FRAME
FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

DELIVERABLE D4.3
Detailed metallogenic studies of key phosphate deposits in Europe

WP 4 “Critical Raw Materials in phosphate deposits and associated black shales”

This project has received funding from the European Union’s Horizon 2020
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1. Introduction

This deliverable is devoted to the detailed metallogenic studies of key, and critical raw materials, phosphate deposits in Europe. These case studies examine both sedimentary and igneous-related phosphate deposits, both medium to large in size. The selection of deposits was as representative as possible. Since the black shales hosting sedimentary phosphorite could provide additional Critical Raw Materials (CRM), they are briefly considered as well.

The aim of this deliverable is to lead to (i) a better understanding of the CRM distribution and enrichment within these deposits and constrain the processes which have led to these enrichments, and (ii) identify and highlight the potential of these deposits regarding the CRM.

Hereafter, a summary of the different phosphate types encountered in Europe is first provided. It is followed by a description of the methodology applied to prepare the deliverable, then by the outcome of this work before the conclusions and prospects. For the outcome, the main results of the metallogenic studies are presented. The detailed studies are provided as annexes that account for a few hundred pages.

2. Summary of the different phosphate deposit types encountered in Europe

In Europe, phosphate deposits and occurrences are abundant and widely distributed (Figs. 1 and 2). They are igneous or sedimentary in origin and their age varies from the Archean to the Pleistocene (Fig. 2). Various sub-types of igneous-related phosphate deposits occur (defined according to Inspire; Fig. 1) and are detailed in the section “2.1. Igneous-related types” here below, listed by type.

2.1. Igneous-related types

In Finland, the Devonian Sokli **carbonatite** complex hosts a large apatite deposit, the reserves of which are estimated at 190 million tonnes (Ahokas 2015). The highest modal values of apatite are observed in phoscorite (up to 50%) (O’Brien and Hyvönen 2015). The Siilinjarvi phosphate deposit is associated with a carbonatitic complex dated at ~2610 Ma (GTK unpublished report in O’Brien et al. 2015). Ore reserves of 234 Mt at an average grade of 4 wt% P_2O_5 are estimated (O’Brien et al. 2015). In Norway, the Neoproterozoic Fen carbonatite complex is known for its Nb and REY mineralization, though it also hosts apatite-rich facies (containing up to 29% apatite; Ihlen et al. 2014). The Seiland Igneous Province (Norway) comprise Neoproterozoic to Cambrian alkaline complexes, among which the Lillebukt Complex that presents an interest for its phosphate content (Ihlen et al. 2014). In Sweden, the Neoproterozoic Alnö carbonatite contains ~2 million tonnes at a grade varying from 2 to 6%

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P_2O_5. Other small occurrences of phosphate associated with carbonatites are known in Italy and Germany.

Unsaturated and saturated syenitic and alkali granitic igneous rocks and pegmatites constitute other rocks that typically host phosphate deposits. The Misværdal Complex (Norway) is a Silurian age alkaline complex comprizing mostly pyroxenites that are the main carrier of apatite. Resources could reach 30 Mt at 4.1% P_2O_5 (Ihlen et al. 2014). The Paleoproterozoic Lofoten-Vesteralen Mangerite Complex (LVMC, Norway) – where nelsonite ore (containing between 2.75 and 4.23% P_2O_5) is present as thick veins and breccias - constitutes another interesting area regarding its potential for P (Ihlen et al. 2014). In southern Norway, the Kodal deposit is found in the Permian Larvik Complex (Oslo Igneous Province). It is made of pyroxenitic ore lenses rich in apatite, with resources of 70 Mt, grading at 4.9% P_2O_5 (Ihlen et al. 2014). The Loch Borralan and Loch Loyal Silurian intrusions (Scotland, UK) host apatite-rich facies that present a potential regarding P (Notholt and Highley 1981; Walters et al. 2013). Other alkaline complexes containing apatite at a near-economic grade are found in Italy (Stoppa et al. 2016).

The best known **lamproite** in Europe is present in Spain, at Jumilla. There, Miocene **jumillites** host an apatite mineralization (Venturelli et al. 1991).

In Norway, phosphate mineralizations related to **mafic to ultramafic intrusions** are widespread. The Neoproterozoic Rogaland Anorthosite Province constitutes one of the most promising targets regarding phosphate exploitation, with resources being above 300 Mt at a grade reaching 8.0-10.2% of apatite for the individual cumulate zones (Ihlen et al. 2014). In Finland, the Paleoproterozoic Kauhajärvi gabbro and appinite at Vanttaus are intrusions enriched in apatite that could present an interest for future P exploration (Kärkkäinen and Appelqvist 1999; Sarapää et al. 2013).

Most of the **iron oxide apatite** (IOA) deposits in Europe are found in Sweden, with (i) the major mining areas in the northern Norrbotten district that have reserves and resources estimated at 2372 Mt of iron oxide-apatite ore (Hallberg et al. 2016). This Paleoproterozoic mineralization comprises mostly magnetite-hematite-apatite and associated calcite, actinolite and diopside (Frietsch and Perdahl 1995); (ii) the Bergslagen district, with the Grängesberg mine that has estimated resources of 148 Mt (Hallberg et al. 2006). In Norway, the Nissedal area is known for occurrences of magnetite–hematite-apatite deposits. The Mesoproterozoic Søftestad deposit presents remaining resources of ~0.5 Mt, with ~55% Fe and 3.9% P_2O_5 (Ihlen et al. 2014, and references therein).

The most important European apatite deposits occurring as **metasomatic replacement/hydrothermal veins** – and (at least spatially) – associated with granite are the post-Variscan quartz-apatite veins occurring in the southern Central Iberian Zone (mining district of Logrosan and Belvis-Navamoral; Vindel et al. 2014). This was one of the most important phosphate source in Europe from the 1850s to the Second World War (Vindel et al.

2014). In the Bamble-Lillesand Block (Norway), the paragneiss at Rossavika hosts pseudo-carbonatite lenses and veins enriched in apatite. The grade of the lenses varies between 7.63 and 21.34 wt.% P_2O_5 in the lenses (Ihlen et al. 2014). In Sweden, the REE-P mineralization occurring at Olserum, Djupedal and Bersummen is present as veins and vein zones hosted in metasedimentary rocks. It is thought to be deposited from high temperature hydrothermal fluids, connected to the granite (Andersson et al. 2019).

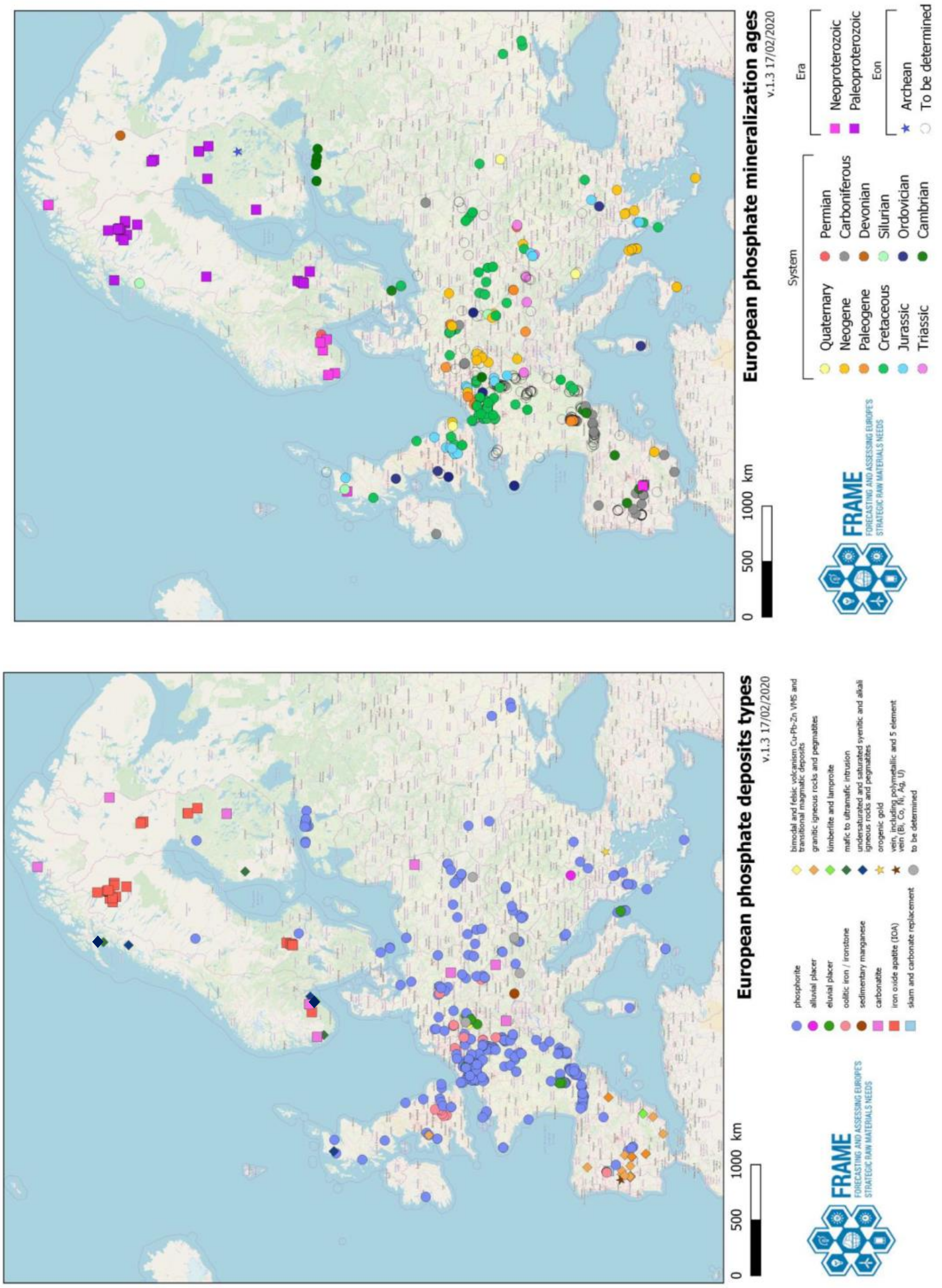

Figure 1. Map illustrating: (left) the mineral deposit type of phosphate mineralization in Europe and (right) the phosphate mineralization in Europe according to their age (System/Period for Phanerozoic mineralization, Era for Proterozoic mineralization, and Eon for Archean mineralization). Report " Deliverable D4.2" of the FRAME project-WP4.

2.1. Sedimentary phosphorites

Three main episodes of phosphogenesis are known during the Lower Paleozoic, the Upper Cretaceous, and the Tertiary. They led to the formation of deposits of major importance.

Lower Paleozoic phosphorites constitute most of the phosphorites in Europe, testifying for the presence of a phosphogenic province within the Avalon and the Baltic Platforms. Such deposits are commonly associated with glauconitic sediments or black shales (Notholt and Brasier 1986). At Fontanarejo (Spain), early Cambrian phospharenite and phospharenorudite constitute resources of about 2,000,000 tonnes (Notholt et al. 1989). In Serbia, Ordovician metamorphosed phosphatic sandstone presents 95 million tonnes grading at ~10% P_2O_5 (Torbica and Lapčević 2012). The sandstones, straddling the Cambrian–Ordovician boundary interval in northern Estonia, contain shelly phosphorite deposits with an estimate of about 750 million tons of P2O5 (Raudsep 1997).

An important sedimentary phosphate unit of Upper Cretaceous age is known throughout the Paris and Mons Basins (France and Belgium), where it forms economic deposits of phosphatic chalk. These deposits reveal a significant phosphogenic episode that occurred during Cretaceous time on the NE margins of the Anglo-Paris Basin (Jarvis 1992) and result in the formation of numerous phosphorite occurrences/deposits. In the Mons and Paris Basins, phosphatic chalk, enriched pockets of residual phosphates, and phosphatic channels infills lead to total resources of 600-900 million tonnes at 8-10.5% P_2O_5 in the Mons Basin (Robaszynski 1989), and 12-15 million tonnes at 7-14% P_2O_5 in the Paris Basin (Monchiardini 1989). The Taplow Cretaceous phosphate chalk (UK) has reserves estimated at 500,000 tonnes (only for its SW side). In addition, reserves of other 246,000 tonnes can be found in Cenomanian condensed phosphatic glauconitic marl of the Cambridge Greensand (UK; Notholt et al. 1979). In Germany (Lower Saxony), the Lengede-Broitstedt deposit presents a grade of about 4% P_2O_5 (Notholt et al. 1979). Cretaceous phosphatic beds associated with iron ore in the Oberpfälz district (Germany) represent reserves of at least 30,000 tonnes at 20% P_2O_5 (Notholt et al. 1979). In Greece (Drymonas deposit), phosphatized limestone horizons of Cretaceous age has reserves of about 7 Mt at ~25% P_2O_5 (Tzifas et al. 2014).

The Cenozoic constitutes another major period of phosphogenesis leading to the formation of many deposits and occurrences in Europe (Arthur and Jenkyns 1981). The largest are known in the area of Salento (Italy), where Miocene phosphate-rich limestones account for at least 60 million tonnes grading at 7-8 % P_2O_5. An additional 10 million tonnes of Upper Pliocene (?) nodular phosphate-rich rocks at a grade in the range 10.5-20.5 % P_2O_5 are present in the same area (Notholt et al. 1979). Oligo-Miocene phosphatic nodule-rich formations in Sicily have resources of 7 million tonnes at about 15% P_2O_5 (Donnalucata district; Notholt et al. 1979; Cultrone et al. 2008). In Germany, phosphorite deposits associated with Lower Tertiary Fe and

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Mn oxide ores in the Lahn district account for 750,000 tonnes at a grade above 20% P_2O_5 (Notholt et al. 1979).

Beside the deposits formed during these three main phosphogenic episodes, it is worth mentioning a few others economically interesting mineralizations. Among these, the Proterozoic Lampinsaari deposit (Finland), made of a lenticular bed of apatite-bearing dolomite, skarn and apatite-rich gneiss, accounts for 39 million tonnes at a grade of 2.6% P_2O_5 (Notholt and Brasier 1986; Notholt et al. 1989). Devono-Carboniferous phosphorites being potentially interesting from an economic point of view are present in Ireland, France, Spain, UK, Romania and Germany (Notholt et al. 1979, 1989). In the County Clare (Ireland), Upper Carboniferous condensed sequences of phosphate rocks have estimated resources of 1.25 million tonnes at 20-25% P_2O_5 (Notholt et al. 1979). The Moncorvo Fe-deposit (Portugal), the north Pyrenean fault zone (France) and the area of the Rhenish Schiefergebirge and Harz Mountains constitute other targets regarding their potential in phosphate mineralization (Notholt et al. 1979).

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3. Methodology

The selection of deposits made for the detailed metallogenic studies aimed at considering the different phosphate types presented above. These case studies examine thus both igneous-related and sedimentary phosphate deposits. In addition, the choice was made to investigate preferably deposits medium to large in size, or targets that look promising for further exploration.

The selection of deposits was as representative as possible (Fig. 2), investigating phosphate mineralization associated with mafic and ultramafic intrusions (the Bjerkreim-Sokndal layered intrusion in Norway), apatite deposits related to carbonatite (Fen in Norway, Siilinjarvi in Finland), saturated and undersaurated syenites (the Kodal-Larvikite and Raftsund intrusion fall in that category), sedimentary phosphorites from various ages (Ordovician in Estonia, Cretaceous in Belgium and the Czech Republic, Tertiary in Italy) and, finally, sedimentary apatite associated with oolitic ironstone (Moncorvo, Portugal).

This extensive selection covered the most representative phosphate deposits encountered in Europe. One exception is the apatite deposit associated with IOA ore. However, for the latter, significant efforts were made in the past (during the last decades) to characterize properly the enrichment in CRM of these deposits, which are mostly present in Sweden. The literature about these deposits is abundant (e.g., Eilu et al. 2012; Martinsson et al. 2016; Sadeghi 2019; Sadeghi et al. 2020). Consequently, there were no need to investigate further this type of mineralization for the present project.

For the study of the deposits considered in the frame of this WP, new field work was done (except for the study of the Siilinjarvi carbonatite, the samples have been provided by the Yara Suomi Oy mining company). A careful petrographic study was then carried out. Mineralogy and rock texture were investigated using a selection of methods, depending on the needs: X-ray diffraction (XRD), optical microscopy (including cathodoluminescence), scanning electron microscopy (SEM) coupled with energy dispersive spectrometer (EDS) and Raman spectroscopy. The chemistry of minerals hosting CRM (such as apatite in phosphate deposits) was further investigated using electron microprobe and LA-ICPMS analyses. In situ analyses were often needed to investigate the changes of apatite chemistry - and from an economic point of view - its REE and F enrichment. This provides crucial information about sedimentary processes/diagenesis in the case of phosphorites, and magmatic processes and the involvement of different types of fluids (late-magmatic/metasomatic/hydrothermal) in an igneous context. Besides, whole rock chemistry provides crucial information about the potential for REE of the deposits.

