

## UNLOCKING RARE EARTH ELEMENTS FROM EUROPEAN APATITE-IRON ORES

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### Abstract

*Rare Earth Elements are known to occur within apatite-magnetite ores of the Kiruna type. Previously it was assumed that the REE was associated to the apatite part of the ore. It is now shown that the REE follows the apatite to a much less degree, and that the REE are contained in the minerals monazite, allanite and some unknown REE-phase still to be identified. Monazite occurs as inclusions in the apatite as well as free particles. Allanite is to some degree in mixed grains with magnetite but also in free particles. Monazite mainly reports to the apatite concentrate while allanite largely goes to the tailings. Laboratory flotation also shows some preferential concentration of heavy REE over light REE to the apatite concentrate. A new EU project, REEcover, will characterise the REE phases in this type of iron ore and among the different process streams within the mineral beneficiation chain.*

### Introduction

Deposits of apatite iron ores are the major source for iron in the European Union and are exploited by LKAB in several mines in the Kiruna area in northern Sweden, which is an important mining province dominated by Fe and Cu deposits. The combined production from two large underground mines and one open pit was for 2013 25.5 M tonnes of pellets and fines and a total ore production of 2275 M tonnes from 11 mines during the last 127 years. These magnetite deposits with/without haematite have mineralogical and textural features that are different to most other types of iron deposits in the world. Most characteristic is the presence of apatite as an important gangue mineral, which contributes to high phosphorus content of the ores. Many apatite iron ores contain 1 to 5 % P on average and apatite has been produced as a by-product at Malmberget during the First and Second World War but also in 1952-1953. In the Kiruna area, apatite has been produced from the Rektorn deposit in 1942 to 1946, and 1985-1988 about 0.4 Mt apatite concentrates were produced by flotation from Kiirunavaara ore<sup>1</sup>. Elevated contents of rare earth elements (REE) in apatite from the apatite iron ores in Northern Sweden was early noticed and investigated in some detail in the 1960's<sup>2</sup>. The samples then consisted of gangue minerals from different ores, flotation concentrates of apatite and handpicked apatite grains. These results

demonstrated a strong enrichment of the LREE in apatite with total REE+Y contents of 1545 to 8855 ppm and that Monazite occurred as inclusions in Apatite<sup>2</sup>. In a recent study<sup>3</sup>, the chemistry and occurrence of REE-minerals in the Kiirunavaara deposit have been further investigated by optical microscopy, scanning electron microscope (SEM) and electron micro probe analysis (EMPA). The samples included apatite concentrates obtained from tailings and ore from drill cores. This study confirmed previous results but showed that allanite and monazite may be common as larger grains in the ore and act as important carrier of the light rare earth elements.

### **TEXTURE AND CHEMISTRY OF REE-BEARING MINERALS**

Three main REE-bearing minerals have been identified by optical microscopy, SEM and EMP analysis and analysed for their chemical composition by electron micro probe<sup>3</sup>. Rarely grains of thorite with moderate enrichment of heavy rare earth elements were found.

#### **Apatite**

Apatite  $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$  occurs mainly as disseminated grains in the ore or form band, schlieren or veinlets. Disseminated apatite occurs interstitial to magnetite as subhedral and equidimensional or prismatic grains up to 0.5 mm large but mostly in the size of 0.05-0.1 mm. In banded type of D-ore, apatite often form prismatic grains with the long axis oriented parallel with the banding. Apatite forming patches-stringers-schlieren may be slightly coarser in grain size (up to 1mm) and occur together with varying amounts of biotite, magnetite and calcite. Locally there occur skeletal ore, which is coarse grained with apatite and/or carbonate occurring interstitial to tabular magnetite crystals.

The apatite is a fluorapatite with 3.75 % F and 0.06 % Cl on average. There is no significant variation in composition for apatite in the tailings and samples of ore. Total content of REE is not possible to obtain by EMPA, due to values below detection limits for most rare earth elements. Highest values were obtained for Ce, while La, Nd and Y were only detected in some apatite grains. Total contents for rare earth element oxides (REO) including only La, Ce and Nd are in the range of 0.04 to 0.91 with an average of 0.25 percent by weight (Table 1). Slightly higher REO contents in apatite has been reported in earlier studies<sup>4,5</sup> (0.07 to 1.57 and averages of 0.38 to 0.85 percent by weight) from spot analyses on individual grains of apatite by EMPA and LA-ICP-MS while complete REO-analyses of concentrates of apatite generated values from 0.45 to 1.04 percent by weight<sup>2,6</sup>. All the reported data demonstrates a strong dominance for the light rare earth elements.

