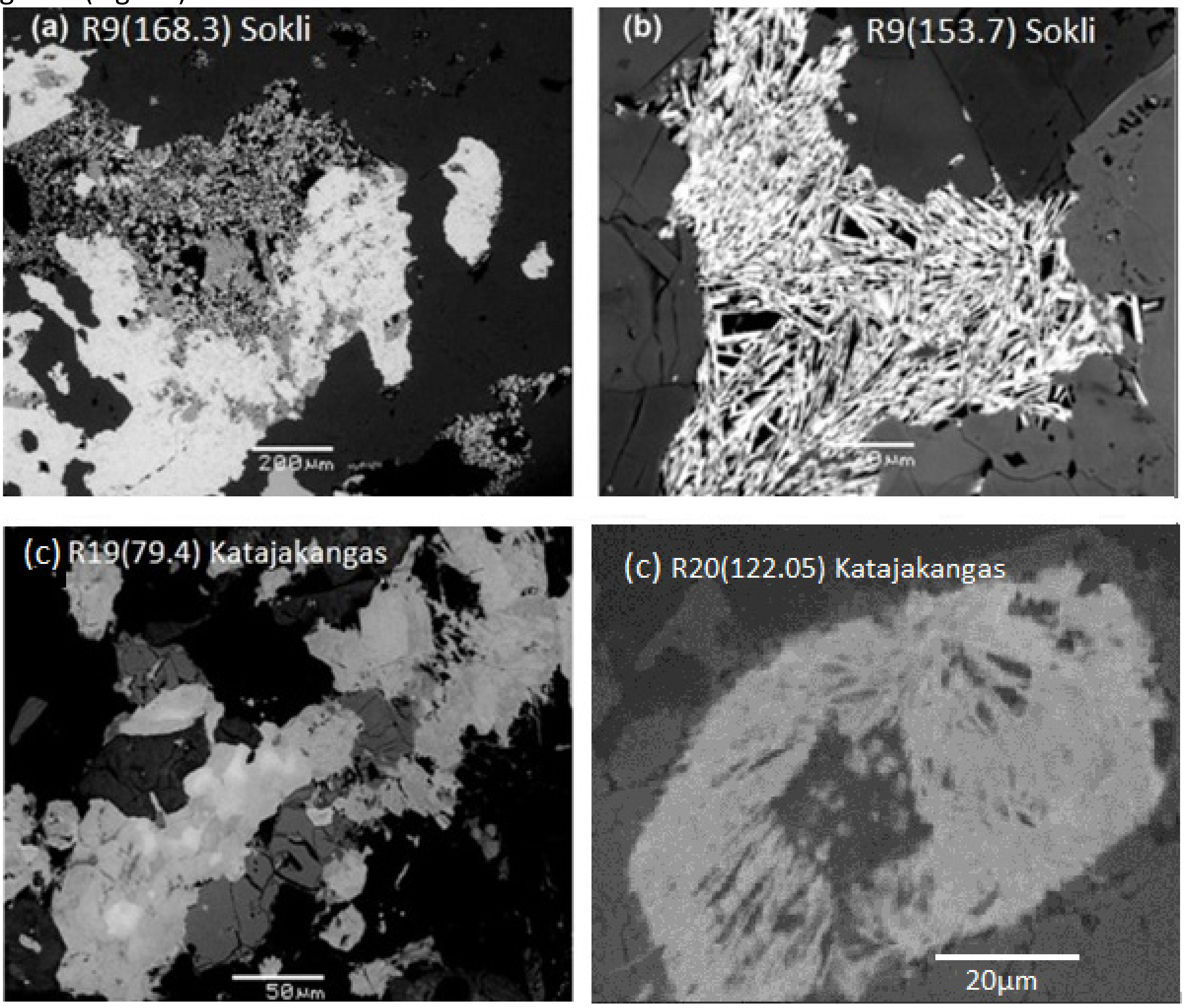

Figure 2: BSE images of REE-bearing and associated minerals in studied rocks (a) Clusters of barite, strontianite (white) and ancylite(grey) within calcite, (b) acicular crystals growth of bastnaesite within apatite and Sr-calcite, (c) irregular fergusonite (Y) grains, the bright core marks enrichment of U and/orTh, (d) acicular crystals of allanite within dolomite.