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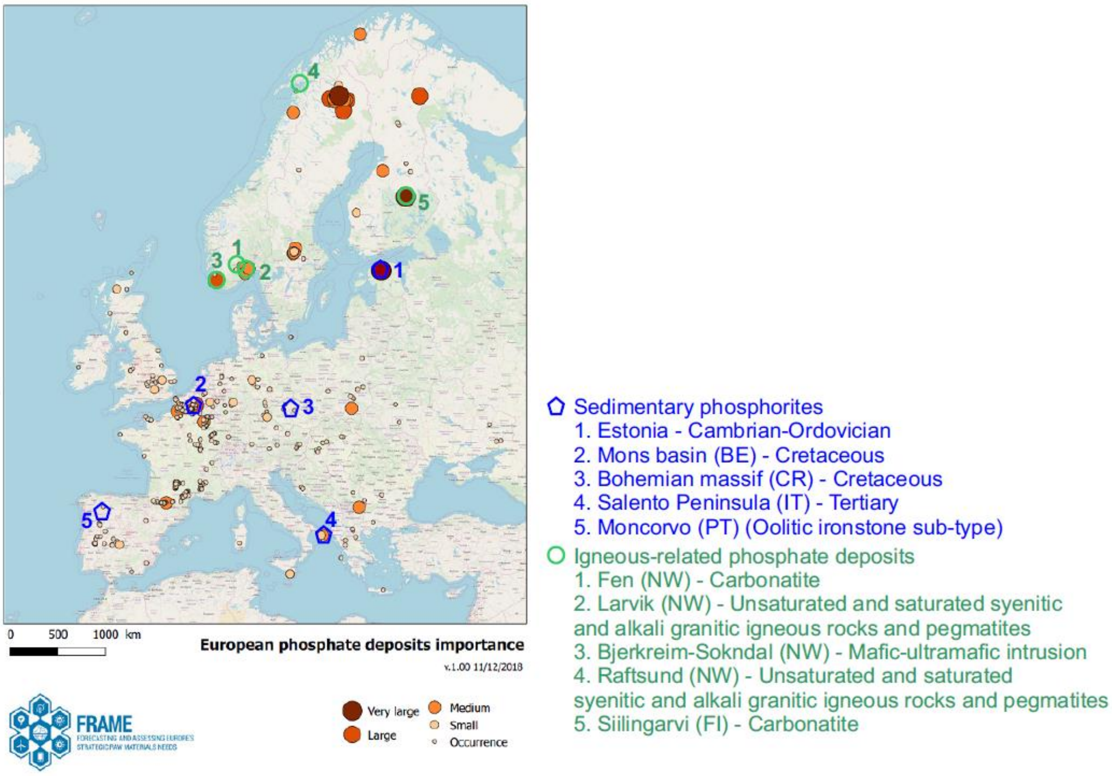


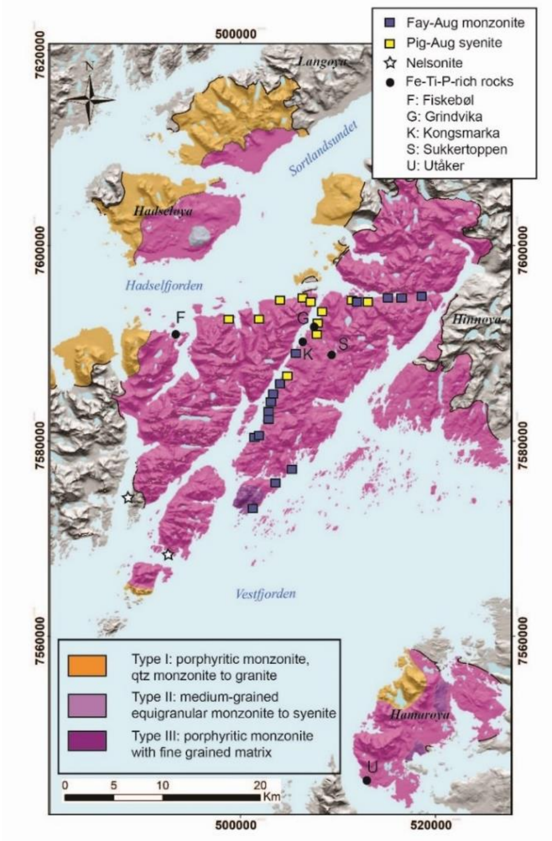
Figure 2. Location of the studied phosphate deposits

4. Outcome

In this section are provided summaries of the different metallogenic studies. The latter are of course provided as annexes (from Annex 1 to Annex 7). The new data gathered for this deliverable (mostly newly acquired data, but also data from the “grey literature”) have been collected and added to the database comprising mineralogical and geochemical data prepared for the Work Package 8 of the FRAME project. This database is provided as Annex 8 of this report.

4.1. Igneous phosphate deposits in Norway

The deposits presenting the most economical potential for phosphorus in Norway are of magmatic origin, and the main mineral hosting phosphorus is apatite. Four intrusions associated with the most promising apatite-rich rocks were investigated as part of this study: the Raftsund intrusion (RI) 1800 Ma, Lofoten-Vesterålen AMCG, Nordland, northern Norway; the Bjerkreim Sokndal layered intrusion (BKSK), 930 Ma, Rogaland Anorthosite Province, Rogaland, southwestern Norway; the Fen alkaline-carbonatite complex, 580 Ma, Telemark, southern Norway; the Larvik Plutonic Complex (LPC), 295-292 Ma, Permian Oslo Rift, Larvik, southern Norway.



The Raftsund intrusion, a monzonitic to quartz-monzonitic batholith (78 x 35 km), is the largest intrusion of the Vesterålen - Lofoten AMCG complex. It was emplaced around 1800 Ma in Archean and Paleoproterozoic granulite-facies migmatitic gneisses (Coint et al. 2020 and references therein).

Fe-Ti-P-rich rocks (black circles in Fig. 3), arbitrarily defined as rocks containing more than 1 wt% P_2O_5, are found scattered in the type II monzonite-syenite unit and are most abundant in the pigeonite-augite syenite (Pgt-Aug syenite). The mineralizations form cm-scale dark veins and lenses (up to 200 x 50 m) that are scattered throughout the unit.

Figure 3. Simplified geological map of the Raftsund intrusion (modified from Coint et al. 2020) and location of the samples used in this study.

The Neoproterozoic Rogaland Anorthosite Province (RAP) consists of several massif-type anorthosite bodies, the Bjerkreim-Sokndal layered intrusion (BKSK), largest layered intrusion in Western Europe, as well as intrusions of norites, jotunites, mangerites and charnockites. Apatite is mostly found associated with lithologies of intermediate composition such as gabbronorites and jotunites (orthopyroxene monzodiorite) (0.08 - 5.51 wt% P_2O_5 with an average of 2.96 wt% P_2O_5; data from Schiellerup et al. 2001). The northern lobe of the BKSK, called the Bjerkreim lobe, hosts the largest volumes of apatite-rich rocks of interest in this study (Fig. 4). It is a very large but low-grade resource of apatite (Ihlen et al. 2014), however the presence of ilmenite and V-rich magnetite significantly increases its economic potential.

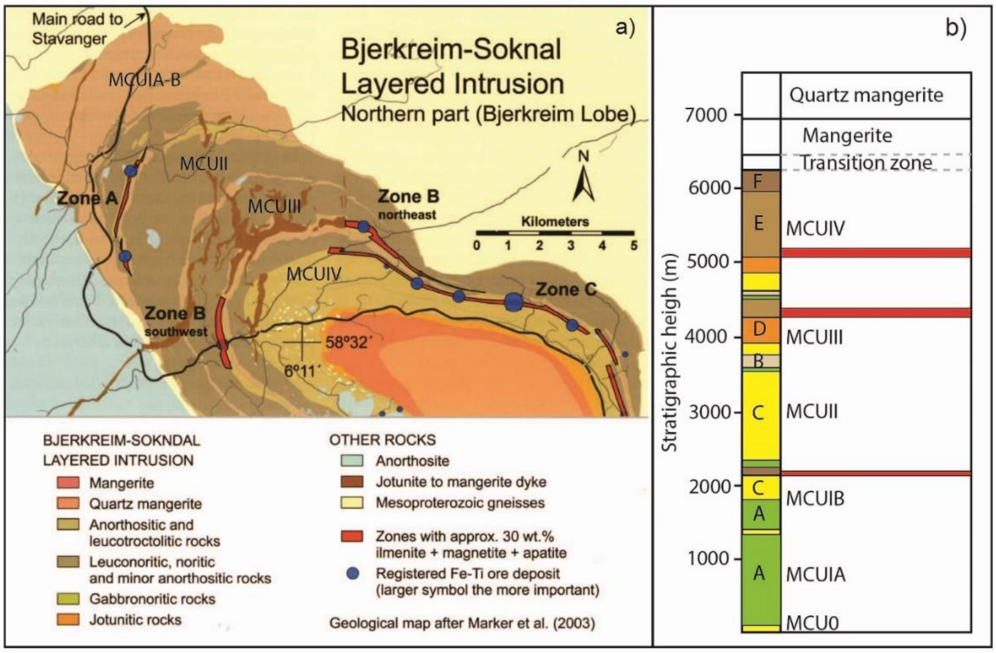


Figure 4. a) Simplified geological map of the Bjerkreim lobe (from Ihlen et al. 2014). b) Simplified stratigraphic column of the layered series. The red horizon are the apatite-rich horizons (modified from Ihlen et al. 2014).

In the BKSK, apatite is constrained to the stratigraphic zones e and f in MCUIB, MCUIII and MCUIV. The most promising resource in the BKSK is confined to the MCU IV and MCU III ore zones having ore potentials of about 400 Mt and 150 Mt, respectively. The calculations are based on average concentrations in samples and cores, extrapolated to 100 m depth: MCU IBe: 45 x 3000 m @ 8.3 % Ap, 15.2 % Ilm, 10.6 Mag; MCU IIIe: 100 x 3000 m @ 7.8 % Ap, 11.4 % Ilm, 6.9 % Mag; MUC IVe: 70 x 8500 m @ 10.2 % Ap, 12.4 % Ilm, 7.3 % Mag.

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The Fen alkaline complex is an Ediacaran (580 Ma, Andersen and Taylor 1988) pipe-like intrusion, composed of variety of carbonatites and associated alkaline rocks (Fig. 5), that was emplaced through Proterozoic gneisses, 20 km west of the Oslo rift (Andersen 1988).

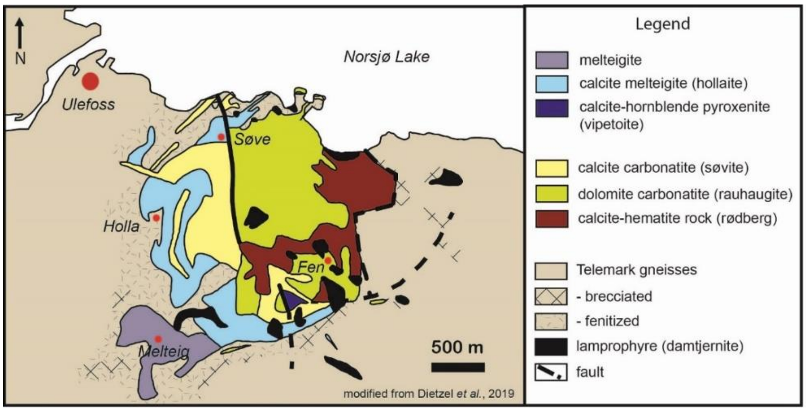

Figure 5. Simplified geological map of the Fen alkaline-carbonatite complex (modified from Dietzel et al. 2019).

Although no systematic sampling has been carried out in the intrusion, the average P_2O_5 for the major rock-types forming the complex, including the calcite-carbonatite (søvite, Fe-rich dolomite carbonatite (rauhaugite), the hematite-calcite rock (rødberg), the nepheline pyroxenite (melteigite) and the amphibole pyroxenite (vipetoite), ranges between 1.86 to 3.69 wt% P_2O_5 (Ihlen et al. 2014). The calcite carbonatite unit contains the most apatite, with local segregation reaching up to 11.3 wt% P_2O_5 (Schilling 2013; Hornig-Kjarsgaard 1998), although one recent whole-rock analysis reported a value of 10.15 wt% P_2O_5 in a REE-mineralized Fe-dolomite carbonatite (Dahlgren 2019).

A series of apatite-phlogopite-amphibole-magnetite lenses, almost free of carbonate, to apatite-rich calcite and dolomite carbonatite have been described in the calcite carbonatite. Samples studied for this project are mainly from the calcium-carbonatite and the Fe-dolomite carbonatite. Apatite is either euhedral to subhedral concentrically zoned crystals or occur as cm-scale clusters of radiating prismatic apatite crystals. Samples from the Fe-dolomite carbonatite contain fragments of apatite-rich rocks that commonly display evidence for hydrothermal alteration. Apatite in that unit is present as both subhedral zoned crystals and as sub-micrometre microcrystalline apatite. In many areas microcrystalline apatite is associated with other minerals such as chlorite, quartz and thorite.

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The Larvik Plutonic Complex (LPC) is the largest monzonitic body associated with the Permian Oslo rift (Neumann 1980). It was emplaced between 297 to 292 Ma (Dahlgren et al. 1998) as a series of nested circular monzonitic bodies (larvikite) which are younger towards the northwest. The magmas forming the intrusion evolved from silica-saturated in the east to silica-undersaturated toward the northwest. The last two units to be emplaced are nepheline syenites (lardalite).

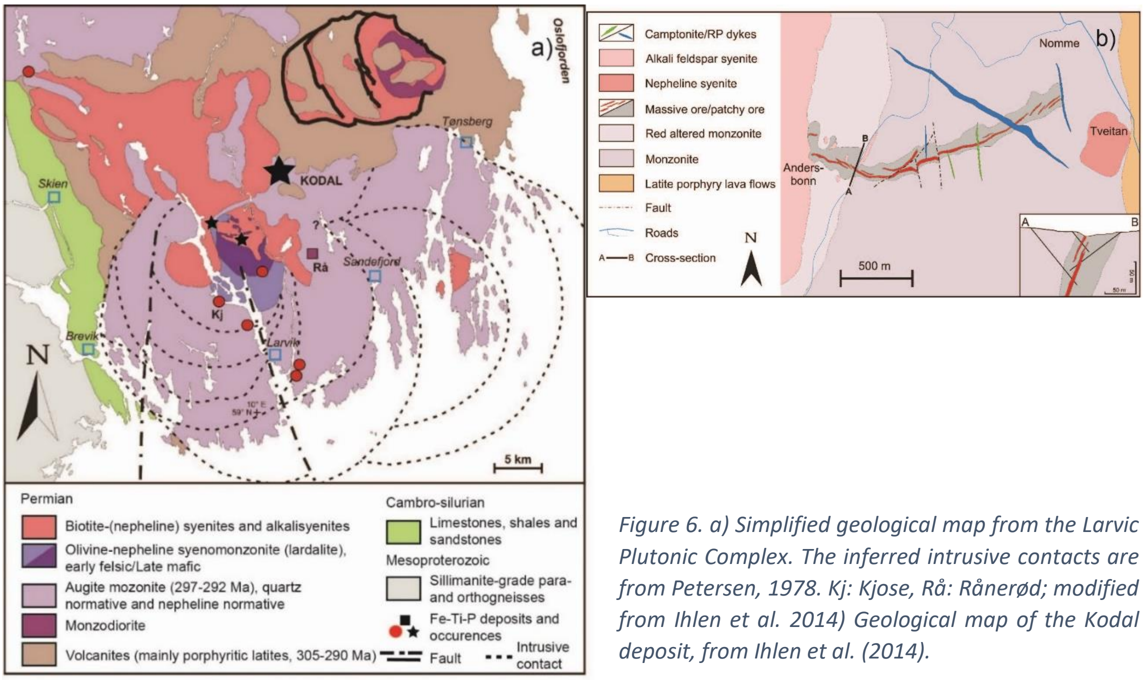


Figure 6. a) Simplified geological map from the Larvic Plutonic Complex. The inferred intrusive contacts are from Petersen, 1978. Kj: Kjose, Rå: Rånerød; modified from Ihlen et al. 2014) Geological map of the Kodal deposit, from Ihlen et al. (2014).

Fe-Ti-P-rich rocks are found throughout the complex (Fig. 6a). They occur as tens-of-centimetre to meter-scale veins, pods, or conduit-like features in both the monzonite and the nepheline syenite (lardalite). The Kodal deposit (Fig. 6b), in the north-eastern part of the intrusion, is the largest deposit in the LPC. It consists of a 1900 m-long, 18-20 m-thick and at least 300 m-deep series of lenses of magnetite, apatite, ilmenite +/- augite rock. Kodal Minerals Ltd. recently conducted systematic core drilling according to JORC-standards and advanced ore dressing tests. Kodal Minerals Plc. estimates a JORC compliant resource of 49 Mt @ 5 % P_2O_5 of inferred and indicated crude ore for the Kodal deposit http://www.kodalminerals.com/; whereas Lindberg (1985) inferred open pit resources of about 70 Mt with an average content of 4.9 wt.% P_2O_5 (massive ore + transition zones) or alternatively underground resources of 35 Mt with an average of 6.8 wt.% P_2O_5 (massive ore zone).

The whole-rock dataset shows that, overall, samples from the BKSK and Kodal intrusions are more enriched in phosphorus than the ones associated with the Raftsund intrusion. Samples from the Kodal deposit contain the highest P_2O_5 concentrations (4-8 wt%). One sample from Kjose also displays high-grade P_2O_5 values (>9 wt%), whereas one sample of the calcite carbonatite from Fen reach concentrations close to 10 wt% P_2O_5.

The three intrusions dominated by silicate minerals display a strong correlation between the total REE found in the rock and the P_2O_5 content, indicating that the whole-rock content of the REE in most of these rocks is controlled by apatite (Fig. 7). The Fen alkaline-carbonatite complex displays different systematics. In carbonate-rich magmas, both phosphates and fluorocarbonates are stable and play an important role in controlling the REE content.