#### **Monazite**

Monazite  $(\text{Ce},\text{La},\text{Nd},\text{Th})\text{PO}_4$  occurs texturally in two different forms within the apatite crystals. The monazite inclusions are mainly forming rods oriented parallel to the c-axis of the apatite grains but may also be tabular with a more random orientation (Figure 1a). In most cases, inclusions are most abundant in the inner part of apatite grains while the rim often lacks inclusions (Figure 1b). The rod-shaped inclusions have

a length of up to 80 µm but are most commonly 10-30 µm in size. The tabular shaped monazite inclusions are mostly 5-20 µm in size. The highest amount of monazite inclusions is found in larger apatite grains within veins and schlieren, while disseminated more fine grained apatite in D-ore might lack visible inclusions. Inclusions of monazite are also rare in samples containing higher contents of biotite. Besides occurring as inclusions in apatite, monazite is also locally found as up to 150 µm large single grains together with magnetite and gangue minerals.

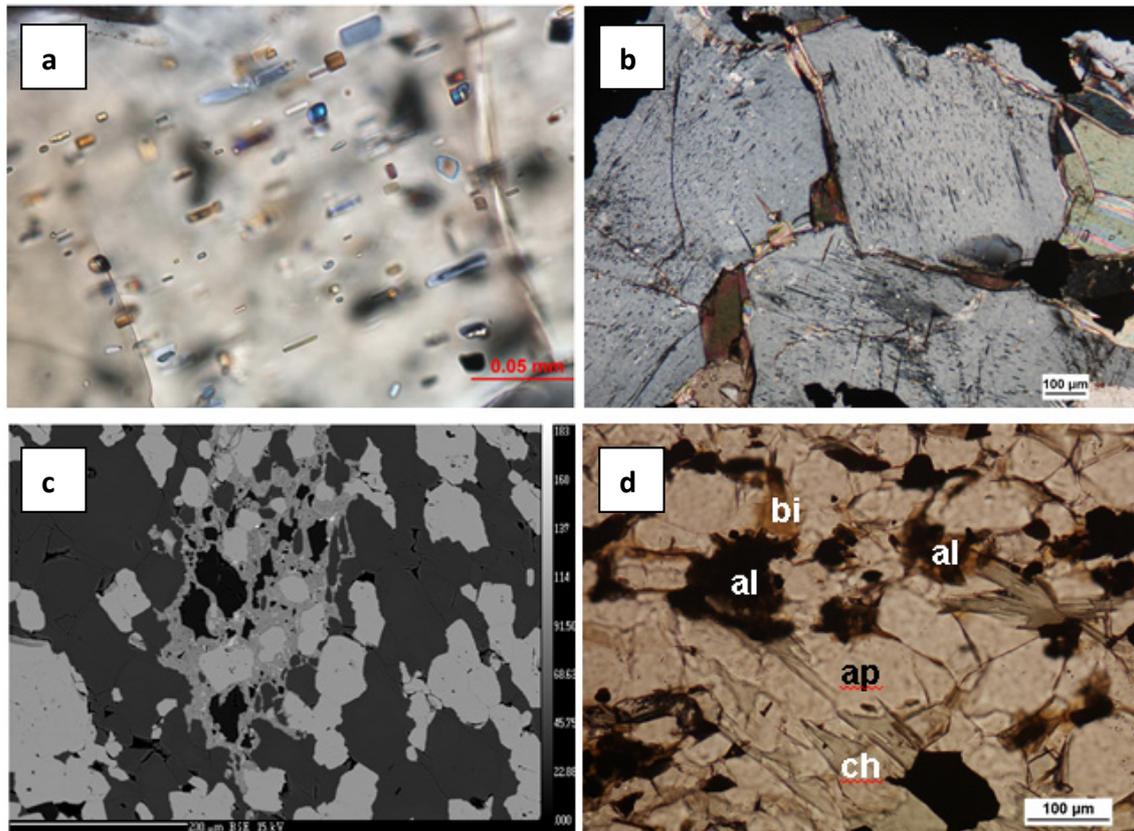
Total content of REO in monazite (La, Ce, Pr, Nd) varies between 68.87 and 71.87 with an average of 70.0 percent by weight (Table 1). Earlier reported chemical data<sup>4</sup> for monazite from Kiirunavaara is similar in contents with REO (La-Dy) varying from 68.11 to 68.92 percent by weight.

