FRAME
FORECASTING AND ASSESSING EUROPE'S STRATEGIC RAW MATERIALS NEEDS

DELIVERABLE D4.4 Development of a procedure to prepare and analyze phosphate deposits to provide internally consistent geochemical data at a European level

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

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

GeoERA RAW MATERIALS

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Development of a procedure to prepare and analyze phosphate deposits to provide internally consistent geochemical data at a European level

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1. Introduction

This deliverable is devoted to geochemistry. It deals with how to provide internally consistent geochemical data at a European level for phosphate mineralization. It aims at establishing a procedure to prepare and analyse phosphate samples.

The first section describes the methodology applied for this deliverable and provides a list of elements that should be analyzed in apatite and/or phosphate rocks according to a selection of methods. It describes the way the laboratories were chosen to do the bulk rock and in-situ analyses and presents the issue regarding standards for bulk rock analyses and in-situ analyses.

The second section details the outcome of this work in terms of quantity and homogeneity of bulk rock and in-situ analyses. It also describes the investigations lead regarding standards before a final section including the conclusions and prospects.

2. Methodology

2.1. List of elements to analyse

The selection of elements to analyse in apatite and phosphate rocks was approved by the partners. This was an achievement of the milestone M4.2.

The elements were selected according to the method/analyse type. The details are given here after:

- Bulk rock analyses on phosphate mineralization/rocks: major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P), trace elements (REE, V) (Co, Sc, Ni, LILE-Ba, Sr, Rb, HFSE-Nb, Ta, Hf, Zr)
- Bulk rock analyses on black shales hosting phosphorites: major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, C total, S total), trace elements (REE, Co, Sb, Be, V, PGE)
- Electron microprobe analyses on apatite: P, Ca, F, Fe, Si, Cl
- Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) on apatite: REE, V, U, Th, Si, P, Ca, Ti, Rb, Sr, Y, Zr, Nb, Ba, Hf, Ta, W, Pb

For FRAME-WP4, mostly bulk rock analyses on phosphate rocks and LA-ICPMS analyses on apatite were performed. Electron microprobe analyses were essentially done to determine the type of apatite (based on the Cl^-, F^- contents) and the Ca concentrations, which is used as internal standard for LA-ICPMS analyses.

2.2. Selection of laboratories

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As for the list of elements to analyse, the selection of laboratories where to perform analyses was an achievement of the milestone M4.2.

Though it was initially planned to let every partner of the project analyse the samples from its own country, it was finally decided to divide the samples into only two separate batches to produce larger homogenized datasets. As such, analyses of apatite and phosphate rocks from Norway were performed at the NGU, and all the other analyses were handled by the GSB, coordinator of the WP.

Since the facilities were not available in-house at the GSB, bulk rock analyses were performed on Inductively Coupled Plasma optical emission spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the ULB (University of Brussels), electron microprobe analyses – though less crucial for homogenization – at the University of Würzburg (Germany) and the LA-ICPMS analyses at the University of Lorraine (France). The equipment and the methodology related are presented in the Annex 1.

For what concerns the NGU, all the analyses were performed in-house apart from the electron microprobe analyses, which were carried out at the NTNU (Norwegian University of Science and Technology, Trondheim, Norway).

2.3. Use of standards

It quickly appeared that the only way to deliver homogenized data from several laboratories was to prepare a standard sample that can be distributed among the institutes and surveys interested in providing geochemical data on phosphate mineralization. First, time was dedicated to find existing standards on the market suitable for bulk analyses of phosphate rocks and in-situ analyses of apatite. One standard was found for whole rock analyses (see below, section 3.1), but no standard large and cheap enough (to be shared between the partners of the project) was available. Hence, partners prepared an “internal” standard for the project.

3. Outcome

3.1. Bulk rock analyses

3.1.1. Standard for bulk rocks analyses

The Institute for Reference Materials and Measurements of the Joint Research Centre has a list of certified materials that can be used as standards. Among these, a natural Moroccan phosphate rock (Certified Reference Material BCR-032; the fiche about this material is provided as Annex) is available and has been tested for the following major elements: Ca, P, C,

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F, Si, S, Al, Mg and Fe (Figure 1). Such material is convenient to precisely analyze major elements in European phosphate rocks, which contain two of the elements present in the critical raw materials (CRM) list, namely P (P_2O_5 content of 32.98 % in the BCR-032) and F (certified value of 40.4 g/kg F in the BCR-032). Aliquots of this standard were distributed among the partners of the WP for further analyses and studies about apatite and phosphate deposits in their respective countries.