Mäkärä-Vaulo

Selection of the Mäkärä and Vaulo areas as REE-Au-target in the Tana Belt was based on LREE- and HREE-anomalies in regional till and bedrock geochemistry and Au intersections in previous drill holes. Earlier studies indicate that the hydrothermal quartz-haematite-pyrite veins in Mäkärä are generally narrow (1 mm - 2 m) and formed as tensional fractures (11). The anomalous REE contents in the Tana belt can be explained by the occurrence of bastnaesite, cerite, allanite and fine xenotime grains in arkosic gneisses. The REE composition of the minerals is characterized by enrichment in Ce, La and to a lesser extent Nd. The total REE content decreases from 75 wt % in cerite (Ce), 60% in bastnaesite to 25 wt % in allanite.

SEM –BSE imaging of arkosic gneiss core samples from Mäkärä and Vaulo reveals that xenotime occurs as scattered grains within Ti-bearing minerals and as overgrowths on zircon. Allanite as the main REE-bearing mineral in the studied samples, occurs as spheroidal aggregates or as fillings vugs or cavities wiz and albite, and the chlorite and bastnaesite replacing the allanite grains (Fig. 3c). Electron microprobe analyses EPMA along the opened fractures in some spheroidal aggregates, have shown needle-like bastnaesite crystals and fine apatite grains filling these spaces (Fig. 3d).