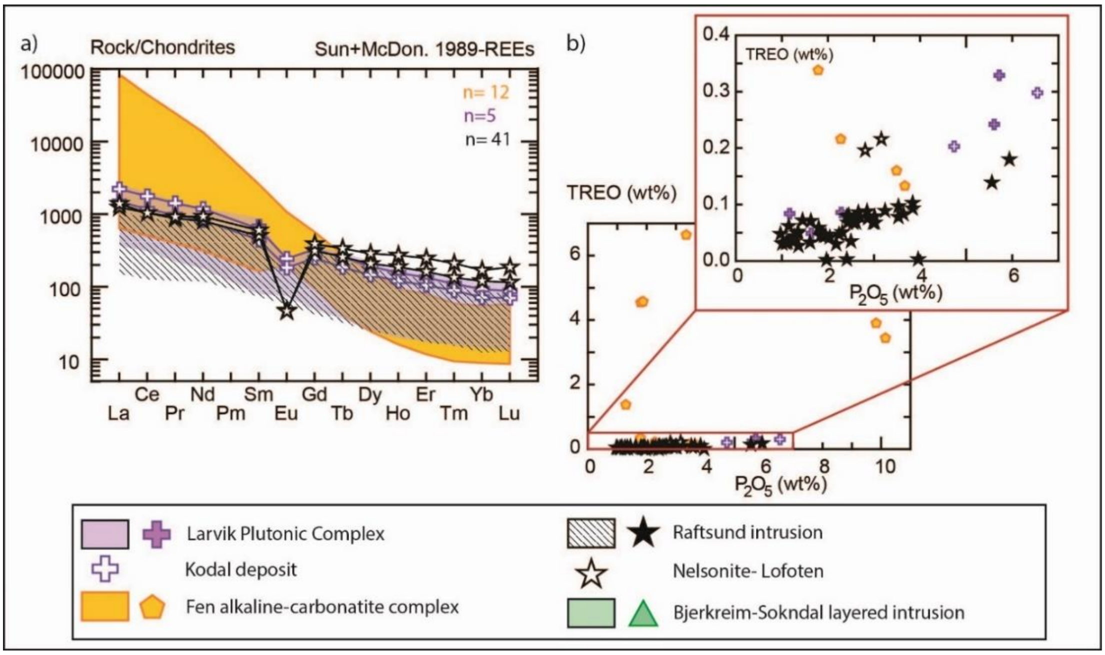


Figure 7. Whole-rock REE concentration. a) REE patterns normalized to chondrite (Sun and McDonough 1989). b) P_2O_5 versus TREO (wt%) concentration with rescaled panel to better display the trend for the Raftsund intrusion and the Larvik Plutonic Complex.

Regarding its trace element composition (LA-ICPMS analyses; Table 1), apatite from the Fen alkaline-carbonatite complex displays the most compositional variations. Microcrystalline apatite is characterized by a strong depletion in LREE and a slight but significant enrichment in HREE compared to the euhedral to subhedral apatite from the same complex (Fig. 8). Their Th content is very high (>100 ppm). It is not certain that all the Th is hosted in the crystal structure of apatite.

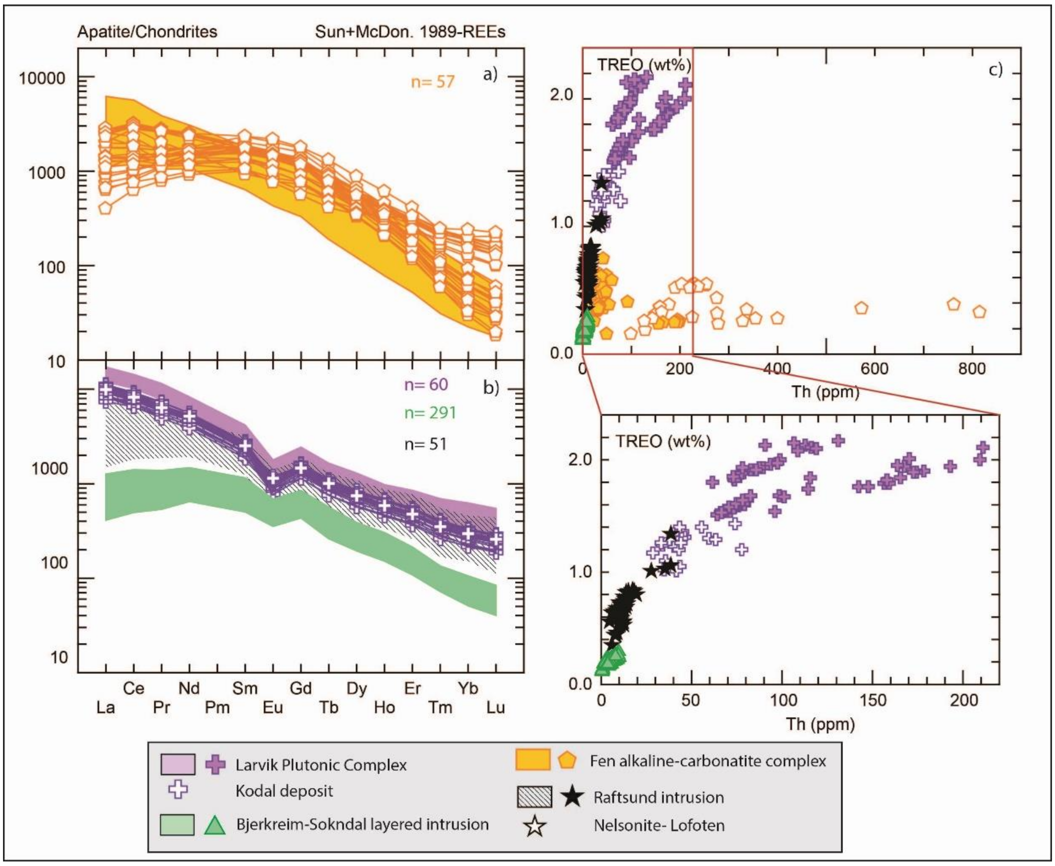


Figure 8. a) and b) apatite REE concentrations normalized to chondrite (Sun and McDonough 1989). c) Total REE (%) content versus Th content (ppm). Apatite that crystalized from silica-rich magmas display little variation in Sr compared to apatite from Fen.

The BKSK apatite, which crystallized from the most mafic magma, display the least amount of variation, and overall contains low concentrations of trace elements including REE and Th (Fig. 8). Apatite from the LPC are the most enriched in REE and contain up to 220 ppm Th (Fig. 8).

Table 1. Summary of Total Rare Earth Oxide, Th and U concentrations in apatite from each considered intrusion. "n" is the number of analyses. µX Ap: microcrystalline apatite. SubH Ap: Subhedral apatite. Clusters of acicular apatite are considered as subhedral apatite in this table

Intrusion	*Texture*	*n*	*TREO (wt%) av*	*TREO (wt%) min-max*	*Th (ppm) av*	*Th (ppm) min-max*	*U (ppm) av*	*U (ppm) min-max*
Fen	µX Ap	30	0.38	0.16-0.55	271	98.82-761	15.32	0.1-139
Fen	SubH Ap	57	0.46	0.16-0.80	50	5.6-199	1.48	bdl-22
LPC	SubH Ap	60	1.81	1.51-2.17	107	64-211	21	3-22
Kodal (LPC)	SubH Ap	23	1.25	0.92-1.29	45	34-78	11	8-17
RI	SubH Ap	51	0.69	0.35-1.34	13	4.7-38.6	4.31	2.14-10.67
BKSK	SubH Ap	291	0.19	0.11-0.29	4.4	0.35-10.04	1.68	0.25-3.61

The investigations carried out for this project can be summarized as followed.

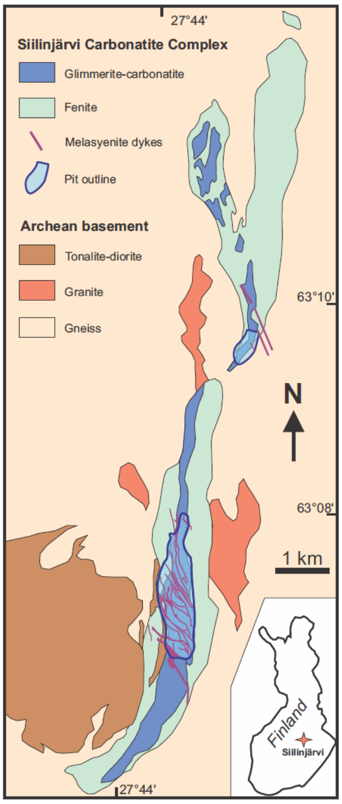
The Bjerkreim-Sokndal layered intrusion (BKSK) is a large low-grade resource of apatite, but is associated with ilmenite, and V-rich magnetite, potential bi-products. The macrocyclic units MCUIII and MCUIV present the most economic potential. Average modal proportions are the following: 7.8-10% apatite, 11.4-15.2% ilmenite and 6.9-10.6% V-rich magnetite. Total Rare Earth Element Oxide (TREO) in apatite (0.11-0.29 wt%) and Th concentrations are low (0.35-10.04 ppm).

The Kodal deposit, the next largest deposit in the country, represents much smaller volumes than the BKSK. The ore contains in average 17% apatite, 25-60% ilmenomagnetite and titanomagnetite, 5-15 % high Mg-ilmenite, 20-40% augite and 3-10% phlogopite. The resource is estimated to 49 Mt of ore @ 5 wt% P_2O_5, according to JORC standards. Apatite from the Kodal ore contains apatite with 0.92-1.29 wt% TREO and 45 ppm Th on average. Other Fe-Ti-P-occurrences in the Larvik Plutonic Complex (LPC; with which the Kodal deposit is associated) represent much smaller volumes, although recent field observations suggest that the process that led to Fe-Ti-P enrichment happened in several areas in the intrusion. Apatite from these occurrences contains higher concentrations of both REE (1.51-2.17 wt% TREO) and thorium (64-211 ppm) than the Kodal apatite. Further investigation, including detailed geophysical survey, will help evaluate the potential for apatite resources in the rest of the LPC.

Apatite resources related to the Fen alkaline-carbonatite complex are not yet well characterized. Whole-rock chemistry suggests high ore grade, however the distribution of the mineralizations and the volumes potentially available are unknown. Calcium carbonatite in the complex has the greatest potential as an apatite deposit, with phosphorus as a biproduct of Niobium mining. Magmatic apatite in the unit contain between 0.16 to 0.80 wt% TREO, associated with variable amount of thorium (5.6-199 ppm). Microcrystalline apatite, resulting from hydrothermal activity, present more challenging compositions with high trace element content, such as Th (up to 762 ppm), Ba and Sr associated with a depletion in LREE. Further investigation of the resource, with characterization of the distribution of these two types of apatite in all units of the intrusion, is necessary to further evaluate the potential for this deposit.

Despite a local enrichment in apatite, the Raftsund intrusion seems the least promising area. Apatite contain as much REE (0.69 wt% TREO on average) as the magmatic subhedral apatite from the Fen intrusion and low concentrations of Th (13 ppm on average). However, only few Fe-Ti-P-rich rock contain more than 4 wt% P_2O_5 and the size of the known mineralizations is restricted. Nevertheless, the process responsible for forming the mineralizations, silica-liquid immiscibility, resulted in the formation of an Fe-Ti-P-rich melt which could have ponded somewhere else in the intrusion, forming a larger deposit. The extreme topography of the area makes further detailed investigation complicated.

4.2. Siilinjarvi carbonatite-related phosphate deposit (Decrée et al. 2020)



The Siilinjärvi phosphate deposit (Finland) is hosted by an Archean carbonatite complex dated at ~2610 Ma (GTK unpublished report in O'Brien et al. 2015). The complex is of lenticular shape, comprises intermixed carbonatite and glimmerite, and dips steeply into a gneissic basement (O'Brien et al. 2015). Fenite is well developed all around the complex (Fig. 9). Almost all the glimmerite-carbonatite rocks constitute phosphate ore, with an apatite content of about ~10 vol%. Apatite-rich carbonatite and glimmerite contain up to 30 vol% apatite, and apatite veins are essentially monomineralic (~80 vol% apatite; O'Brien et al. 2015). The Siilinjärvi mine produces about 11 Mt/yr, with ore reserves of 234 Mt at an average grade of 4 wt% P_2O_5 (data for January 2014; O'Brien et al. 2015).

Figure 9. Geological sketch map of the Siilinjärvi Carbonatite Complex (modified and redrawn from O'Brien et al., 2015). The upper insert shows the location of Siilinjärvi in Finland

In rocks of the glimmerite and carbonatite series (including silica carbonatite and carbonate glimmerite), apatite is mostly present as isolated elongated euhedral to anhedral crystals (from about 1 mm to a few centimeters in size) or as clusters of crystals. The magmatic origin of apatite in the glimmerite-carbonatite series is confirmed by the dominant blue cathodoluminescence of this mineral, the enrichment in LREE and the lack of complex textures such as turbid or conversion textures under CL (e.g., Zirner et al. 2015; Broom-Fendley et al. 2017). A major evolution trend regarding the distribution of REE in apatite is revealed by CL imaging (Fig. 10).

An increase in rare earth elements (REE) content during apatite deposition (also observed in the REE patterns; Fig. 13a) is explained by re-equilibration of early apatite (via sub-solidus diffusion at the magmatic stage) with a fresh carbonatitic magma enriched in these elements. Apatite seems to be associated with a conspicuous Na- and K-rich zone within the carbonatite matrix (which is evidenced by the LIBS images, Fig. 11), which could be related to a separate – and late – carbonatite generation.

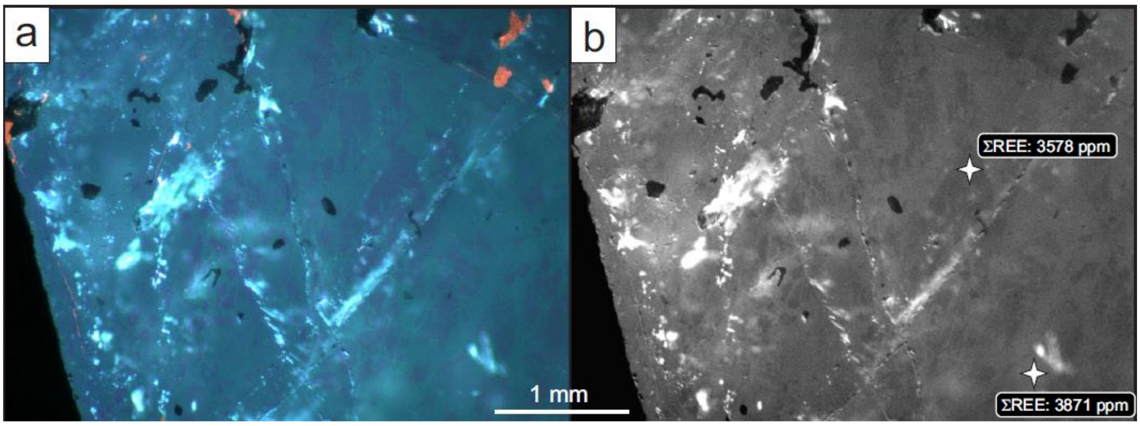


Figure 10. Cathodoluminescence (CL) photomicrographs of the Siilinjärvi glimmerite-carbonatite series. Color CL in (a). Spectral CL (Nd3+ emission filtered at 880 nm) in (b). Related REE content is indicated in a black box. (a-b) Apatite crystal in apatite rock (sample Si11) exhibiting a heterogeneous texture; a blue-luminescent apatite is partly altered/replaced by a green-luminescent apatite, which is characterized by a stronger Nd activation

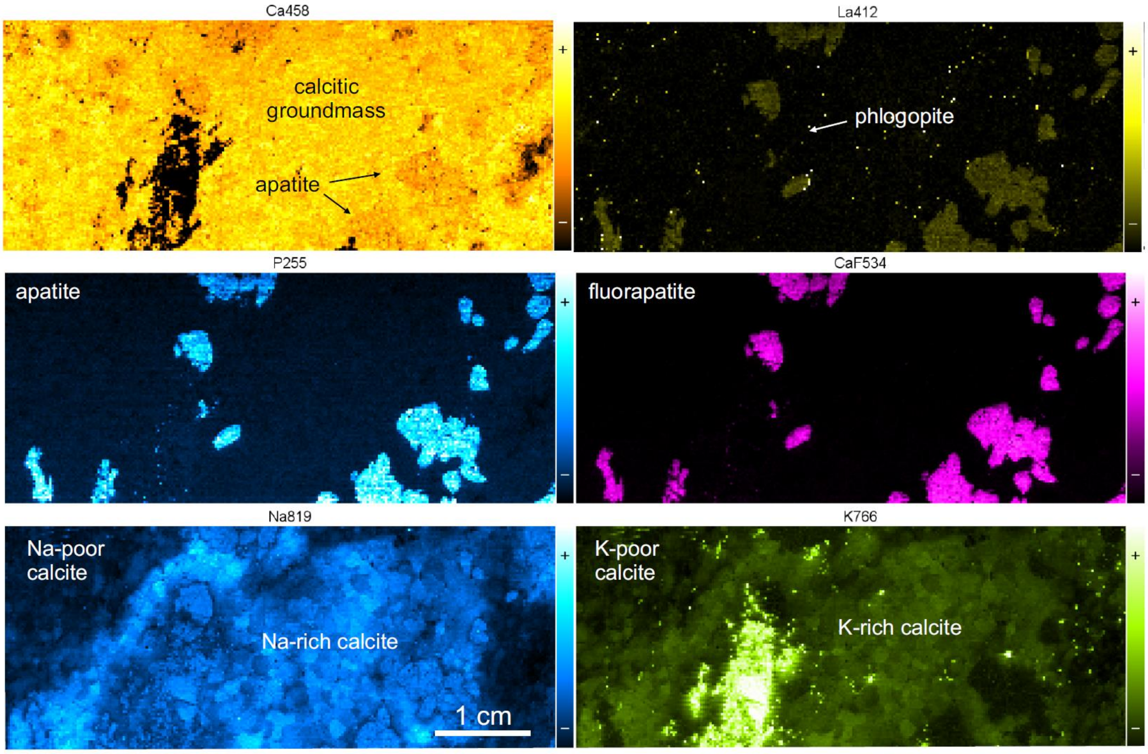


Figure 11. LIBS analysis of an apatite rock (apatite-rich carbonatite, sample Si11) from Siilinjärvi. Element names are followed by the integer part of the emission wavelength that was used. (a) Selected LIBS maps that show the distribution of both the major minerals (calcite, phlogopite and fluorapatite) and minute REE-minerals (as inferred from the bright spots in La and Ce maps). Although REE are detected in apatite, REE-minerals are scattered throughout the matrix but not included in apatite nor in phlogopite. The map of molecular CaF emission confirms the apatites are all fluorapatites. Note the Na- and K-rich zone within the calcitic groundmass of the carbonatite.