Only indicative values are given for the following minor and trace elements: As, B, Cd, Cr, Co, Cu, Hg, Mn, Ni, Ti, V, Zn. Consequently, a standard for bulk rock analyses could be developed in the future for trace elements and more precisely for the CRM (REE at first instance, and potentially V). Alternatively, one can consider that the use of the BCR-032 for major elements (and more particularly P and F), combined with other standards that typically serve for high-precision measurements of trace elements in a wide variety of rock types (e.g. USGS standards BHVO-2 and AGV-2), is sufficient to obtain reproductible and homogenized analyses on phosphate-rich rocks.

NATURAL MOROCCAN PHOSPHATE ROCK
(Phosphorite)

	Mass fraction based on dry mass		Number of accepted individual measurements
	Certified value [1)] [g/kg]	Uncertainty [2)] [g/kg]	
Ca expressed as CaO	518	4	70
Total P expressed as P_2O_5	329.8	1.7	85
Carbonate Carbon expressed as CO_2	51.0	0.8	60
F	40.4	0.6	80
Si expressed as SiO_2	20.9	1.2	60
Total S expressed as SO_3	18.4	0.8	75
Al expressed as Al_2O_3	5.5	0.6	80
Mg expressed as MgO	4.0	0.1	65
Fe expressed as Fe_2O_3	2.3	0.1	65

1) The certified value is the unweighted mean of individual measurements obtained by different laboratories. The certified value is traceable to SI.
2) The uncertainty is estimated standard deviation of reproducibility which. It accounts for the precision and bias of the participating laboratories as well as for any inhomogeneity of the material.

Figure 1. Major element content of the standard BRC-032 (JRC 2011)

3.1.2. Data obtained on phosphate rocks from European deposits

As mentioned previously, the bulk rock analyses were obtained in two laboratories, at the ULB and at the NGU.

Most of the analyses were performed at the ULB (University of Brussels), collaborator of the GSB for this task, using ICP-OES and ICP-MS. The standard BCR-032 was introduced in the

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analytical procedure for all the samples analysed. About 90 samples representative of ~75 phosphate occurrences and deposits (sedimentary or igneous in origin) were analyzed for the deliverable D4.2 'New mineralogical and geochemical data on samples from phosphate deposits/occurrences' (Table 1). In addition, 43 samples were analyzed to further study 4 deposits in the frame of deliverable D4.3 'Detailed metallogenic studies of key phosphate deposits in Europe' (Table 2).

At the NGU, 59 samples from four Norwegian deposits/occurrences were all analyzed using XRF on glass disks for major elements and pressed pellets for trace elements. Additional data for REE and HFSE were obtained on glass disks using LA ICP-MS for the deliverable D4.3 (Table 3). Since these data were performed at the very beginning of the project, the standard BCR-032 was not included in the analytical routine.

Consequently, more than 130 harmonized bulk rock analyses were performed with the use of a standard for high P and F concentrations. Additional 59 analyses are considered as internally consistent regarding the analytical procedure applied.

3.2. In-situ (LA-ICPMS) analyses

3.2.1. Data obtained on apatite from European deposits

The LA-ICPMS analyses were obtained at the NGU and at the University of Lorraine (France), which is collaborator of the GSB for this task. The analyses were performed for the metallogenic studies that are part of the deliverable D4.3 'Detailed metallogenic studies of key phosphate deposits in Europe', which includes the publications of Coint et al. (2020) and Decrée et al. (2020).

In that way, 43 analyses were performed by the GSB at the University of Lorraine to investigate the potential of the apatite deposit at Siilinjarvi and 175 analyses were obtained at the NGU on apatite from the Norwegian deposits/occurrences of Fen, Kodal/Larvik and Raftsund (Table 3).

Initial plans to analyse apatite in all the samples were altered due to limitations imposed by the pandemic situation and the subsequent closure of the labs.