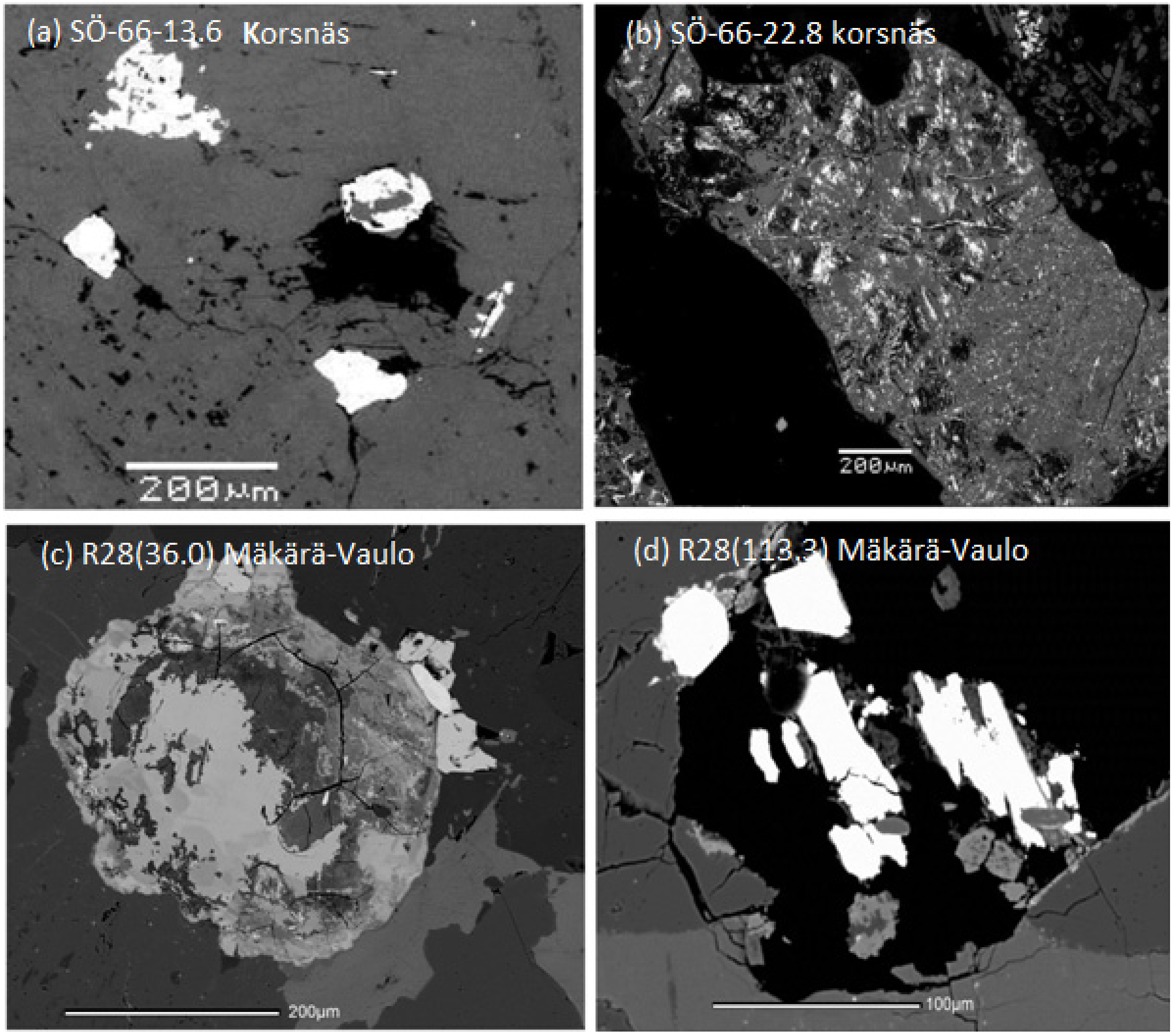

Figure 3: BSE images of REE-bearing and associated minerals in studied rocks. (a) Ca-ancylite grains disseminated through calcite, (b) discrete and coarse crystal of apatite with exsolution-induced domains of monazite clustering, (c) vug-filling texture; chlorite altered to allanite (in the rim) and later to bastnaesite in the center(light grey), (d) euhedral to subhedral bastnaesite grains filling the vugs and fractures within quartz.

Enontekiö

The Enontekiö area is characterised by variable rock types; albitites, syenite and carbonatite veins. In this study four samples were selected for chemical and mineralogical analyses. The carbonatite vein sampled contains 2.8% P_2O_5, 0.45% REE and 256 ppm Nb and characterized by high content of REE minerals as allanite, ancylite, bastnaesite and xenotime. The albitites samples characterized by high content of U-Pb minerals such as davidite- (Ce), mausuyite and sayrite as well as high content of apatite, allanite and monazite. The allanite presents as fine-grained aggregates associated with monazite, apatite and zircon and exhibits a well-developed chemical zonation with Fe- and REE poor core and an Fe- and REE-rich margin. Despite the good abundance of allanite in the Enontekiö samples (<1%) it represents an important mineral phase in this locality since it contains more than 40% LREE (Ce, La, Nd). Monazite is, after allanite, the most important LREE carrier in albitites rocks of Enontekiö, where it appears as isolated minute crystals with a diameter usually smaller than 50—60 µm. Multigrain analyses show that the monazite-(Ce) is rich in LREE as Ce (~38%), La (~20%), Nd (~10%), CaO (1.5%), P_2O_5 (28%) and F (<1%). Bastnäsite is found in most studied samples of Enontekiö rocks, it crystallised around davidite or occurs as vein filling (Fig). EPMA analysis of bastnasite grains indicate that F more than 3%, and the predominance of LREE (> 65%), with Ce2O3 (35-37%), La2O3 (14-17%) and Nd2O3 (11.5-13.5%). Davidite as most common U-Pb minerals in Enontekiö area occurs in association with bastnaesite and allanite. Davidite is zoned, as shown by bastnaesite inclusions found near the rim of one grain, and a darker central region in the same grain (Fig. 4a). Reconnaissance EPMA traverses show that this zoning, at least in part, reflects the uneven distribution of elements Fe, Y, Si and U. Uranium, Cr, Ti and Pb tend to be relatively concentrated toward the central (more altered) portion of grains at the expense of Pb. Darker areas thus have maximum U, Pb and minimum Ti (Fig. 4b).

Honkilehto

The Kuusamo Schist Belt is an Au-Co-Cu-U occurrence with no resource estimate available. It is mainly hosted by albitised, biotitised and sulphidised sericite quartzite (12, 13). The studied samples characterized by occurrences of REE-minerals (bastnaesite, allanite) and U-Pb (davidite) with high content of Cr-magnetite and apatite.

Bastnaesite crystals are envelope-shaped around the U-Pb minerals or as isolated fine grains around the U-minerals (Fig. 4c). In Honkilehto, two phases of U-rich minerals recognized; firstly U-Pb rich minerals (richtetite) contain high uranium content 75% U, 20 Pb and 5% Y, Fe , secondly the U-Si rich mineral (bijvoetite) contain less UO2 (~65) with Si(~15%). Intergrowth of these two minerals exhibit cauliflower form in most studied U-Pb and U-Si phases (Fig. 4d). All of these U-minerals are associated mostly with bastnaesite and allanite.

Conclusions

Detailed mineralogical characteristic revealed three distinct types of REE-mineralization as phosphates, carbonates and silicates in studied areas. Mineralogical and mineral chemical analysis demonstrate that hydrothermal processes were responsible for the REE mineralization in the studied rocks and confirms that such processes are predominant in the formation of REE minerals in carbonatites, calc-silicate rocks and albitites. During late-stage processes apatite and carbonate minerals have been replaced by various assemblages of REE–Sr–Ba minerals in carbonatites.