In amphibole- and pyroxene-rich fenites, apatite displays a complex zonation (alteration and conversion textures), which can be regarded as the product of apatite re-equilibration with highly evolved melts and/or fluids (e.g., Zirner et al. 2015; Broom-Fendley et al. 2017). The REE content and distribution follow two major evolution trends in the investigated apatite within fenite: (i) Apatite grains can exhibit an increasing Nd activation under CL towards their outer rim, as overgrowths after resorption (Fig. 12a); (ii) The second trend is characterized by a strong decrease in Nd-activation in green-luminescent rims and overgrowths (Fig. 12b). This decrease in REE is coupled with a substantial LREE loss (Fig. 13b).

Considering the above contrasting trends, at least two types of melt/fluid-rock interactions could explain the observed phenomena. The REE enrichment could involve Na-K-rich fluids during early (pre-emplacement) evolution of the carbonatite. These fluids are likely enriched in P and REE. Interacting with them, the early formed apatite would have been enriched in REE through coupled dissolution–reprecipitation processes (e.g., Zirner et al. 2015). Conversely, the decrease in LREE in apatite is commonly attributed to the mobilization of these elements during fluid flow through the rock (e.g., Harlov et al. 2002). The LREE are more easily mobilized than M/HREE during fluid-rock interactions and show greater stability as chloride or fluoride complexes.

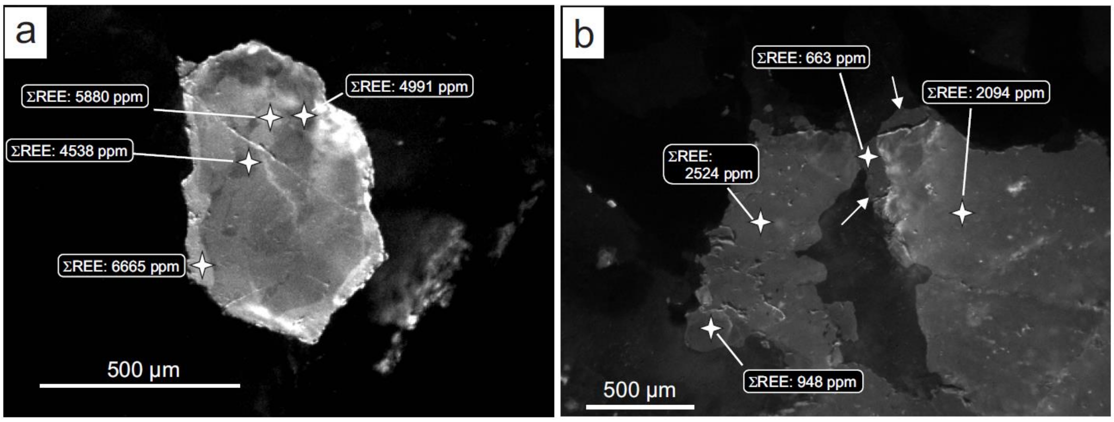


Figure 12. Cathodoluminescence photomicrographs of the Siilinjärvi fenites. Spectral CL (Nd3+ emission filtered at 880 nm) in (a) and (b). The four-pointed stars represent the spots where EPMA and LA-ICPMS analyses were performed. Related REE content is indicated in a black box. (a) Zoned apatite crystals with a blue-violet CL core and green CL rim in a pyroxene-rich fenite (sample Si4); textures suggest the partial replacement of the early-formed (violet-luminescent) grain by an apatite with stronger Nd-activation; (b) Closely-packed cluster of apatite crystals in a pyroxene-rich fenite (sample Si5); apatite overgrowth (indicated by arrows) shows a dark blue-greenish luminescence that is characterized by a decrease in Nd-activation

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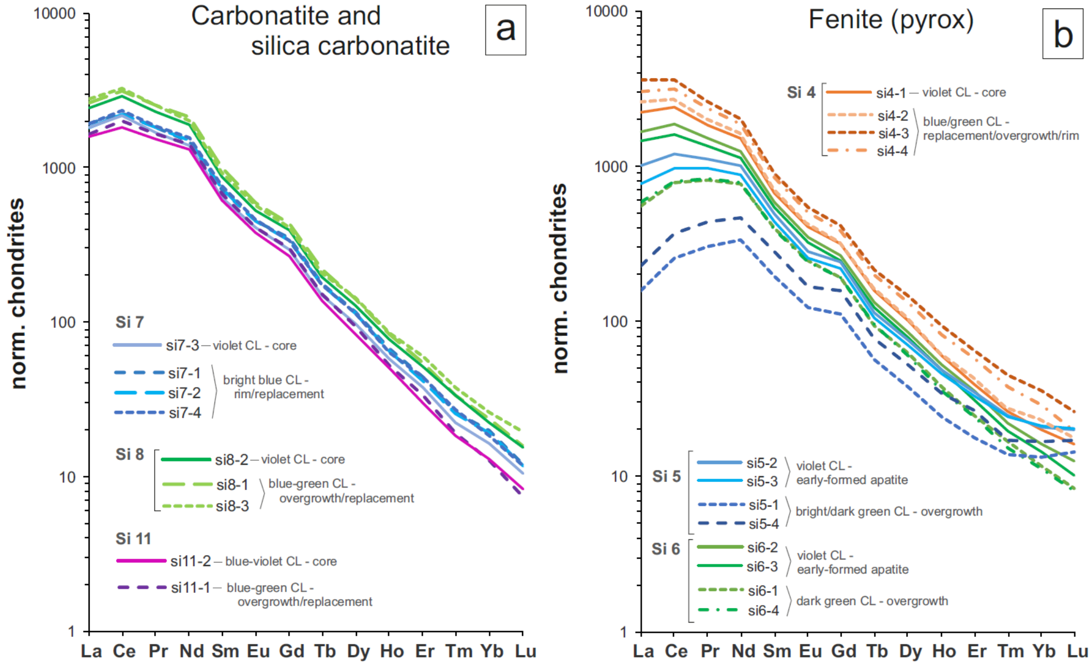

Figure 13. Selected representative REE patterns of apatite in different rock types of the Siilinjärvi Complex; (a) carbonatite and silica carbonatite and (b) pyroxene-rich fenite; REE patterns are normalized to chondrite values from McDonough and Sun (1995)

The estimation of the ore reserves at Siilinjärvi as per January 2014 was 234 Mt at an average grade of 4 wt% P_2O_5. Almost all the rocks of the glimmerite-carbonatite series can be considered economic for apatite exploitation (O'Brien et al. 2015). The analyses performed in the frame of this study confirm the enrichment in phosphate of these rocks ($2.32<P_2O_5<34.18$ wt%), apart from the carbonate glimmerite that contains only 0.23 wt% P_2O_5. In the Siilinjärvi mine, fenites are stockpiled separately (O'Brien et al. 2015), though some of these rocks show a promising phosphate content (two samples at 2.4 and 2.9 wt% P_2O_5), close to the average grade of the rocks that are currently mined. In the rocks pertaining to the glimmerite-carbonatite series or in fenites, the REE content of the rocks correlates well with their P_2O_5 concentration (Fig. 14). These correlations can be used to roughly estimate the REE reserves at Siilinjärvi. Based on the latter and on an average content of 4 wt% P_2O_5 in the rocks exploited (O'Brien et al. 2015), two average hypothetical REE contents were calculated, depending on the correlation used: (i) 576 ppm, using the equation based on all rock types (Fig. 14), and (ii) 697 ppm using the equation considering only the rocks currently mined as phosphate (i.e. the glimmerite-carbonatite series; Fig. 14). As a reserve of roughly 200 Mt remains to be exploited, the REE reserve should approximate ~133,000 t of Total Rare Earth Oxide (TREO) (using an average grade of 576 ppm) or ~161,000 t of TREO (using an average grade of 697 ppm) in the phosphate deposit. A large part of the REE must be present in apatite. Apatite from the glimmerite-carbonatite series has indeed high total REE contents (3195 - 6665 ppm). Similar trends are observed for apatite from several studied fenite samples, in which apatite exhibits REE and LREE enrichment (ΣREE = 3835 – 6665 ppm; LaN/YbN = 97 – 200). Apatite in other fenite samples is generally less rich in REE and LREE (LaN/YbN = 12-103; ΣREE =663-4567). The exploitation of REE as a by-product of the apatite could be interesting at Siilinjärvi, and probably in other alkaline complexes as well.

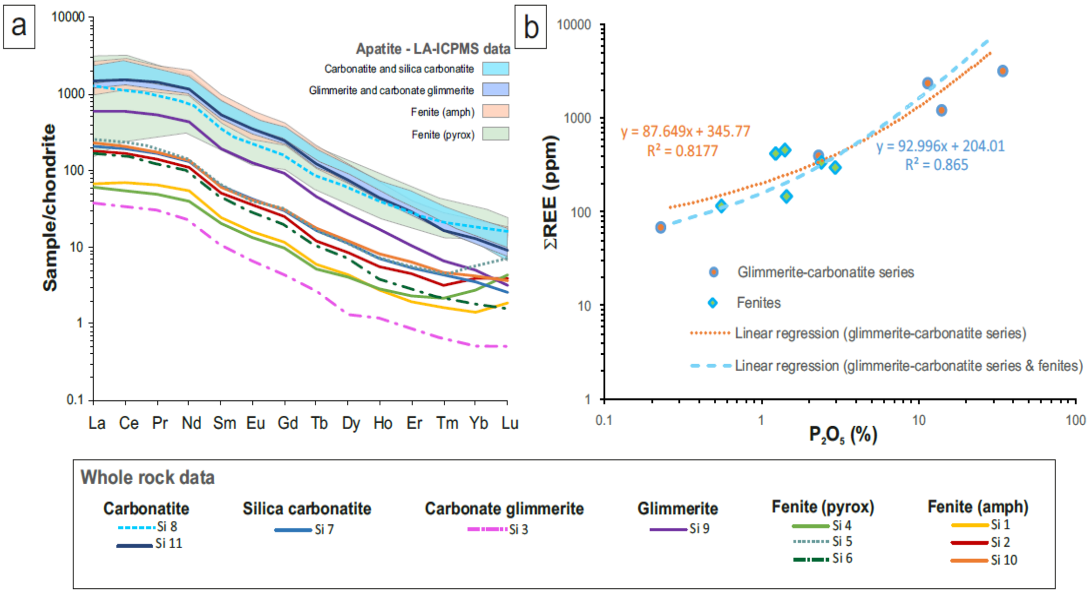

Figure14. (a) REE patterns for whole rock data of the Siilinjärvi rocks. REE patterns of apatite (LA-ICPMS data) are given for comparison. Data are normalized to chondrites (McDonough and Sun, 1995), (b) correlation for whole rock analyses between total REE content and P_2O_5 content

This study also shows that spectroscopic methods (LIBS, cathodoluminescence, Raman spectroscopy) constitute powerful and inexpensive tools for exploration. They bring crucial information about mineralization events, give clues regarding enrichment in REE of apatite, enable fast qualitative assessments of the REE enrichment in apatite, with some insight into (semi)-quantification (Fig. 15).

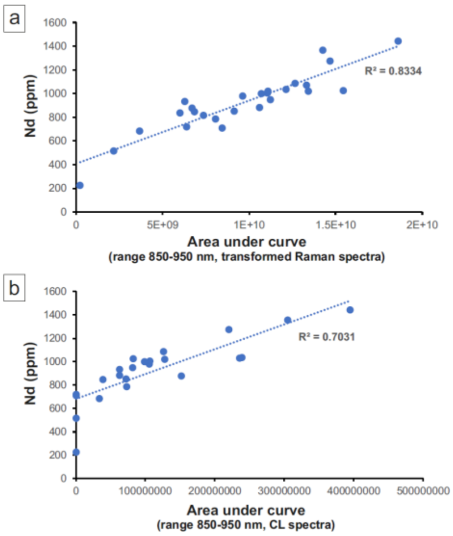

Figure 15. Correlation between Nd content and area under curve between 850 and 950 nm for (a) transformed Raman spectra (Raman shift converted into wavelength) and (b) CL spectra

4.3. Cambrian-Ordovician phosphorites in Estonia

The presence of phosphatised inarticulated brachiopod coquinas in natural outcrops along the steer Baltic Clint cliff, bordering the southern coast of the Gulf of Finland, was known already in the middle of 19th century. Commercial mining of shelly phosphorites was first commenced in the beginning of 1920^{ies} at Ülgase (near Maardu), about 25 km east of Tallinn. Phosphate rock from the Maardu deposit was beneficiated and the finely-ground concentrate was then either used directly as a soil conditioner or processed further for phosphate fertilisers. The Maardu phosphorite deposit was exhausted by the end of 1980ies.

The sedimentary phosphorite deposits in northern Estonia are located in the Baltic Shelly Phosphorite Basin which which extends as a narrow (30–40 km) east-westward strip from Tallinn area to the southern shore of Lake Ladoga in northwestern Russia (a distance about 400 kilometres). The phosphorites are composed of shell accumulations of inarticulated brachiopods who lived in the Furongian–Tremadocian age (about 480–490 million years ago) in sandy tidal flat areas of the high-latitude Paleobaltic Sea.

Lithostratigraphically, the phosphatised, brachiopod-bearing, light-yellowish to dark-grey quartzose (Fig. 16), variably lithified sandstones and siltsones form the Kallavere Formation in Estonia, whereas in the Leningrad Oblast of NW Russia this lithostratigraphic interval is known as the Tosna Formation. The Kallavere phosphate-bearing siliciclastics are overlain by the Tremadocian metallifeous black shales of the Türisalu Formation. The lower contact of the Kallavere Formation with the underlying Tiskre Formation sandstones of the Cambrian Stage 3 represents a hiatus in sedimentation, lasting at least 20 million years.

Quartz is the most abundant (up to 90%) mineral and the principal gangue mineral in Estonian phosphorites, followed by carbonate-fluorapatite. The other minor components in Estonian phosphorites are dolomite, calcite, pyrite, glauconite, ferrous hydroxides, clay minerals and feldspars.

As for chemical composition, the Estonian phosphorites have considerably lower levels of environmentally harmful elements like U (< 60 ppm) and Cd (<1 ppm) compared to the phosphorites from North African deposits which at present are the major source material for fertiliser industry in Europe. Although only few samples have been analysed so far for rare earth element contents, the first analytical results have shown considerable enrichment of REEs (total REE content varies between 400–1300 ppm). In case further studies confirm enrichment in REEs, then the Estonian phosphorites can be considered as an economically attractive multisource CRM commodity – a major raw material for fertiliser industry coupled with potential for REE extraction.

The biogenic phosphorites of the Baltic Phosphate Basin are shell accumulations of inarticulated brachiopods in which the phosphatised shell debris content varies between 5–90% (Fig. 16). Carbonate-fluorapatite is the major mineral of the phosphatised brachiopod shells. The brachiopod shells may contain up to 36% P_2O_5, however the carbonate-fluorapatite content may be highly variable even within single shells due to the variable share of the original bioapatite and diagenetically formed apatite.

Figure 16. Phosphorite sample from the Iru locality (Estonia)

Large-scale geological exploration drillings in northern and north-central Estonia in 1960–1970ies, led to the discoveries of several large sedimentary phosphorite deposits (Toolse, Rakvere and Aseri) in northern Estonia. These three phosphorite deposits have been historically explored by several geological drilling campaigns. The primary purpose of the historical phosphorite drilling campaigns, which altogether yielded several thousand drill cores, was to determine the amount and quality of sedimentary phosphorite rock for setting up the fertiliser industry in this region. It should be pointed that the drilling network in different drilling campaigns was different and it has not been uniform even within a single deposit. Besides geological and geochemical investigations, the beneficiation and wet acid production technological studies were accomplished as well. However, it should be noted that the reported data of historical phosphorite exploration campaigns do not directly conform with CRIRSCO standards and therefore the historically calculated phosphate rock resources need a verification by new drillings. The historical phosphate rock resource data given in this report should therefore be considered as provisional. One of major complications, influencing resource calculations of shelly phosphate resources is that the lensoidal phosphate debris accumulations (alternating with barren sandstones and siltstones) may be spatially highly variable.

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The Toolse, Rakvere and Aseri phosphorite deposits (Fig. 17) were historically erected and delineated by 4% P_2O_5 cut-off criterion. Based on currently known information (geological setting, socio-economic development possibilities, environmental restrictions, etc), the Toolse and Rakvere phoshorite deposits can be considered of having a highest economic potential for further detailed studies. The development of both deposits is hindered at the moment due to imposed environmental restrictions.