### **Allanite**

In general, allanite  $\text{Ca}(\text{REE}, \text{Ca})\text{Al}_2(\text{Fe}^{+II}, \text{Fe}^{+III})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$  is rare in samples containing apatite with abundant inclusions of monazite but is rather common in samples containing biotite. Allanite occurs partly as single grains in association with apatite but also strongly intergrown with magnetite in up to 1 mm large aggregates (Figure 1c). Euhedral grains of allanite may be up to 300 µm in size but most commonly allanite occur in fine grained and anhedral to subhedral aggregates together with apatite, biotite and locally chlorite (Figure 1d). The REO content (La, Ce, Pr, Nd) of allanite varies from approx. 15 to 25 with an average of 22.5 percent by weight and with dominance for the LREE (Table 1). Others reported<sup>4</sup> values of approx. 25.5 % REO (La, Ce, Pr, Nd, Sm, Gd, Dy) for allanite from Kiirunavaara.

## **MATERIALS AND METHODS**

This part is an update on earlier reported flotation results<sup>7</sup>. The materials received at LTU were: General sample consisting of sub-samples from a large number of drill-holes in the tailings pond, 5.85 %  $\text{P}_2\text{O}_5$  and  $\approx 1250$  mg/kg REE; Coarse, low-phosphorus sample, 3.8 %  $\text{P}_2\text{O}_5$ ; Fine high-phosphorus sample, 6.6 %  $\text{P}_2\text{O}_5$ . Both the general sample and the coarse product have wide particle size distributions, cf. Figure 2. A visual inspection of the samples gave that this was due to pebble chips, size 5-10 mm, from the pebble mills. These chips must be removed prior to any flotation. They may be removed by screening/wet classification or by grinding. A slight grinding is preferable since it will also fresh the mineral surfaces for flotation.



**Figure 1.** Micrographs of apatite, monazite and allanite from the Kiirunavaara deposit<sup>3</sup>  
 a) photomicrograph of apatite grain with rod shaped and tabular inclusions of monazite, crossed nicols b) photomicrograph of apatite (grey) with monazite inclusions mainly in the inner part of grains, crossed nicols c) SEM backscatter micrograph of allanite (medium gray) intergrown with magnetite (light gray) and apatite (dark grey) d) photomicrograph of apatite (ap) with some biotite (bi), chlorite (ch), and aggregates of allanite (al).

**Table 1.** Monazite, allanite and apatite from Kiruna tailings (% by weight)

Mass-%	Monazite, n=11	S.D.	Allanite, n=14	S.D.	Apatite, n=39	S.D.
SiO <sub>2</sub>	0.18	0.11	32.66	1.51	0.07	0.09
TiO <sub>2</sub>	0.01	0.01	0.13	0.09	0.01	0.02
Al <sub>2</sub> O <sub>3</sub>	0.03	0.06	15.58	2.00	0.16	0.60
FeO	0.21	0.15	15.09	1.20	0.12	0.07
MnO	0.03	0.03	0.34	0.16	0.02	0.02
MgO	0.00	0.01	0.32	0.10	0.01	0.01
CaO	0.13	0.07	11.97	1.76	54.55	0.53
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.07	0.06
BaO	0.03	0.04	0.01	0.02	0.02	0.03
La <sub>2</sub> O <sub>3</sub>	14.816	1.879	6.989	3.006	0.020	0.042
Ce <sub>2</sub> O <sub>3</sub>	37.840	0.857	11.442	1.826	0.200	0.160
Nd <sub>2</sub> O <sub>3</sub>	11.951	1.106	2.446	1.106	0.027	0.050

Pr <sub>2</sub> O <sub>3</sub>	5.147	0.316	1.271	0.391	-	
Y <sub>2</sub> O <sub>3</sub>	0.280	0.088	0.319	0.250	0.014	0.017
ThO <sub>2</sub>	0.471	0.282	0.062	0.056	0.017	0.017
UO <sub>2</sub>	0.024	0.031	0.000	0.000	0.000	0.002
P <sub>2</sub> O <sub>5</sub>	28.61	1.01	0.12	0.05	42.34	0.43
F	0.65	0.05	0.24	0.05	3.86	0.37
Cl	-		-		0.03	0.02
SUM REO	70.034		22.467		0.252	