The results obtained provide a useful reference basis for possible future feasibility studies, as well as important mineralogical insights into the varied rock types and mineralizing processes associated with the occurrence of elevated REE in northern Finland.

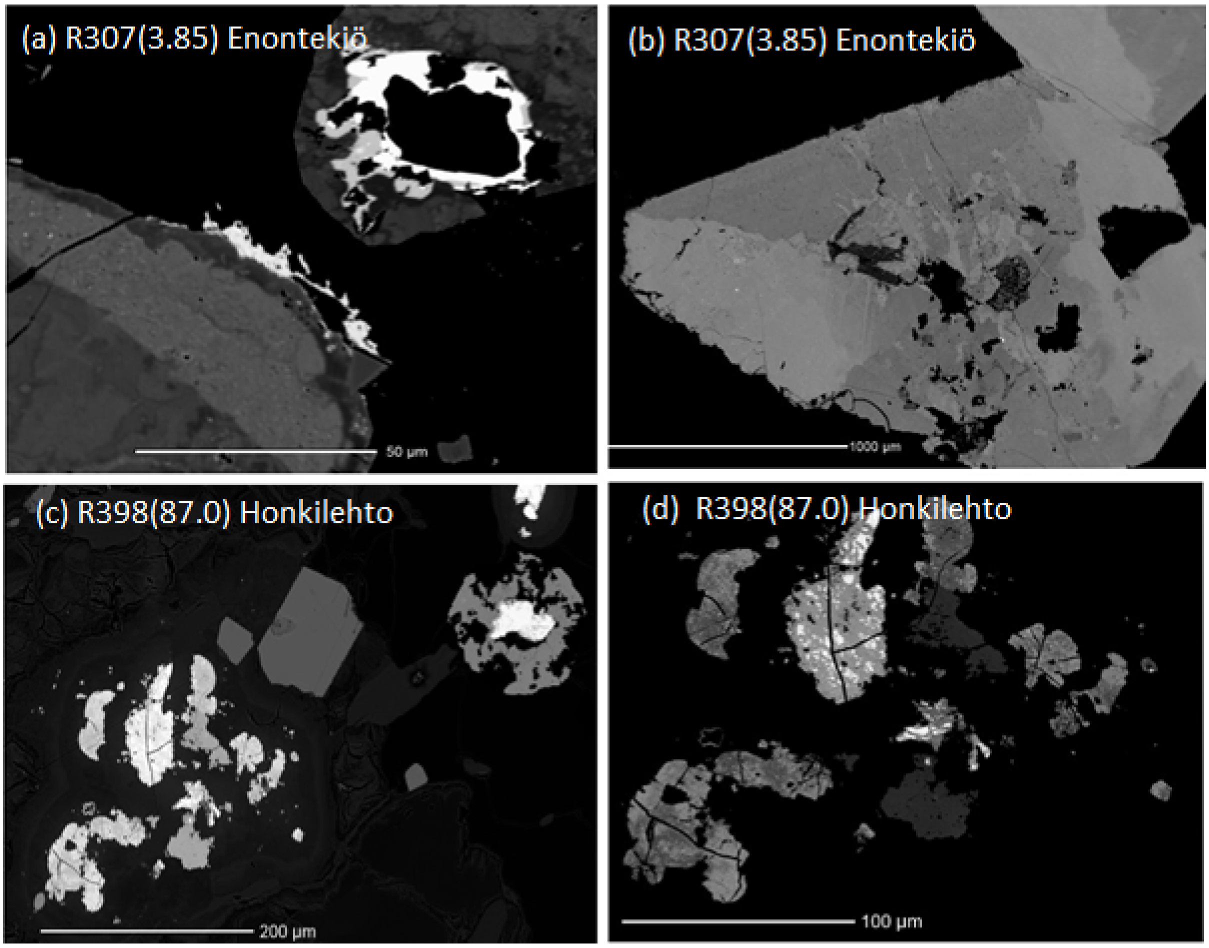

Figure 3: BSE images of REE-bearing and associated minerals in studied rocks. (a) Bastnaesite growth in the rim of davidite or filling vugs within albite, (b) zoning in davidite grain related to the concentration of (Pb-U) versus Ti, (c, d) U-Pb minerals (bright) surrounded by bastnäsite (grey).

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