Figure 17. Location of the Toolse (T), Rakvere (R) and Aseri (A) phosphorite deposits in northern Estonia (map: Estonian Land Board)

The Toolse phosphorite deposit covers an area of about 110 km^2. The phosphate rock bed of mineable interest varies between 1–4 m and is covered by 10–40 m thick overburden of mostly carbonate rocks. Average P_2O_5 content is about 10%, but the maximum P_2O_5 values may reach over 15%. The average chemical composition for commercial bed is: SiO_2 (71%), CaO (14%), P_2O_5, (10%), FeO (0.7%) and Al_2O_3 (0.6%). A few geochemical data are available on rare earth elements, indicating that T_{REE} content may reach up to 1800 ppm, with enrichment in MREE (Fig. 18). The resource is estimated 646 million tons of phosphate rock with average grade of 9% P_2O_5 in area of 109 km^2. The resource estimate can be considered as 'Indicated' to 'Measured resource' by CRIRSCO code.

The Rakvere phosphorite deposit, with an area 140 km^2, is located southwards of the Toolse deposit. The phosphate bed overburden at the Rakvere deposit is thicker than in the Toolse deposit – ranging between 60 –110 meters. The average P_2O_5 content in the mineable bed complexes of the Kallavere Formation is 13%, but the maximum values in some coquina beds may exceed 20%. The average chemical composition of the Rakvere deposit phosphorites is SiO_2 (57%), CaO (21%), P_2O_5, (13%), FeO (0.3%) and Al_2O_3 (0.6%). The resource is estimated 1 938 million tons of phosphate rock with average grade of 13% P_2O_5 in area of 140 km^2. The resource estimate for the Rakvere deposit can be considered as 'indicated' to 'Measured resource' by CRIRSCO code. In addition, there is low confidence level estimate 8,4 billion tons of ore in surrounding area of 826 km^2. This resource estimate can be considered as 'Exploration Result' by CRIRSCO code.

The Geological Survey of Estonia has commenced this year a project to revise the data of historically explored Furongian–Tremadocian phosphorites and black shales. This project focusses on digitising the available drill hole data as well as on drilling new drill holes within the limits of the Rakvere, Toolse and Aseri deposits. Main objectives of this drill program will be: to validate the available geological-geochemical data, to obtain geotechnical data on target rocks and overburden, and to analyse new drill cores for the rare earth elements content and spatial distribution.

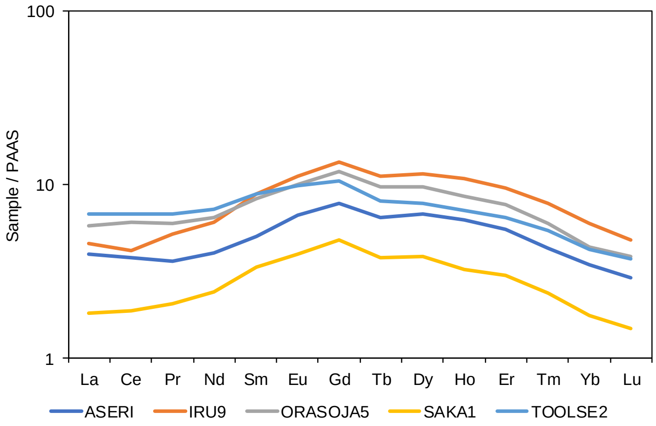

Figure 18. Shale-normalised REE concentrations of bulk phosphate samples. PAAS values from McLennan (1989)

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4.4. Cretaceous phosphorite in the Mons Basin (Belgium) (Jacquemin 2020)

The Ciply Phosphatic Chalk (CPC) in the Mons basin (Belgium) has been exploited for its enrichment in phosphorus in the early part of the twentieth century to produce fertilisers. It represents a facies developed during Cretaceous times in the Mons Basin, which could be regarded as a gulf at the north-eastern margin of the Paris Basin Sea (Robaszynski and Martin 1988). The Mons Basin is a subsiding area where up to 300 m thick sediments accumulated during the Meso-Cenozoic. Subsidence mechanisms are attributed to evaporite dissolution (Visean evaporites have been discovered in the borehole of Saint-Ghislain; Dejonghe et al. 1976). In the Ciply area, the CPC occurs as a lens lying on the southern flank of a syncline and dipping to the north (Fig. 19). Its thickness varies from several meters at the southern border to a little more than 70 m at the axis of the lens.

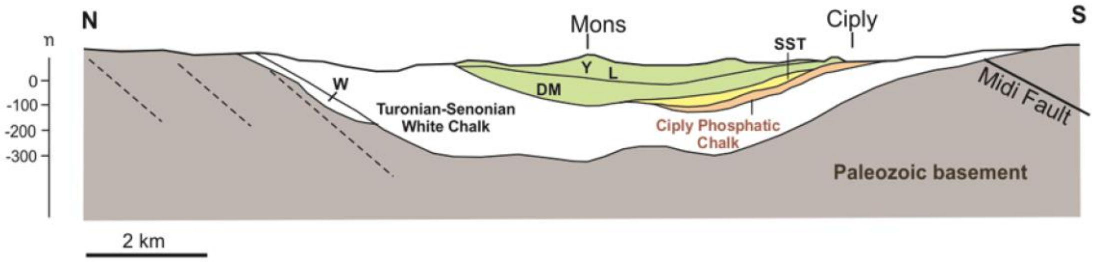

Figure 19. North-south geological section of the Mons Basin. W: Wealden facies; SST: Saint-Symphorien Tuffeau; DM: Danian and Selandian (former Montian); L: Thanetian (former Landenian); Y: Ypresian. From Robaszynski and Martin (1988)

The samples analysed came from two different localities. Most of them originated from the Hyon borehole that was drilled in 1985. Out of the entire sequence, two-thirds could be sampled, which represent approximately 50 m of phosphatic chalk. The second site is the La Malogne underground quarry, which is located on the border of the Mons Basin to the west. In this quarry, kilometres of galleries are spreading through the Maastrichtian phosphatic chalk. A notable feature at La Malogne is the presence of cryptokarsts filled with "phosphatic sand". The latter results from the selective dissolution of the carbonated part of the CPC and the relative enrichment in insoluble phosphate.

The phosphatic chalk of the Mons basin is not a phosphorite sensu stricto, which is defined as containing more than 18 % P_2O_5. It is a light brown phosphatic calcarenite with P_2O_5 grades around 10% (Robaszynski and Martin 1988). The colour of the rock is directly linked to the abundance of phosphatic particles, varying from a white-yellow colour for samples with low contents of phosphatic particles, to a brownish colour for samples rich in phosphate. Phosphate grains comprise (i) peloids, which are dominant and can record several

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phospatization events (Fig. 20a,b), (ii) ooids that can have a bacterial origin (Fig. 20c), (iii) fossil tests filled by CFA and (iv) bone fragments (Fig. 20d).

Regarding its chemistry, The P_2O_5 concentration ranges from 0.15 to 6.7 % for the CPC in the Hyon borehole. The La Malogne underground quarry has similar abundances with 3.7 % for the phosphatic calcarenite, 5.8 % for the conglomeratic bed, 0.81 % for the hardground, and 11 % for the 'phosphatic sands'. The CPC possess an average ΣREE of 350 ppm for the Hyon borehole (63 to 696 ppm), the REE being hosted in francolite (a carbonate-fluorapatite (CFA) [$Ca_5(PO_4,CO_3)_3F$]) (as demonstrated by the positive correlation between the total REE content and P_2O_5 in Fig. 21). Their shale-normalised patterns are similar to other Cretaceous phosphate deposits, which typically display negative Ce-anomaly. The latter suggests that a part of the phosphatization occurred under an oxidizing environment.

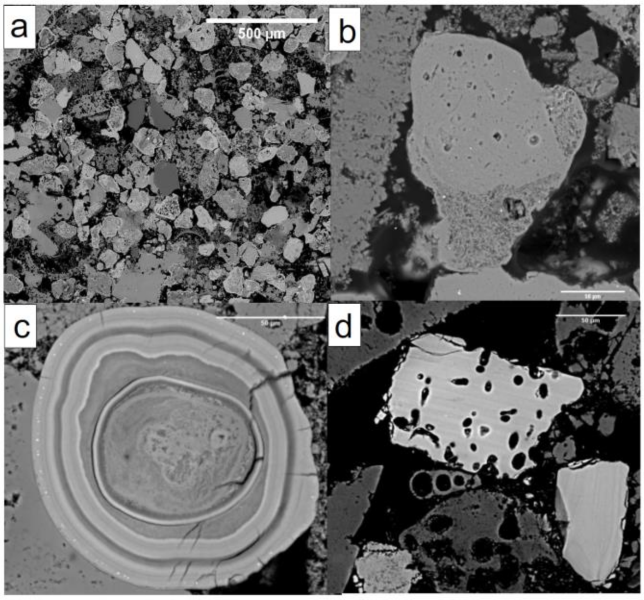

Figure 20. SEM - backscattered electron - images. (a) Representative view of the enriched part of the Ciply Phosphatic Chalk. The majority of the phosphatic grains are composed of peloids, which show different degrees of phosphatisation. (b) Peloids that attest that the previously formed phosphatic sediment was reworked and possibly underwent multi-stage phosphatisation and reworking. The right-hand side image suggests that a previously formed phosphatic was reworked and deposited. Then the sediment in which it deposited underwent a phosphatisation event. (c) Phosphatic ooids. The nucleus is essentially phosphatic. Its origin is unknown, though it may have a bacterial origin suggested by the presence of microspheres. (d) Bioeroded bone fragments

More precisely, the phosphatic calcarenite of the Mons Basin was probably formed under the influence of minor upwelling systems that brought nutrients, such as phosphorus and silicon, to the shallow epicontinental sea of the Mons Basin during transgressive/regressive events. The formation of the phosphate is linked to an overall period of eustatic sea-level highstand, with reworking during subsequent regressive conditions. Phosphogenesis occurred in the sediment mainly in the form of interparticle carbonate-fluorapatite cement. Microbial breakdown of organic matter along with Fe-redox cycling are the likely processes of phosphorus pore water enrichment. The primary phosphatic sediment was reworked in the form of phosintraclasts. Several phosphatisation and reworking events took place. The rare earth elements were incorporated in CFA during phosphogenesis. The source of REE in phosphorites is most likely seawater and the REE patterns recorded in the phosphatic chalk should retain to some extent the primary signature of seawater at the time.

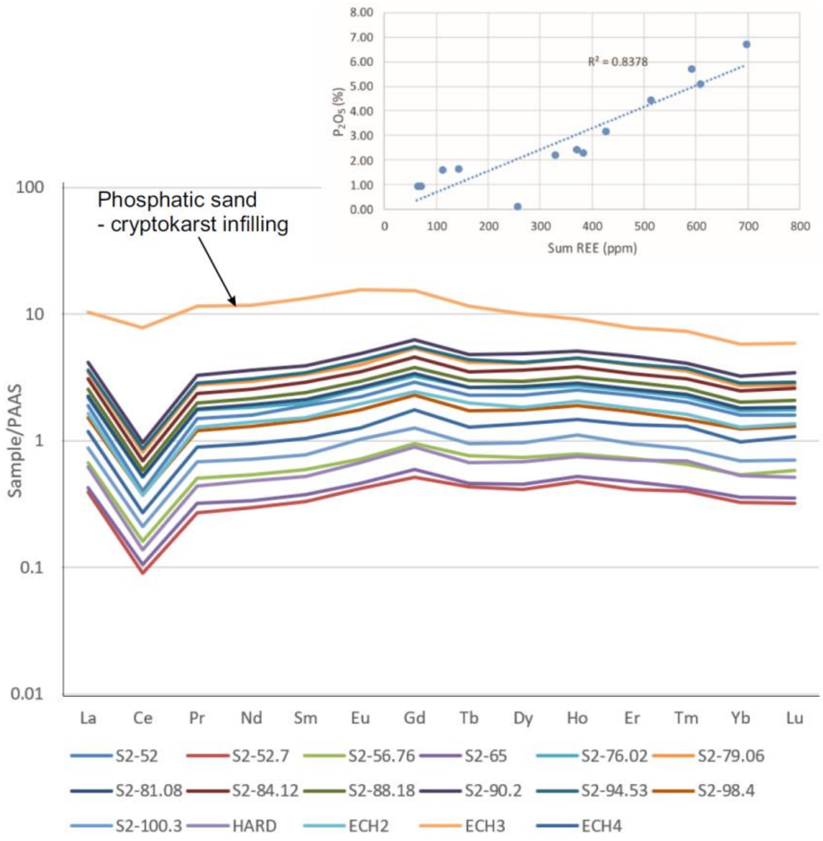

Figure 21. Shale-normalised REEs patterns of the samples from the Hyon borehole. Regardless of the REE abundances, all patterns are similar except that of the phosphatic sands filling the cryprokarsts at La Malogne. The insert shows the positive correlation between the REE and the phosphate content

Regarding the economic potential of the Ciply Phosphatic Chalk, Robaszynski and Martin (1988) estimated its resources at 960 million tons @ 5-10 % P_2O_5. By taking 5 % P_2O_5, around 47 million tons could be retrieved from the Mons Basin while 96 million tons could be recovered by taking 10 % as the average value.

The REE contents average is around 350 ppm for the Hyon borehole. The REE as considered as being part of apatite structure, considering the good correlation between the total REE content and P (Fig. 21). By taking 350 ppm as the average value of the Mons Basin, the total REE that could be recovered amount to approximately 33 600 tons of REE based on the estimation of the resources of Robaszynski and Martin (1988). For the LREE, taking the average of the Hyon borehole, 19 584 tons are potentially retrievable while for the HREE, taking the Hyon borehole average, 14 112 tons.

4.5. Cretaceous phosphorites in the Bohemian Massif (Czech Republic)

Phosphate occurrences have been reported in the Mid-Cretaceous sediments of the Bohemian Basin (BCB) of the Czech Republic. The BCB (Cenomanian–Santonian) is an intracontinental depositional depression that formed by the reactivation of a fault system in the Variscan basement of the Bohemian Massif in the Mid-Cretaceous and acted as a seaway between the North Sea and the Tethys Ocean. The Cenomanian – Lower Turonian sequence in the BCB is represented by the Peruc-Korycany Formation (Cenomanian) and the Bílá Hora Formation (Lower Turonian). The Middle – Upper Turonian sequence is represented by the Jizera and Teplice formations.

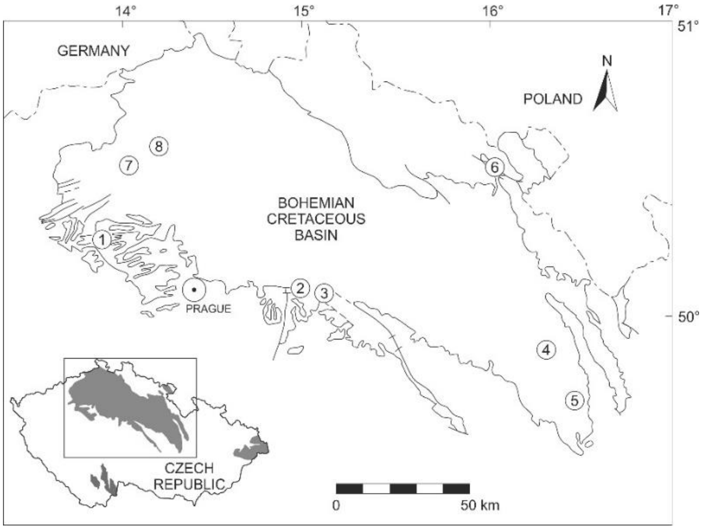

Figure 22. Map of the Bohemian Cretaceous Basin showing location of the Cenomanian–Turonian phosphate-bearing sections: 1) Pecínov quarry; 2) Plaňany quarry; 3) Nová Ves quarry;, 4) Česká Třebová "Třebovské stěny", 5) Březinka – Chvalka, 6) Rtyně v Podkrkonoší, 7) Úpohlavy quarry, 8) Býčkovice road-cut.

The Early Turonian phosphate mineralization is most persistent in the BCB and extends for about 200 km in a NW–SE direction along the southern margins of the BCB (Fig. 22). It is present as phosphate nodules in the Pecínov quarry, accumulation of phosphatized bivalve shells, skeletal remains, shark teeth and phosphatized sponges in the Plaňany and Nová Ves quarries and as phosphatic and bioturbated hardground in the Březinka – Chvalka and Česká Třebová sections (Fig. 23). The phosphate mineralization in these sections is associated with stratigraphic condensation, glauconite, omission surface, bioturbation and hardgrounds. The phosphogenic event marks the onset of the Early Turonian global eustatic transgression in the BCB. The phosphate horizon at the base of the Bílá Hora Formation is thin, usually < 1 m, and the lithology of the host rocks consists of black mudstones, siltstones, quartz-sandstone, bioturbated phosphatic and silty mudstone hardgrounds and/or heterogeneous mixture of bioclasts and intraclasts. With the exception of phosphatic hardgrounds, the other phosphate components in this part of the sequence show evidence of reworking.

The basal part of the Teplice Formation (Upper Turonian) is marked by two remarkable beds of phosphatic marl, holding phosphatized coprolites, sponges, skeletal remains and shell fragments. These basal phosphate-bearing glauconitic marl horizons rarely exceed 0.5m in thickness at the Úpohlavy quarry and show evidence of sequence condensation.