At LTU, the general sample was sieved into fractions from 20 to 600 μm with sieve ratio 2, and the sieve fractions were sent for chemical analysis. The results did show that there was hardly any P<sub>2</sub>O<sub>5</sub> in the fractions >300 μm, but approx. 30 % by weight <20 μm. The REE do mostly follow the P<sub>2</sub>O<sub>5</sub> distribution, but do not have the same peak between 38-250 μm, and there is more REE in the fractions >300 μm. To further investigate, the correlation between P<sub>2</sub>O<sub>5</sub> (apatite) and the REE, the mass and element distributions for all sieve fractions were subjected to Principal Component Analysis (PCA). A loadings (variable) plot (Figure 3) in the directions PC2 and PC3 shows that REE is correlated, but not totally, with the P<sub>2</sub>O<sub>5</sub> distribution. In contrast, the correlation to Ca is strong and this implies that REE to a large extent substitutes for Ca. The conclusion is that REE in the Kiruna tailings pond is, besides in apatite, also present in some other Ca mineral, and that might be allanite or another REE-containing mineral.



**Apatite from tailings**  
Grinding at LTU

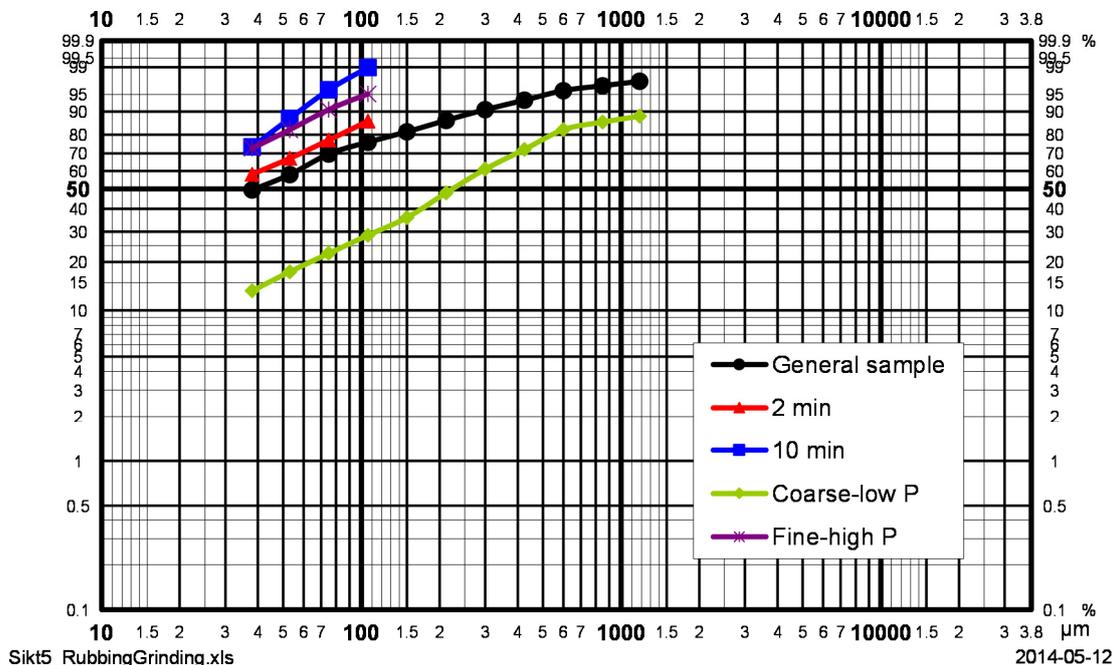


Figure 2. Particle size distributions for samples and after grinding<sup>7</sup>

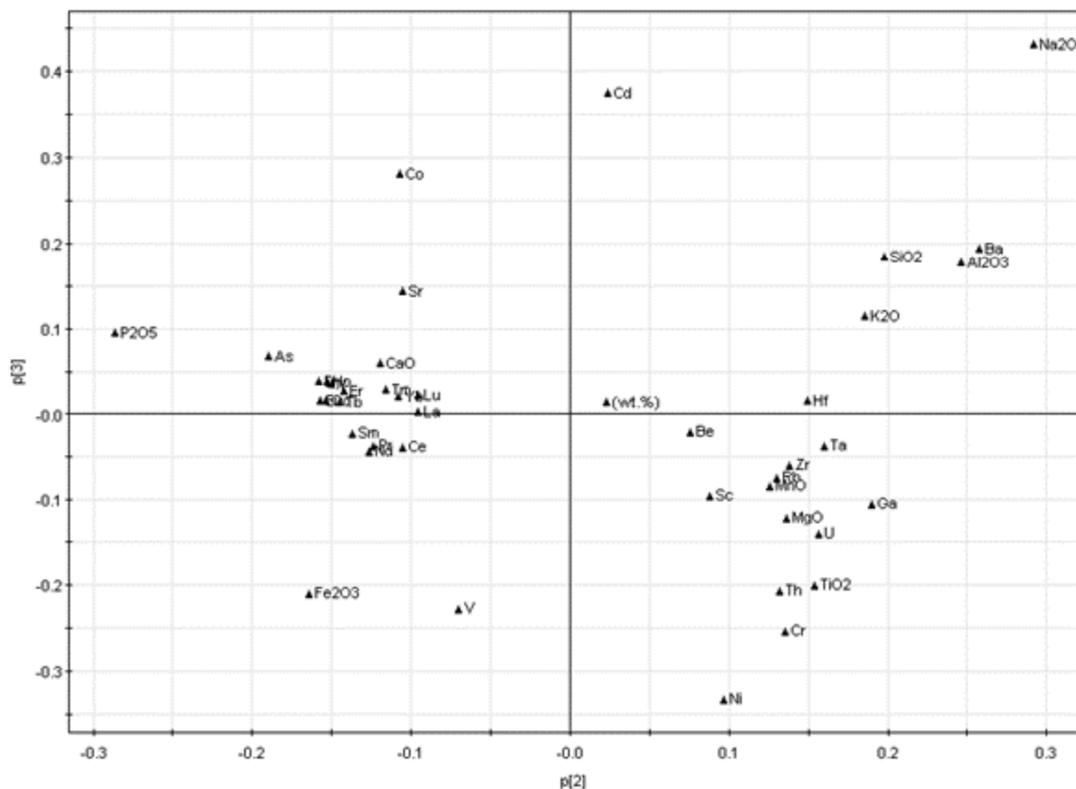
Based on a pre-study, the grinding time to freshen the mineral surface was locked at 10 minutes in a stainless steel rod mill (to not introduce colloidal iron). All flotation tests were run with a talc pre-float, to lower the Mg load, and an apatite rougher flotation followed by three cleaner stages. The tests were run with process water from Kiruna. This was sent to LTU in a 1 m<sup>3</sup> tank and used in grinding, dilution after grinding, in flotation cells and as rinsing water in flotation.

A full factorial statistical test plan with three parameters was used: pH adjusted by NaOH solution, 9 – 11; Reagent (Collector) – Atrac 1563, 130 – 260 g/ton; Depressant – water glass, 500 – 1000 g/ton.

## RESULTS

### Flotation tests

The tests were evaluated with grade-recovery, selectivity curves, and difference indices for the main analyses. Product balances were calculated for all analyses, including individual REE, total REE, HREE and LREE. An example is given in Table 2 and Figures 4a-b. They show that it seems possible to achieve >30 % P<sub>2</sub>O<sub>5</sub> in the concentrate with approx. 70 % recovery and fair selectivity towards MgO, SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. The selectivity diagram (Fig. 4b) also shows that REE is discharged in the rougher and the first cleaner stage. Heavy REE (Y, Eu to Lu) follows apatite better, but are also lost in the same way.



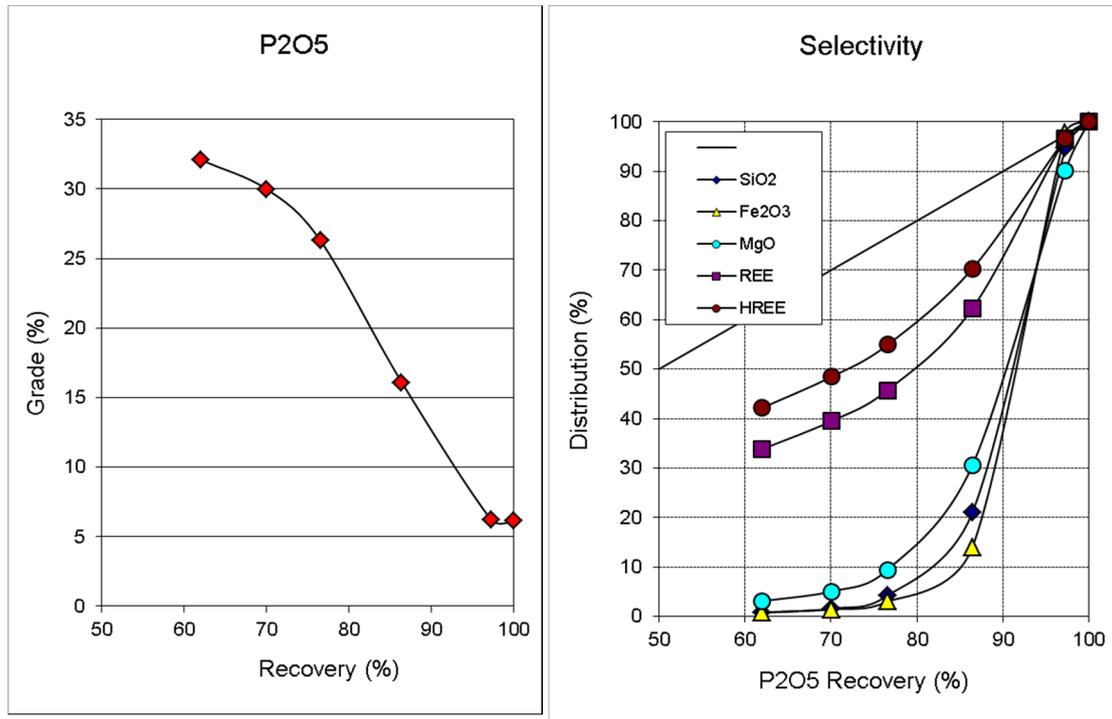
**Figure 3.** Multivariate loadings (variable) plot over mass and element distributions in the general sample<sup>7</sup>