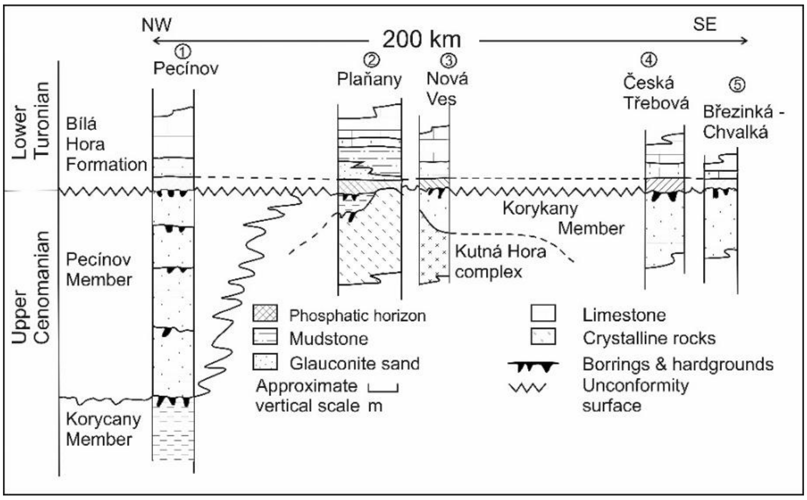

Figure 23 Stratigraphic correlation of the investigated Early Turonian phosphate occurrences of the BCB (See Fig. 22 for geographic location).

In these phosphatic horizons, the micro phosphate components are present as peloids, skeletal grains, fish teeth, intraclasts, sponges and as cementing material, mostly associated with glauconite in siliciclastic sediments. The phosphate in the nodules and in the cement appears as cryptocrystalline brown material with abundant pyrite, silt-size quartz (<0.1mm) and glauconite (~0.1mm) grains. Phosphatized bivalve shell fragments, brown, up to 1mm long, phosphatic angular skeletal fragments, 0.1 – 0.2 mm in size and phosphatized sponges are common. Phosphate peloids and phosphate intraclasts are scarce. Phosphate cement is found in sandstone and in the hardgrounds. Phosphate coprolites contain relatively less mineral impurities, but richer in organic matter, and often show microbial structures of <3 µm in size.

These various phosphate components present an enrichment in P_2O_5 ranging from 19.6 wt % to 39 wt. % P_2O_5. Total REE concentration in the extracted phosphate samples reported by Al-Bassam and Magna (2018) ranges from 631 to 1132 ppm in the phosphate nodules and 398 to 874 ppm in the phosphate coprolites. The analysis of REE (La, Ce and Nd) in the new localities show elevated concentrations in the phosphate samples of the Česká Třebová phosphate-bearing hardground (samples no. 60A and 70) of 1151 and 1525 ppm respectively compared to $\sum$REE of 316 and 488 ppm in the phosphate samples from the hardground at Březinka – Chvalka (samples 80A and 80B respectively), in contrast to $\sum$REE of mostly < 200 ppm in the associated siliciclastic samples.

The Ce anomaly and Ce/La values found in the Early Turonian phosphates of the BCB suggest initial phosphate deposition in restricted environment below sediment-water interface. The REE pattern of distribution in the Early Turonian phosphate components show enrichment in the light REE (LREE) and in some samples a hump (bell-shape) in the middle REE (MREE) (Fig. 24). This suggests deposition in suboxic conditions below sediment-water interface. The Upper

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Turonian coprolitic phosphates at the base of the Teplice Formation mark another phosphogenic event that can be related to condensed sedimentation and low sea-level stand before the following transgressive cycle and the subsequent elevation of the sea-level (Vodrážka et al. 2009). Phosphatisation of the initial coprolite fecal material took place under variable redox conditions; but more oxic than that of the phosphate nodules and other Early Turonian phosphates.

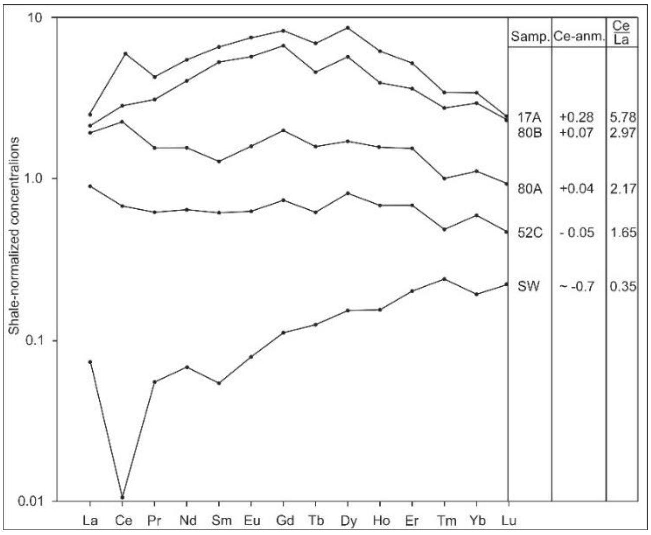

Figure 14. Rare earth elements distribution patterns in selected Early Turonian phosphate samples compared to seawater pattern. Sample 17A: phosphate nodule (Pecínov) (data from Al-Bassam and Magna 2018), Samples 80A & 80B: phosphate tube-fill (Březinka – Chvalka) (new results), Sample 52C: phosphatized carbonate clasts (Nová Ves) (data from Al-Bassam and Magna 2018), SW: seawater

Regarding the potential of the phosphate mineralization in the BCB, despite the consistency of the phosphogenic event during the Early Turonian, the investigated occurrences are present in thin horizons and can not be categorized as deposits in the economic sense, but certainly they are occurrences of great scientific significance. Most of the extracted phosphate components contain anomalous concentrations of REE and some other critical elements, but they represent individual cases (Al-Bassam and Magna 2018). The phosphate-bearing horizons, documented untill now in the Mid-Cretaceous sequences of the BCB, are mostly < 1 m, in all the sampled localities and the bulk rock grade is generally low, not exceeding 5 wt. % P_2O_5. The phosphate components, mostly with >25 wt. % P_2O_5, are diluted by various lithologies of the host rocks, including mudstones, sandstones and carbonates. Selective open cast mining of these phosphates is economically not feasible due to the high stripping ratio and low P_2O_5 grade, but when the country rocks are excavated for other purposes, such as raw material for cement industry (e.g., Pecinov quarry), special attention may be paid to the Early Turonian phosphates (base of Bílá Hora Formation) during excavation. Nevertheless, the Early Turonian phosphate-bearing horizon can be recommended as the main exploration target for marine sedimentary phosphorites in the BCB. However, the potential of discovering sizable high grade phosphate deposits of economic importance as source of REE and/or other valuable critical metals is not so encouraging.

4.6. Tertiary phosphorites in the Salento Peninsula (Italy)

This study focuses on the phosphate-rich deposits in the Mio-Pliocene sedimentary succession in the Salento area (Puglia region, South of Italy). The aim of this study was to characterize the content in P of different units and the REE content for see the feasibility of future exploitation. The Miocene was an epoch of preferential phosphogenesis and accumulation of phosphate-rich deposits. Miocene phosphorites are widespread (Föllmi et al. 2015). In total five main areas were studied: Punta Ristola, Baia del Ciolo, Cava Cursi, Melpignano and Lecce (Fig.25).

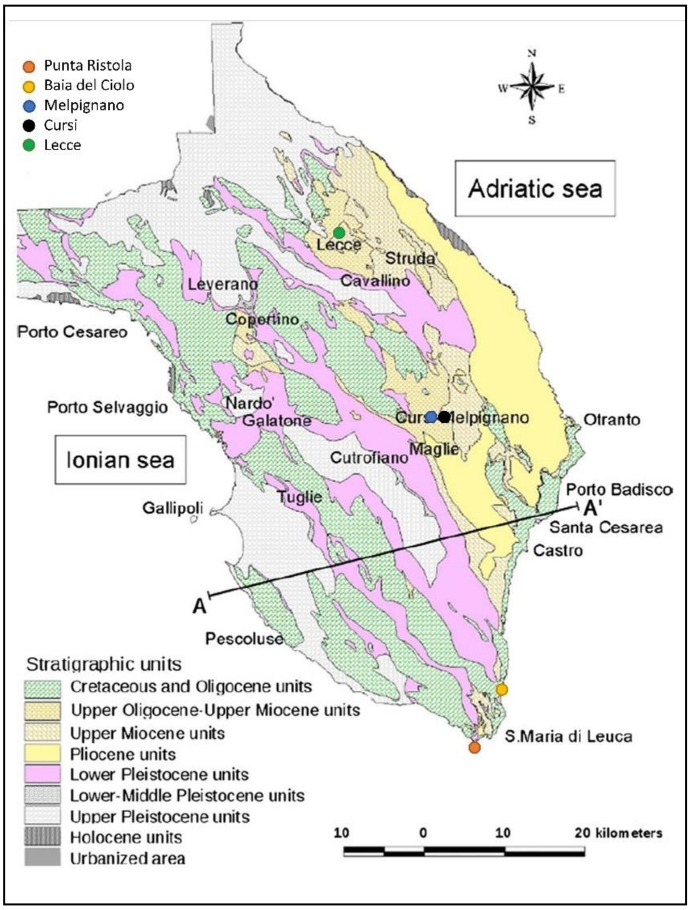

Figure 25. Geological map of Salento (from (Sansò et al. 2015)) and the general location of the investigated deposits

The Oligocene deposits includes two units: the Castro Limestone overlaid by the Porto Badisco Calcarenite. The Novaglie formation is of Early Messinian age and belongs to the Late Miocene shallow-water carbonates (Bosellini et al. 1999; Föllmi et al. 2015). In the interval between the Chattian and Messinian platform carbonates it can be found a thin interval, between 10-15 cm thick, of deep-water, outer-shelf sediments, preserved also as glauconite and phosphate-rich deposit. This layer appears in the Baia del Ciolo section as a fossiliferous phosphatic hardground including phosphatized pebbles and particles (Livello ad Aturia) (Delle Rose 2001; Föllmi et al. 2015) superimposing the Chattian platform carbonates and overlain by Messinian carbonates.

The Pietra Leccese formation of Late Burdigalian to Early Messinian age (Föllmi et al. 2015) superimpose in the area of Cursi a succession of Cretaceous deposit. The Cretaceous consists mostly of dolomitic limestones. The Pietra Leccese is a yellowish biomicrite rich in foraminifera, containing at least two levels enriched in phosphatic and glauconitic particles (Föllmi et al. 2015; Mazzei et al. 2009 and references therin). This unit is the most extensive tertiary formation and it cover an area of about 150 km^2. A notable feature of the Pietra Leccese is the presence of pockets (cryptokarst?) enriched in phosphates and Fe oxides (Fig. 26). The origin of these pockets needs to be further studied. Overlying the Pietra Leccese, there is a sandy, fossiliferous limestones and yellowish sands, with subordinates shale, of Pliocene to Quaternary age (Notholt et al. 1979).

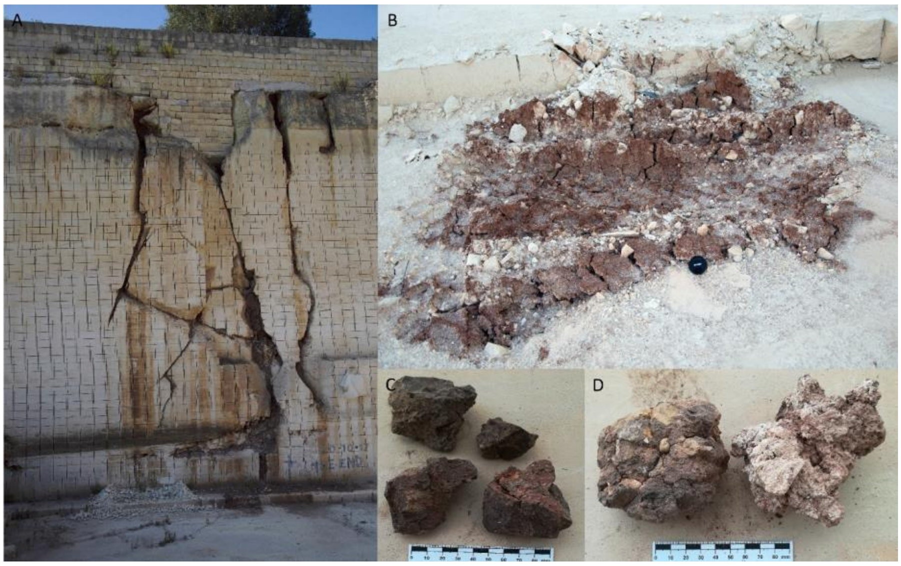

Figure 26. (A) Wall of a Pietra Leccese quarry in Cursi. The fractures are hosting the pocket rich in phosphates and Fe oxides. (B) Closer view of a P-rich pocket. The samples C1 (C) and C2 (D) belongs to one of those pockets

Along the Adriatic cost of Salento sedimentary phosphate rock can then be found in the form of phosphatic nodules and concretions and phosphatic limestones. Nodular phosphate beds (Upper Pliocene) occur at various localities in the southern part of the Salentino peninsula. Phosphate rock from the Capo Santa Maria di Leuca (Punta Ristola) in phosphatic conglomerate from 50 cm to 1 m thick occurs near the top of the transgressive Pliocene Calcareniti di Salento formation (Notholt et al. 1979). In all the Miocene formation of the peninsula it has been recorded phosphate in variable concentration, making the Pietra Leccese the best target for this study. The Miocene Salento occurrences were associated to an episode of profound deepening and the installation of pelagic conditions on the Salento platform. The phosphogenesis and glauconite precipitation might have been facilitate by the generation of a current-dominated depositional system during the upwelling of a westbound current system (Föllmi et al. 2015)

The mineralogical and geochemical data were acquired through scanning Electron Microscopy (SEM), EDX, X-ray diffraction (XRD), Raman spectroscopy and whole rock chemistry analysis. The data obtained are consistent with those provided by Föllmi et al. (2015) and Notholt et al. (1979) regarding the potential in P of the phosphate formations occurring in the Salento

Peninsula. The Pietra Leccese show a low P grade (1-4% P_2O_5); phosphate nodule formations at Punta Ristola and Baia del Ciolo are in the range of 6.32-23% P_2O_5 (with an average of 16%). The P-rich pockets have a relatively low grade (2-6%), further analysis and study are needed to better understand how this pocket are formed and what is the primary source of the P-enrichment. The ∑REE content varies significantly depending on the formation, from 16 to 429 ppm. It is the lowest in nodular phosphate formations and the highest in the Pietra Leccese.

The Pietra Leccese formation extend in the Salento peninsula for ~150 km^2 with an average thickness in the Lecce area of 80 m. It commonly shows a relatively low grade (3–4% P_2O_5; Notholt et al. 1979). Considering the totality of the formation with a 3.5% P_2O_5 grade, the tonnage is of ~600 million tons. Regarding the REE, based on the correlation illustrated in figure 27 (leading to an average content of 170 ppm REE) and with a mean content of 3.5% P_2O_5, one could recover 102 000 tonnes of REE. Of course, these calculations about the potential of P and REE in the area are theoretical and one must consider that the Pietra Leccese is used as the main local building stone. Notholt et al. (1979) have also reported 60 million tonnes of phosphatic limestone, with a content of 7–8 % P_2O_5. With the same way of reasoning, ~22 000 tonnes of REE could be recovered based on a mean content of 7.5 % P_2O_5 and 370 ppm REE. Finally, Notholt et al. (1979) reported 10 million tonnes at grades in the range 10.5–20.5 % P_2O_5 of Upper Pliocene nodular phosphate deposits. The latter likely correspond to the Punta Ristola occurrence. Considering an average grade of 38 ppm of ΣREE for a grade of 15% P_2O_5, based on the correlation observed for the Punta Ristola samples (Fig. 27), then one could recover 380 tonnes of REE.

The phosphate deposits of the Salento Peninsula could show promising potential regarding its REE content. Further studies are nevertheless necessary to well define the extend of the formation and its potential.

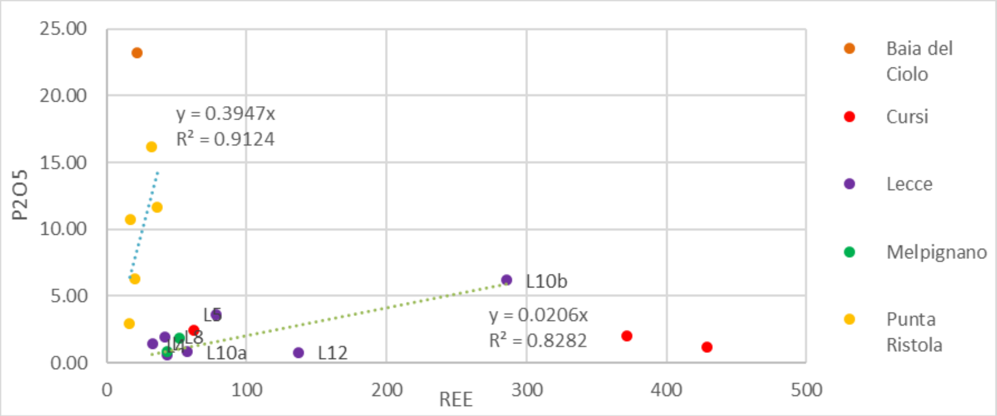

Figure 27. Plot total REE content (ppm) vs P_2O5 (%)

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4.7. Lower Paleozoic sedimentary phosphate mineralization associated with ironstones at Moncorvo (Portugal)

The Moncorvo ore deposit, located in the northern part of Portugal, is composed of six ore bodies that are: Cabeço da Mua, Vale de Porros, Carvalhosa, Santa Maria, Cotovia (Reboredo), Pedrada and Fraga de Apriscos (Fig. 28). This deposit is hosted in Lower Paleozoic sediments enriched in iron and deposited in a marine platform. It is dated as Ordovician. Deformation and low-grade metamorphism affected the sedimentary sequence during the Variscan Orogeny. The main mineralization is made of hematite (specularite and martite) and magnetite. Phosphorous minerals are lazulite - and its weathering products - and apatite were also observed. D'Orey (1999) describes" *initially a compact magnetite/quartzite layer, detrital in character (the magnetite occasionally showing chromite cores), was deposited by entrapment in near shore lagoons where rivers debouched, rather than in the open sea. This stage was followed by oscillating and transgressive shorelines which gave rise to breaks in sedimentation in combined river delta and shallow water marine environment where detrital material and fine iron oxide and clay suspensions were deposited in fluctuating environments. These events gave rise to layers of both magnetite (martite) and specularite intergrown with quartz, silicates and phosphates*."

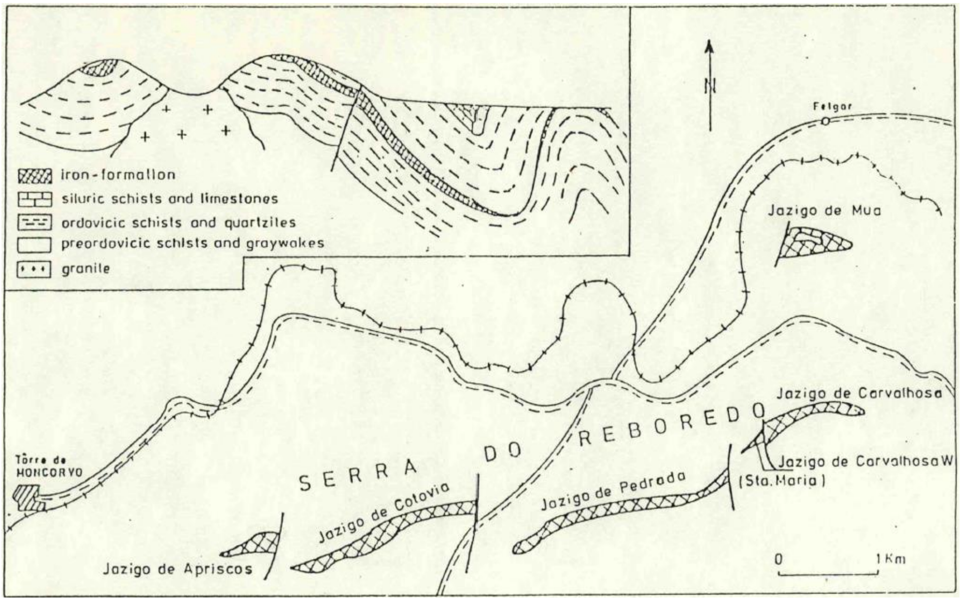

Figure 28. Geological map of the Moncorvo iron ore deposit (Ferrominas, 1978). Sampling was made in drillholes from Cotovia ore in Serra do Reboredo

In the Moncorvo ironstores, the phosphorous in the rocks is controlled by the iron considering that, in marine environment, phosphorous precipitates along with the iron oxi-hydroxides in colloidal forms. D'Orey (1999) shows that limonitic material has adsorbed substantial amounts of phosphorus. According to the feasibility study (MTI Ferro de Moncorvo 2015), martite occurs in the Reboredo ore until 90 m depth and bellow that, magnetite is about 10 to 35% abundant where apatite occurrence is also observed. Urbano (2017) observes that apatite is also abundant in the Felgueiras sector. Figueiras et al. (2015) in detailed petrographic and EPMA study of the phosphates present in the Mua, Carvalhosa and Reboredo ore bodies shows that phosphates are common phases in all these ores and that Fe(±Al,Mg,Mn)-bearing phosphates are the most abundant showing large chemical variability. The present mineral phases are mostly lazulite but also barbosalite and scorzalite and that by replacement of Fe^{3+} and Al^{3+} by REE other intermediate phases are present. Compositions close to rockbridgeite, occasionally enriched in Mg (replacing Fe^{2+}) and bearing REE traces (in Fe^{3+} positions), are also common; some analyses of this subset are relatively enriched in Mn (instead of Fe^{2+}), getting close to frondelite. Other hydrated phases such as gormanite and ludlamite are also present. Ca(±Fe,Mg,Al)-bearing phosphates are also frequent where apatite is the most common. Two different apatite species occur; the more REE-enriched variety is Ca-apatite withup to 4.87 Ca a.p.f.u (Figueiras et al. 2015)

For this study**,** and having in mind the previous studies, drillholes from the Cotovia (Reboredo) ore deposit were studied. The chemistry was investigated using pXRF and whole rock (wet chemistry) analyses, whereas mineralogical characterisation was undertaken using XRD and thorough microscopic observations. The thin sections will also serve as LA-ICPMS samples and for further EPMA analyses. The ore minerals observed in the thin sections are mostly hematite and magnetite. Magnetite occurs in anhedral masses or clusters that incorporate hematite crystals and sometimes Ti-bearing phases of which titanite (sphene) is the most common.

Preliminary geochemical studies show that the Cotovia ore contains up to 4.5 % P_2O_5, with an average value of 1% P_2O_5 on the analyzed samples. Regarding critical elements, the V content ranges from 95 to 695 ppm. The total REE content varies from 129 to 313 ppm, with an overall enrichment in heavy HREE of the ore ($0.14<(La/Yb)_N<1.1$), as observed in the PAAS-normalized REE patterns.

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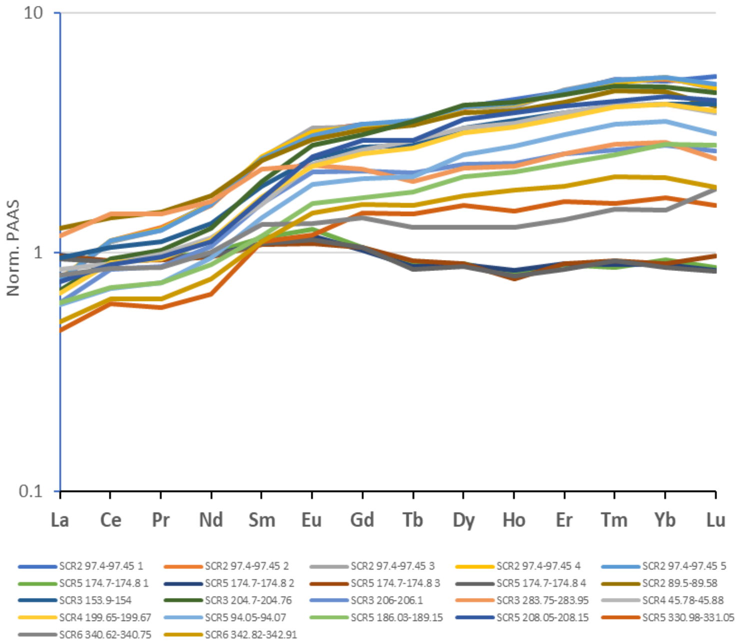

Figure 29. Shale-normalised REEs patterns (whole rock analyses) of the samples from Cotovia-Moncorvo. Normalization to the Post-Archean Australian Shales (PAAS; Condie 1993)

Most of the samples collected in the drillholes of Cotovia- Reboredo were classified as Fe-Sand samples probably related with a detritic origin. Nevertheless, the Ce anomaly (Ce/Ce*) vs. Nd diagram and the Ce anomaly vs. Y_{SN}/Ho_{SN} fall in a mixed diagenetic/hydrogenetic field. The representativity of the samples cannot indicate a general overview of the iron ores of Moncorvo in relation with its REE phosphate potential. However, with further analysis of the potential for REE accessed by LA-ICP-MS analysis and EPMA analysis, some conclusions may be taken. Therefore, the data obtained for Cotovia show that it is worth investigating further the deposit regarding its P, V and REE content. In addition, more analyses and a proper assessment of the reserves/resources in P should be done in the future.

4.8. Short synthesis regarding the potential of black shales hosting phosphorites

The Ordovician black shales hosting phosphorite deposits in the northern part of Estonia were investigated to assess their potential for CRM (Vind 2018). Comparable studies were led on the mudstones and other phosphate-bearing siliciclastic sediments in the Mid-Cretaceous sediments of the Bohemian Basin (BCB) of the Czech Republic.

The Estonian black shales is clearly of interest with future resource for several metals, as V, U, Mo, Pb and Zn. Preliminary assessment of the resources shows that 19.2 Mt MoO_3, 6.7 Mt U_3O_8 and 88 Mt V_2O_5 might exist in the total basin, of which only a fraction might be recoverable. Nevertheless, the black shale deposit occur under a shallow cover. Thus, they constitute an easy prospective area for further exploration (Vind 2018). The Geological Survey of Estonia has commenced in 2019 a project to revise the data of historically explored Furongian–Tremadocian phosphorites and black shales. This project focusses on digitising the available drill hole data as well as on drilling new drill holes within the limits of the Rakvere, Toolse and Aseri deposits. Main objectives of this drill program will be: to validate the available geological-geochemical data, to obtain geotechnical data on target phosphorite rocks and on overburden, and to analyse new drill cores for the rare earth elements content and their spatial distribution.

Regarding the phosphate-bearing siliciclastic sediments in the Mid-Cretaceous sediments of the Bohemian Basin (Czech Republic), the chemical analysis reported by Al-Bassam et al. (2019) for the mudstones and other phosphate-bearing siliciclastic sediments show that they generally contain lower concentration of most critical elements compared with Average Shale of Turekian and Wedepohle (1961). However, the glauconitic dark gray and black mudstones of the upper part of the Pecínov Member (Upper Cenomanian) and those of the lower part of the Bílá Hora Formation (Lower Turonian) in the Pecínov section might be interesting targets for Nb, Th, W and occasionally for REE, Y and U (Table 2).

The mudstones and siltstones hosting the phosphates generally contain lower concentrations of REE, Y and U; with the exception of sample 23A (phosphatic silty tube-fill from the Pecínov Member, Upper Cenomanian) which contains the highest REE concentration of 2496 ppm coupled with 864 ppm Y and 20.7 ppm U. Some samples in the mudstones of the Bílá Hora Formation (Lower Turonian) may be noticed for their elevated Y and U concentrations relative to other mudstone samples (Table 2), probably enhanced by the presence of minor quantities of apatite. Critical elements analysed in the siliciclasts samples of the new localities show lower concentrations of most trace elements compared to the black mudstones in the Pecinov section and to Average Shale of Turekian and Wedepohl (1961). Exception of this is sample 60B, collected from the hardground at Česká Třebová section, which contains high W concentration of 15 ppm (Table 2).

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Table 2. Concentration of critical elements in the Cenomanian and Turonian phosphate-bearing black mudstones at Pecínov quarry (Al-Bassam and Magna 2018; Al-Bassam et al. 2019) and siliciclastic hardground at Česká Třebová (sample 60B)

Elements (ppm)	**Cenomanian mudstones**			**Turonian mudstones**		
	Range (10 samples)	Mean	23A*	Range (8 samples)	Mean	60B
Nb	11.9 – 16.0	13.7	11.7	6.1 – 16.0	10.2	4.0
W	3.0 – 6.3	4.0	4.2	1.9 – 7.7	3.3	15.0
Th	10.5 – 17.8	12.0	22.1	5.9 – 12.6	9.3	2.5
Y	14.2 – 25.4	20.5	864	14.2 – 70.4	26.3	12.0
U	2.5 – 11.0	3.8	20.7	2.2 – 37.1	8.8	1.2
∑REE	116 – 149	123	2496	107 – 329	160	67

*****Contains 7 wt. % P_2O_5

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5. Conclusions and prospects

The studies carried out for this task “Detailed metallogenic studies of key phosphate deposits in Europe” result in a better knowledge of the phosphate deposits, their origin and associated potential for CRM. Hundreds of new whole-rock and LA-ICPMS analyses have been performed (see Annex 8). These data will be integrated into the GeoERA Information Platform.

Several studies provide new approximate numbers about resources in REE of phosphate deposits/district in Europe, as for the carbonatite-related Siilinjarvi deposit (Finland), the phosphatic chalk of the Mons basin (Belgium) and the Salento Peninsula (Italy).

In addition, interesting concentrations of some critical elements have been reported in the course of these studies (as in the Bohemian Cretaceous Basin, Czech Republic), paving the way for discovering new CRM (P and REE) occurrences not reported before.

Finally, new exploration – spectroscopic – tools were tested/developed to better characterize the phosphate mineralization and easily determine the distribution (and abundance) of REE in apatite and its host rock (see the study of the Siilinjarvi deposits).

The most striking results – by case study - are the following ones:

- In Norway, the Bjerkreim-Sokndal layered intrusion (BKSK) presents a well-known large low-grade resource of apatite, the interest of which is also found in the accompanying Fe-Ti-V mineralization. The Kodal deposit, the next largest deposit in the country, represents much smaller volumes than the BKSK. However, the grade in phosphate is higher. Apart from the Kodal deposit, recent field observations suggest that the process that led to Fe-Ti-P enrichment happened in several areas in the Larvik intrusion (LPC). Further investigation, including detailed geophysical survey, will help evaluate the potential for apatite resources in the rest of the LPC. In the Fen alkaline-carbonatite complex, whole-rock chemistry suggests high ore grade. However, is necessary to further evaluate the potential for this deposit. Despite local enrichment in apatite, the Raftsund intrusion is the least promising area. Nevertheless, the process resulting in the formation of an Fe-Ti-P-rich melt which could have ponded somewhere else in the intrusion, forming a larger deposit. The extreme topography of the area makes further detailed investigation complicated.
- The Siilinjärvi phosphate deposit (Finland), which is hosted by an Archean carbonatite complex, has ore reserves of 234 Mt at an average grade of 4 wt% P_2O_5 (data for January 2014; O’Brien et al. 2015). Almost all the glimmerite-carbonatite rocks constitute phosphate ore, with an apatite content of about ~10 vol%. The analyses performed on these rocks in the frame of this project confirm the general enrichment in phosphate of these rocks ($2.32<P_2O_5<34.18$ wt). In the Siilinjärvi mine, fenites are stockpiled separately (O’Brien et al. 2015), though some of these rocks show a promising phosphate content (two samples at 2.4

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and 2.9 wt% P_2O_5), close to the average grade of the rocks that are currently mined. The REE content of the rocks correlates well with their P_2O_5 concentration. These correlations are used to roughly estimate the REE reserves at Siilinjärvi. Based on the latter and on an average content of 4 wt% P_2O_5 in the rocks exploited (O'Brien et al. 2015), an average hypothetical REE content between 576 and 697 ppm is calculated. As a reserve of roughly 200 Mt remains to be exploited, the REE reserve should be between 133 000 t and 161 000 t of Total Rare Earth Oxide in the phosphate deposit. A large part of the REE must be present in apatite (as confirmed by LA-ICPMS analyses; total REE content in apatite from the glimmerite-carbonatite varies from 3195 and 6665 ppm). Consequently, the exploitation of REE as a by-product of the apatite could be interesting at Siilinjärvi.

- ❖ In north Estonia, the Toolse, Rakvere and Aseri Ordovician phosphorite deposits were historically delineated by 4% P_2O_5 cut-off criterion. So far, Toolse and Rakvere phoshorite deposits can be considered of having a highest economic potential. The Toolse phosphorite deposit covers an area of about 110 km^2. The phosphate rock bed of mineable interest varies between 1–4 m. Average P_2O_5 content is about 10%, but the maximum P_2O_5 values may reach over 15%. A few geochemical data indicate that the total REE content may reach up to 1800 ppm. The Rakvere phosphorite deposit, with an area of 140 km^2, is located southwards of the Toolse deposit. The phosphate bed overburden at the Rakvere deposit is thicker than in the Toolse deposit – ranging between 60 and 110 meters. The average P_2O_5 content in the mineable bed complexes of the Kallavere Formation is 13%, but the maximum values in some coquina beds may exceed 20%. The resource is estimated 1 938 million tons of phosphate rock with average grade of 13% P_2O_5. New drills will be performed by the Geological Survey of Estonia within the limits of the above-mentioned deposits to validate the available geological-geochemical data, to obtain geotechnical data on target rocks and overburden, and to analyse new drill cores for the rare earth elements content and spatial distribution. In case further studies confirm enrichment in REE highlighted by the first analytical results, then the Estonian phosphorites can be considered as an economically attractive multisource CRM commodity.

- ❖ The Ciply phosphatic chalk of the Mons basin (Belgium) hosts the second most important phosphorite in Europe known so far. Resources were estimated at 960 million tons @ 5-10 % P_2O_5 (Robaszynski and Martin 1988). The study led in the frame of this project (Jacquemin 2020) brings new information about the genesis of the deposit and the enrichment in REE of the phosphatic chalk. These data allow assessing (roughly) the resources in REE of the Mons basin. Taking into account the numbers from Robaszynski and Martin (1988), one can estimate that between 47 and 96 million tons of phosphates could be retrieved from the Mons Basin. The REE contents average is around 350 ppm for the dominant phosphatic chalk facies (Jacquemin 2020). Based on these data, the total REE that could be recovered amount to approximately 33 600 tons of REE, with 19 584 tons LREE and 14 112 tons HREE. One prospect in the future could be to reassess in the same way comparable deposits located in France and the UK.

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- The investigations led in the Mid-Cretaceous sediments of the Bohemian Basin (CBC, Czech Republic) show that, despite the consistency of the phosphogenic event during the Early Turonian, the studied phosphate occurrences are only present in thin horizons and can not be categorized as deposits in the economic sense. Nevertheless, it is worth mentioning that most of the extracted phosphate components contain anomalous concentrations of REE and some other critical elements, though representing individual cases (Al-Bassam and Magna 2018). Consequently, the Early Turonian phosphate-bearing horizon can be recommended as the main exploration target for marine sedimentary phosphorites in the BCB, though the potential of discovering sizable high grade phosphate deposits of economic importance as source of REE and/or other valuable critical metals is not so encouraging.