**Table 2.** Products balance for a good test<sup>7</sup>; pH, collector, depressant – all low

Product		Mass		Assays (%)									
Notation	Name	(g)	(%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
1	Talc conc	42.9	4.3	41.90	5.00	10.80	13.20	1.31	12.80	0.18	1.58	3.96	0.61
mp 1	Feed to flotation	965.8	95.7	32.66	6.03	12.77	25.99	1.62	5.21	0.17	2.08	6.24	0.73
2C	Apatite conc	119.6	11.9	2.04	0.23	51.10	1.77	0.14	1.45	0.31	0.16	32.10	0.07
2CR	Cl-middl 3	25.0	2.5	11.60	1.61	39.10	6.18	0.54	4.36	0.35	0.83	19.90	0.28
2B	Clean conc 2	144.6	14.3	3.69	0.47	49.03	2.53	0.21	1.95	0.32	0.27	29.99	0.11
2BR	Cl-middl 2	35.7	3.5	24.40	4.01	25.70	11.20	1.01	6.83	0.28	1.39	11.30	0.40
2A	Clean conc 1	180.3	17.9	7.79	1.17	44.41	4.25	0.37	2.92	0.31	0.49	26.29	0.17
2AR	Cl-middl 1	152.3	15.1	36.60	6.81	12.00	18.40	1.80	7.71	0.19	2.24	4.01	0.36
2	Rogher conc	332.6	33.0	20.98	3.75	29.57	10.73	1.02	5.11	0.26	1.29	16.09	0.25
mp 2	Tail	633.2	62.8	38.80	7.22	3.94	34.00	1.94	5.26	0.12	2.49	1.06	0.99
	Calc.Feed	1008.7	100.0	33.06	5.98	12.68	25.44	1.61	5.53	0.17	2.06	6.14	0.73

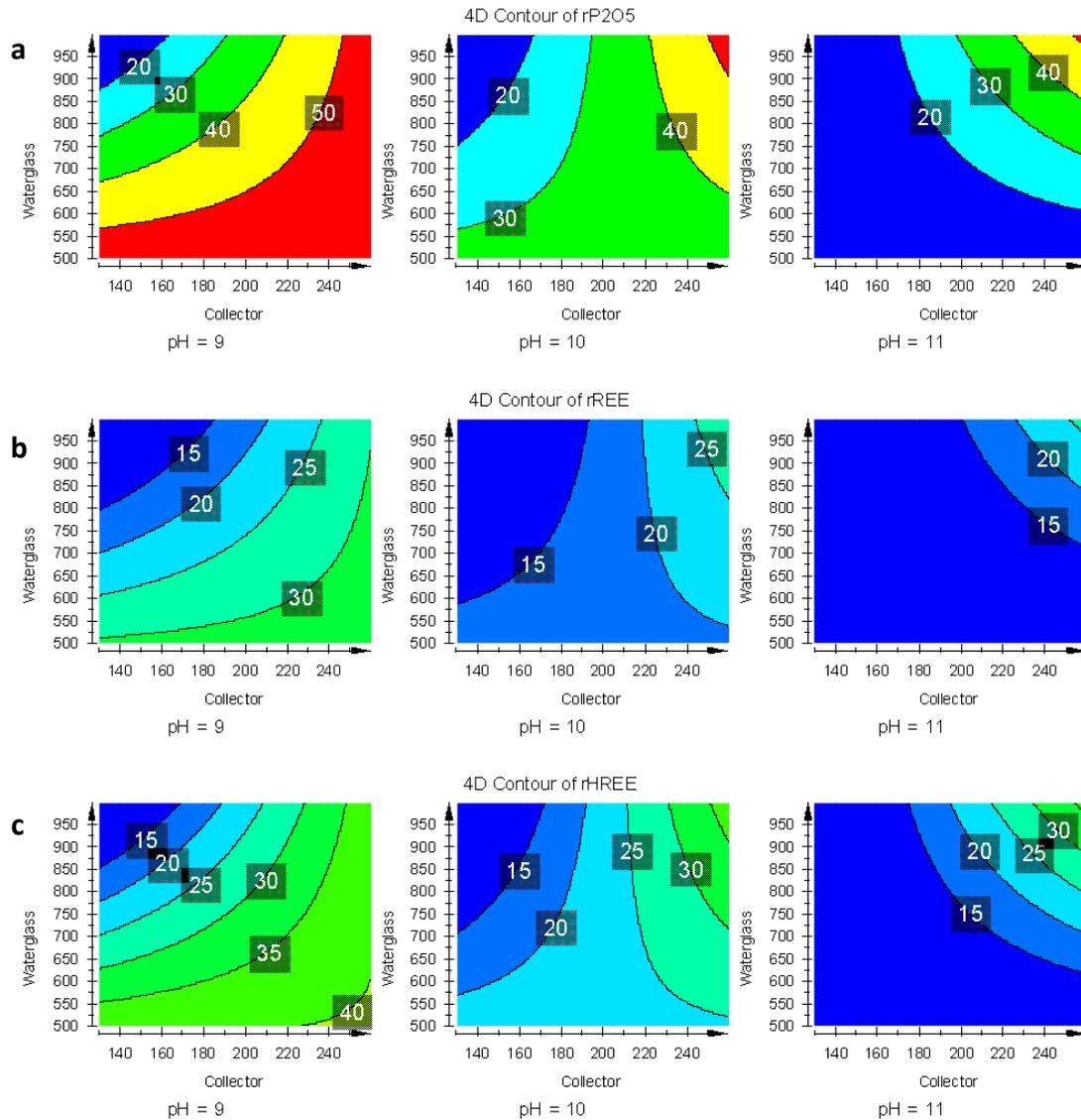
Product		Mass		Distributions (%)									
Notation	Name	(g)	(%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
1	Talc conc	42.9	4.3	5.4	3.6	3.6	2.2	3.5	9.8	4.6	3.3	2.7	3.6
mp 1	Feed to flotation	965.8	95.7	94.6	96.4	96.4	97.8	96.5	90.2	95.4	96.7	97.3	96.4
2C	Apatite conc	119.6	11.9	0.7	0.5	47.8	0.8	1.1	3.1	22.1	0.9	62.0	1.1
2CR	Cl-middl 3	25.0	2.5	0.9	0.7	7.6	0.6	0.8	2.0	5.2	1.0	8.0	0.9
2B	Clean conc 2	144.6	14.3	1.6	1.1	55.4	1.4	1.9	5.1	27.3	1.9	70.0	2.1
2BR	Cl-middl 2	35.7	3.5	2.6	2.4	7.2	1.6	2.2	4.4	5.9	2.4	6.5	2.0
2A	Clean conc 1	180.3	17.9	4.2	3.5	62.6	3.0	4.1	9.4	33.1	4.3	76.6	4.1
2AR	Cl-middl 1	152.3	15.1	16.7	17.2	14.3	10.9	16.9	21.0	17.3	16.4	9.9	7.4
2	Rogher conc	332.6	33.0	20.9	20.7	76.9	13.9	21.0	30.5	50.5	20.7	86.4	11.4
mp 2	Tail	633.2	62.8	73.7	75.8	19.5	83.9	75.6	59.7	45.0	76.0	10.8	85.0
	Calc.Feed	1008.7	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0



**Figure 4.** a) grade-recovery and b) selectivity diagrams for a good test<sup>7</sup>

## Response surfaces

To get a better view of how the parameters influence the responses, contour plots were made for recoveries of  $P_2O_5$ , REE and HREE, cf. Figures. 5a-5c. The overall view is that the best recoveries are for pH 9, high collector dosage and low water glass addition. Note that in all cases there is a local maximum for pH 11, high collector and high water glass. Therefore, the experimental space is 3-dimensional with a saddle point at the centre of the test series. It is interesting to note that said recoveries show the same general pattern. This indicates that the REE and HREE are either locked with apatite or in free-floating minerals with similar flotation properties as apatite.