- The Salento Peninsula hosts phosphatic nodule-rich formations and phosphatic limestones, the "Pietra Leccese", dated to the Tertiary. The Pietra Leccese shows a low P grade (1-4% P_2O_5). The phosphate nodule formations at Punta Ristola and Baia del Ciolo are in the range of 6.32-23% P_2O_5 (with an average of 16%). The ∑REE content varies significantly depending on the formation, from 16 to 429 ppm. It is the lowest in nodular phosphate formations and the highest in the Pietra Leccese. The Pietra Leccese formations extend in the Salento peninsula for ~150 km^2 with an average thickness in the Lecce area of 80 m. It commonly shows a relatively low grade (3–4% P_2O_5; Notholt et al. 1979). Considering the totality of the formation with a 3.5% P_2O_5 grade, the tonnage is of ~600 million tons. Regarding the REE, based on correlations determined thanked to the newly aquired analyses (leading to an estimated average content of 170 ppm REE), one could recover 102 000 tonnes of REE. Of course, these calculations about the potential of P and REE in the area are theoretical and one must consider that the Pietra Leccese is used as the main local building stone. Notholt et al. (1979) have also reported 60 million tonnes of phosphatic limestone, with a content of 7–8 % P_2O_5. With the same way of reasoning, ~22 000 tonnes of REE could be recovered, based on a mean content of 7.5 % P_2O_5 (and an average content of 370 ppm REE). Finally, Notholt et al. (1979) reported 10 million tonnes at grades in the range 10.5–20.5 % P_2O_5 of Upper Pliocene nodular phosphate deposits. The latter likely correspond to the Punta Ristola occurrence. Considering an average grade of 38 ppm of ΣREE for a grade of 15% P_2O_5, based on the correlation observed for the Punta Ristola samples, then one could recover 380 tonnes of REE. The phosphate deposits of the Salento Peninsula could show promising potential regarding its REE content. Further studies are nevertheless necessary to well define the extend of the formation and its potential.

- The Moncorvo iron deposit (Portugal), Ordovician in age, is mostly made of hematite and magnetite, with a known mineralization of lazulite and apatite, among other phosphates. The preliminary study of one of its orebodies - Cotovia (Reboredo) – shows that the ironstones exhibit concentrations in phosphate as high as 4.4% P_2O_5. Enrichment in V and REE is also locally reported (up to 695 ppm and 313 ppm, respectively). Considering the large range of P, V and REE contents, more data about the resources/reserves of the deposit in P are needed and additional chemical analyses are necessary before stating the potential of the deposit in CRM.

- The black shales and mudstones hosting phosphorites in Estonia and the Czech Republic have been investigated regarding their possible CRM contents. Only the Estonian black shales represent resources for several metals, of which V that is a CRM. Even though much work is needed to further assess the deposit, the close association of these black shale deposits with the phosphorites would make these metals valuable by-product for phosphorus producers (Vind 2018). In the Mid-Cretaceous sediments of the Bohemian Basin (Czech Republic), preliminary analyses of phosphate-bearing siliciclastic sediments show that the glauconitic dark gray and black mudstones of the upper part of the Pecínov Member (Upper Cenomanian) and those of the lower part of the Bílá Hora Formation (Lower Turonian) in the Pecínov section might be interesting targets for Nb, Th, W and occasionally for REE, Y and U. Further works are needed, though probably not of great economic significance.

From these studies, it appears that an (even rough) assessment of the REE potential of the phosphate mineralization - whether it is sedimentary or igneous in origin - should be systematically done during the exploration (or exploitation) phase. One of the most important limitations to assess this potential is the general lack of information about the reserves and resources of the phosphate deposits themselves.

This work also emphasizes the so-far underestimated potential of the deposits related to mafic rocks, as those occurring in Norway. The latter are seemingly not very large, but the contents in P and REE is most promising. Works are needed to further assess these mineralizations. They are ongoing.

It is worth mentioning here that even if the size/morphology/potential of the mineralized body do not seem favourable for exploitation now, it could be otherwise in the future, considering - for instance - the rapid developments in the field of robotics in mining.

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6. References

Ahokas K (2015) Finland's phosphorus resources are more important than ever. Geofoorumi 2, 10-12

Al-Bassam KS, Magna T (2018) Distribution and significance of rare earth elements in Cenomanian–Turonian phosphate components and mudstones from the Bohemian Cretaceous Basin, Czech Republic. Bulletin of Geosciences 93 (3), 347 –368

Al-Bassam KS, Magna T, Vodrážka R, Čech S (2019) Mineralogy and geochemistry of marine glauconitic siliciclasts and phosphates in selected Cenomanian–Turonian units, Bohemian Cretaceous Basin, Czech Republic: Implications for provenance and depositional environment. Geochemistry 79, 347 – 368

Andersen T (1988) Evolution of Peralkaline Calcite Carbonatite Magma in the Fen Complex, Southeast Norway. Lithos 22, 99-112

Andersen T, Taylor PN (1988) Pb Isotope Geochemistry of the Fen Carbonatite Complex, Se Norway - Age and Petrogenetic Implications. Geochimica Et Cosmochimica Acta 52, 209-215

Andersson SS, Wagner T, Jonsson E et al (2019) Apatite as a tracer of the source, chemistry and evolution of ore-forming fluids: The case of the Olserum-Djupedal REE-phosphate mineralisation, SE Sweden. Geochim Cosmochim Acta 255, 163-187

Arthur MA, Jenkyns HC (1981) Phosphorites and paleoceanography. Ocean Acta, Special issue, https://archimer.ifremer.fr/doc/00245/35660/34169.pdf

Bosellini A, Bosellini FR, Colalongo ML, Vescogni A (1999) Stratigraphic architecture of the Salento coast from Capo d'Otranto to S. Maria di Leuca (Apulia, southern Italy). Rivista Italiana di Paleontologia e Stratigrafia 105(3), 397

Broom-Fendley S, Brady AE, Wall F, Gunn G, Dawes W (2017) REE minerals at the Songwe Hill carbonatite, Malawi: HREE-enrichment in late-stage apatite. Ore Geology Reviews 81, 23-41

Coint N, Keiding JK, Ihlen PM (2020) Evidence for silicate-liquid immiscibility in monzonites and petrogenesis of associated Fe-Ti-P-rich rocks: example from the Raftsund intrusion, Lofoten, northern Norway. Journal of Petrology. DOI:10.1093/petrology/egaa045

Condie KC (1993) Chemical composition and evolution of the upper continental crust: contrasting results from surface samples and shales. Chemical geology 104, 1-37

Cook PJ, Shergold JH (Editors) (1986) Phosphate deposits of the world. Volume 1: Proterozoic and Cambrian phosphorites. Cambridge University Press

Cultrone G, Anfuso G, Sebastián E (2010) Mineralogy of Miocene phosphatic nodules in SE Sicily (Italy). Geol Quarterly 52, 61-70

Dahlgren S (2019) REE mineralization in the Fen Carbonatite Complex, Telemark, Norway- A world-class exploration terget for the high-tech and “green-shift” industry? Buskerud Telemark Vestfold County Council Report 2019-1, p.85

Dahlgren S, Corfu F, Heaman L (1998) Datering av plutoner og pegmatitter i Larvik pluton-kompleks, sydlige Oslo Graben, ved hjelp av U–Pb isotoper i zirkon og baddeleyitt. Norsk Bergverksmuseum Skrift 14, 32–39

Decrée S, Savolainen M, Mercadier J, Debaille V, Höhn S, Frimmel H, Baele JM (2020) Geochemical and spectroscopic investigation of apatite in the Siilinjärvi carbonatite complex: Keys to understanding apatite forming processes and assessing potential for rare earth elements. Applied Geochemistry 123, 104778

Dejonghe L, Delmer A, Groessens E (1976) Discovery of anhydrite in Prenamurian Formations of soundings in Saint-Ghislain. Bulletin de la Classe des Sciences de l'Académie royale de Belgique 62, 80-83

Delle Rose M (2001) Salento Miocene : A preliminary paleoenvironmental reconstruction. http://siba-ese.unisalento.it/index.php/thalassiasal/article/view/i15910725v25p41/1889

Dietzel CAF, Kristandt T, Dahlgren S, Giebel RJ, Marksa MAW, Wenzel T, Markl G (2019) Hydrothermal processes in the Fen alkaline-carbonatite complex, southern Norway. Ore Geology Reviews, 111

d'Orey FLC (1999) The Detrital Origin of the Moncorvo Ordovician Ironstones. Ciências da Terra (UNL) Lisboa 13, 131-140

EC (European Commission) (2015) Report on Critical Raw Materials for the EU. Critical Raw Materials Profiles. http://ec.europa.eu/DocsRoom/documents/11911/attachments/1/translations. Accessed 9 December 2016

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731166

Eilu P (ed) (2012) Mineral deposits and metallogeny of Fennoscandia. Geological Survey of Finland, Special Paper 53, 401 p https://tupa.gtk.fi/julkaisu/specialpaper/sp_053.pdf

Figueiras J, Mateus A, Rodrigues P et al. (2015) Phosphate phases in the Moncorvo iron ores; consequences to the mineral resource characterization and its economic assessment. Book of Abstracts, Iberian Geochemistry Congress, 78-81

Föllmi KB, Hofmann H, ChiaradiaM. de Kaenel E, Frijia G, Parente M (2015) Miocene phosphate-rich sediments in Salento (southern Italy). Sediment Geol 327, 55–7.

Hallberg A, Bergman T, Gonzalez J et al (2016) Chapter 7 – Sweden. In: Boyd R, Bjerkgård T, Nordah B et al (eds) Mineral Resources in the Arctic. Geological Survey of Norway Special Publication, http://www.ngu.no/upload/Aktuelt/CircumArtic/7_Sweden.pdf

Harlov DE, Andersson UB, Förster HJ, Nyström JO, Dulski P, Broman C (2002) Apatite–monazite relations in the Kiirunavaara magnetite–apatite ore, northern Sweden. Chemical Geology 191(1-3), 47-72

Hornig-Kjarsgaard I (1998) Rare Earth Elements in Sövitic Carbonatites and their Mineral Phases. Journal of Petrology 39, 2105–2121

Ihlen PM, Schiellerup H, Gautneb H, Skår Ø (2014) Characterization of apatite resources in Norway and their REE potential—a review. Ore Geol Rev 58, 126-147

Jacquemin D (2020) The phosphatic chalk of the Mons Basin, Belgium. Petrography and geochemistry of the Ciply Phosphatic Chalk and implications on its genesis. Memoirs of the Geological Survey of Belgium, Vol. 64 (submitted and accepted for publication)

Jarvis I (1992) Sedimentology, geochemistry and origin of phosphatic chalks: the Upper Cretaceous deposits of NW Europe. Sediment 39, 55-97

Kärkkäinen N, Appelqvist H (1999) Genesis of a low-grade apatite-ilmenite-magnetite deposit in the Kauhajärvi gabbro, western Finland. Miner dep 34, 754-769

Lindberg PA (1985) Fe-Ti-P Mineralizations in the Larvikite-Lardalite Complex, Oslo Rift. NGU Bulletin 402, 93-98

Martinsson O, Billström K, Broman C, Weihed P, Wanhainen C (2016) Metallogeny of the northern Norrbotten ore province, northern Fennoscandian Shield with emphasis on IOCG and apatite-iron ore deposits. Ore Geology Reviews 78, 447-492

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731166

Mazzei R, Margiotta S, Foresi LM, Riforgiato F, Salvatorini G (2009) Biostratigraphy and chronostratigraphy of the Miocene Pietra Leccese in the type area of Lecce (Apulia, southern Italy). Boll Della Soc Paleontol Ital 17

Monchiardini C (1989) The Senonian (Cretaceous) phosphatic chalks of the Paris Basin, France. In: Notholt AJG, Sheldon RP, Davidson D (eds) Phosphate deposits of the world: volume 2, phosphate rock resources, Cambridge University Press, Cambridge, pp 407-410

McLennan SM (1989) Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. Geochemistry and Mineralogy of Rare Earth Elements. Reviews in Mineralogy vol 21, 169–200

MTI, Ferro de Moncorvo SA (2015) Projeto De Reativação Das Minas De Ferro De Moncorvo Relatório Síntese. EIA Volume II.Estudo de Impacto Ambiental, 547p

Neumann ER (1980) Petrogenesis of the Oslo region larvikites and associated rocks. Journal of Petrology 21, 499-531

Notholt AJG., Highley DE (1981) Investigation of the phosphate potential of the Loch Borralan Complex, north-west Highlands, Scotland. Open File Report, Institute of Geological Sciences (now BGS)

Notholt AJG, Brasier MD (1986) Proterozoic and Cambrian phosphorites-regional review: Europe. In: Cook PJ, Shergold JH (eds) Phosphate deposits of the world: volume 1, Proterozoic and Cambrian phosphorites, Cambridge University Press, Cambridge

Notholt AJG, Highley DE, Slansky M (1979) Raw Materials Research and Development IV. Dossier on Phosphate, Commission of the European Communities, Brussels

Notholt AJG, Sheldon RP, Davidson D (1989) Europe-Introduction. In: Notholt AJG, Sheldon RP, Davidson D (eds) Phosphate deposits of the world: volume 2, phosphate rock resources, Cambridge University Press, Cambridge

O'Brien H, Hyvönen E (2015) The Sokli carbonatite complex. In: Mineral Deposits of Finland, Elsevier, pp 305-325

O'Brien H, Heilimo E, Heino P (2015) The Archean Siilinjärvi carbonatite complex. In: Mineral Deposits of Finland, Elsevier, pp 327-343

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731166

Raudsep R (1997) Phosphorite. In: Raukas A and Teedumäe A (eds) Geology and mineral resources of Estonia, Estonian Academy Publishers, 436 p

Robaszynski F (1989) The phosphatic chalk of the Mons Basin, Belgium. In: Notholt AJG, Sheldon RP, Davidson D (eds) Phosphate deposits of the world: volume 2, phosphate rock resources, Cambridge University Press, Cambridge, pp 370-375

Robaszynski F, Martin M (1988) Late Cretaceous Phosphate Stratiform Deposits of the Mons Basin (Belgium). Mineral Deposits within the European Community, Springer, Berlin, Heidelberg, 515-529

Sadeghi M (ed) (2019) Rare earth elements distribution, mineralisation and exploration potential in Sweden. Sveriges geologiska undersökning, Rapporter och meddelanden 146, 168p http://resource.sgu.se/produkter/rm/rm146-rapport.pdf

Sadeghi M, Arvanitidis N, Ladenberger A (2020) Geochemistry of Rare Earth Elements in Bedrock and Till, Applied in the Context of Mineral Potential in Sweden. Minerals 10(4), 365

Sansò P, Margiotta S, Mastronuzzi G, Vitale A (2015) The Geological Heritage of Salento Leccese Area (Apulia, southern Italy). Geoheritage 7, 85–101

Schiellerup H, Meyer GB, Tegner C, Robins B, Korneliussen A (2001) Resources of apatite, ilmenite and magnetite in the Bjerkreim-Sokndal Layered Intrusion, Rogaland, South Norway. Geological Survey of Norway report 2001.092, p 33

Schilling J (2013) Petrography, mineralogy and whole-rock data of the major lithologies of the Fen complex. Geological Survey of Norway report 2013.034, p.18

Stoppa F, Pirajno F, Schiazza M, Vladykin NV (2016) State of the art: Italian carbonatites and their potential for critical-metal deposits. Gondwana Res 37, 152-171

Sun SS, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts; implications for mantle composition and processes. In: Saunders AD, Norry MJ (eds.) Magmatism in the ocean basins: Saunders AD and Norry MJ, 313-345

Torbica S, Lapčević V (2012) Concept of underground mining of phosphate deposits in Lisina near Bosilegrad. Podzemni radovi, 23-29

Turekian KK, Wedepohl K (1961) Distribution of the elements in some major units of the Earth's crust. Geol Soc Amer Bull 72, 175 – 192

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731166

Tzifas IT, Godelitsas A, Magganas A et al (2014) Uranium-bearing phosphatized limestones of NW Greece. J Geochem Explor 143, 62-73

Urbano EEMC, Meireles CAP, Gomes MEP et al. (2015) Comparative petrographic study between the iron ore from the northern and southern limb of Moncorvo syncline. VIII Seminário Recursos Minerais, Ambiente e Ordenamento do Território

Venturelli G, Capedri S, Barbieri M et al (1991) The Jumilla lamproite revisited: a petrological oddity. Europ J Miner, 123-146

Vind J (2018). Review of the Exploration Potential of the Estonian Black Shale (Graptolitic Argillite) Deposit. Geological Survey of Estonia / Research Report EGF-8995, 52p https://fond.egt.ee/fond/egf/8995

Vindel E, Chicharro E, Villaseca C et al (2014) Hydrothermal phosphate vein-type ores from the southern Central Iberian Zone, Spain: Evidence for their relationship to granites and Neoproterozoic metasedimentary rocks. Ore Geol Rev 62, 143-155

Vodrážka R, Sklenář J, Čech S, Laurin J, Hradecká L (2009) Phosphatic intraclasts in shallow-water hemipelagic strata: a source of palaeoecological, taphonomic and biostatigraphic data (Upper Turonian, Bohemian Cretaceous Basin). Cretaceous Res 30, 204 – 222

Walters AS, Goodenough KM, Hughes HS et al (2013) Enrichment of Rare Earth Elements during magmatic and post-magmatic processes: a case study from the Loch Loyal Syenite Complex, northern Scotland. Contrib Miner Pet 166(4), 1177-1202

Zirner AL, Marks MA, Wenzel T, Jacob DE, Markl G (2015) Rare earth elements in apatite as a monitor of magmatic and metasomatic processes: The Ilímaussaq complex, South Greenland. Lithos 228, 12-22

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731166