**Figure 5.** Contour plots for a) recovery of  $P_2O_5$ , b) recovery of REE and c) recovery of HREE to apatite concentrate

## DISCUSSIONS

The flotation results show that the best conditions for both apatite and REE winning are pH 9, high collector dosage (260 g/t) and low depressant addition (500 g/t). For this condition, laboratory scale flotation gives an apatite concentrate with 30 % P<sub>2</sub>O<sub>5</sub> at 70 % recovery.

REE follows apatite in the cleaning, but not totally. The recovery of total REE to apatite concentrate is approx. half of that for apatite. For the heavy REE, it is slightly better. The final grade of REE in the flotation concentrate is fairly constant and related to the P<sub>2</sub>O<sub>5</sub> grade in the apatite concentrate. This implies that REE is not totally in apatite, and that there must be at least one unknown REE phase present. In later investigations it has been seen that a shorter grinding time leads to slightly higher REE recoveries, implying that a not so fine grinding gives better recoveries of liberated REE minerals.

When a full-scale recovering-dredging operation of the tailings pond is running during the winter, the feed to the concentrator will be just above freezing. Unfortunately, preliminary tests indicate unacceptable losses of apatite and REE when the flotation is run below 10 °C with the present reagent mix.

It appears that a large proportion of the REE is lost already in the rougher flotation and the first cleaner flotation. If this loss is caused by REE present in allanite, a test of the magnetic properties of the tailings might give some indication of the possibility to use high-gradient magnetic separation and/or amine based flotation to increase the total REE recovery.

## FUTURE WORK

In the attempts to recover some of Europe's most critical REEs from existing mine waste, it is fundamental to understand the occurrence of all REE containing minerals in the tailings and adapt flotation and other techniques to fit these specific minerals. This is one of the objectives in the recently started European project REEcover, where several European countries collaborate on finding new, and more efficient, techniques for characterization, analysis, extraction, and metal production of REEs.

As can be seen in the data presented in this paper, there is a need improving the accuracy of the characterization of REE-bearing minerals, and also on improving the detection of elements of very low concentrations, e.g. the HREE's. To establish in detail the distribution and character of REE-bearing minerals with the purpose to develop the right extraction technique, quantitative analysis using Inca software will be performed on the Kiirunavaara material, as well as LA ICP MS analysis to be able to detect the absolute concentrations of REE's in different mineral phases.

In a recent mineralogical survey by LKAB on an apatite concentrate, the mineral grades according to Table 3 were found. The mineral analyses come from Table 1. The calculated combined REO contents in mg/kg are compared with chemical analyses (ICP-MS) from flotation tests<sup>7</sup>. The two flotation tests gave nearly the same concentrate quality. The agreement between calculated and analysed contents is not so good, but what stands out is that chemically analysed Y grades are approx. five

times higher than theoretically calculated. This indicates that the missing REE phase carries a relatively high Y content, and possibly other HREE's.

**Table 3.** Comparison of REE-content in apatite concentrate

Concentrate		Analysed grades in minerals					
Mineral	Grade (%)	%SumREO	%La2O3	%Ce2O3	%Pr2O3	%Nd2O3	%Y2O3
Apatite	70.65	0.252	0.020	0.200		0.027	0.014
Monazite	0.32	70.034	14.816	37.840	5.147	11.951	0.280
Allanite	0.40	22.467	6.989	11.442	1.271	2.446	0.319
		Calculated concentrate grade contribution (mg/kg)					
		SumREO	La2O3	Ce2O3	Pr2O3	Nd2O3	Y2O3
		1 780	141	1 415	0	189	100
		2 241	474	1 211	165	382	9
		899	280	458	51	98	13
Combined REO		4 920	895	3 084	216	669	122
N101:Test REE		3 550	608	1 290	164	603	472
N105:Test REE		3 484	617	1 250	161	587	486
Conversion REE/REO		0.8000	0.8527	0.8537	0.8545	0.8574	0.7874
Test equivalent bulk chemistry REO		4 396	718	1 488	190	694	608
Difference (Bulk-EMPA) eq REO		-524	-177	-1 596	-25	25	487

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