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Table 1. Samples processed to obtain bulk rock analyses in the frame of the deliverable D4.2 'New mineralogical and geochemical data on samples from phosphate deposits/occurrences'

Sample name	Locality	Country	Deposit type name	Sample name	Locality	Country	Deposit type name	Sample name	Locality	Country	Deposit type name
Au-Lz	Pleshing, Linz	Austria	Phosphorite	DE-DE12	Rauen, Windmühlenberg	Germany	Phosphorite	MNHN11	Lezennes-59	France	Phosphorite
GH 2743	Grand Halleux (boring)	Belgium	Phosphorite	DE-DE10	Sprochkövel	Germany	oolitic iron / ironstone	MNHN12	Etaves-02	France	Phosphorite
GH 2952	Grand Halleux (boring)	Belgium	Phosphorite	DE-DE1	Oberpfalz, Amberg, Bavaria	Germany	Phosphorite	MNHN13	Cierp-32	France	Phosphorite
Thy 1	Thy-le-Chateau	Belgium	Phosphorite	ASERI	Aseri	Estonie	Phosphorite	MNHN17	Saint-Pol-62	France	Phosphorite
Berch 1	Berchem	Belgium	Phosphorite	IRU9	Iru	Estonie	Phosphorite	MNHN18	Liverdun-54	France	oolitic iron / ironstone
Berch 2	Berchem	Belgium	Phosphorite	ORASOJA5	Orasoja	Estonie	Phosphorite	MNHN19	Mollans-70	France	Phosphorite
STN 1	Sint Niklaas	Belgium	Phosphorite	SAKA1	Saka	Estonie	Phosphorite	NHM2	Loch Borralan	United Kingdom	alkaline igneous rocks*
STN 2	Sint Niklaas	Belgium	Phosphorite	TOOLSE2	Toolse	Estonie	Phosphorite	NHM4	Loch Borralan	United Kingdom	alkaline igneous rocks*
MO	Moen, Bossuit Canaal	Belgium	Phosphorite	Font 1	Fontanajero	Spain	Phosphorite	NHM5	Cwmystwyth, Wales	United Kingdom	Phosphorite
MA	Marke, Kockelberg	Belgium	Phosphorite	Font 2	Fontanajero	Spain	Phosphorite	NHM6	Taplow	United Kingdom	Phosphorite
LM1	La Malogne	Belgium	Phosphorite	RA7823	Jumilla, Murcia	Spain	kimberlite and lamproite	NHM7	Loch Borralan	United Kingdom	alkaline igneous rocks*
LM4	La Malogne	Belgium	Phosphorite	Z1232	Jumilla, Murcia	Spain	kimberlite and lamproite	NHM8	Taplow	United Kingdom	Phosphorite
LM3	La Malogne	Belgium	eluvial placer	RB 7210	Cacerès	Spain	granitic igneous rocks and pegmatites	NHM9	Cwmystwyth, Wales	United Kingdom	Phosphorite
Hb56.76	Hyon (boring)	Belgium	Phosphorite	DE-SP1	Logrosan	Spain	granitic igneous rocks and pegmatites	GR1	Kastritsa	Greece	Phosphorite
Hb79.06	Hyon (boring)	Belgium	Phosphorite	RA4064	Estramadura, Caceres, Logrosan	Spain	tic igneous rocks and pegm	GR2	Kastritsa	Greece	Phosphorite
Hb90.2	Hyon (boring)	Belgium	Phosphorite	RB7185	Sierra Patanos, Belmez, Cordoba	Spain	tic igneous rocks and pegm	HU1	Úrkút	Hungary	Phosphorite
Mz-PS1918	Straimont	Belgium	alluvial placer	RC3167	Cap Blanc-Nez	France	Phosphorite	HU2	Úrkút	Hungary	Phosphorite
Mz-PS1903	Martilly	Belgium	alluvial placer	Le Corrijou 1&2	Crozon	France	Phosphorite	B2	Baia de Ciolo	Italy	Phosphorite
Mz-PS1910	Straimont	Belgium	alluvial placer	Le Corrijou 2011	Crozon	France	Phosphorite	PR1	Punta Ristola	Italy	Phosphorite
40A	Rtyně v Podkrkonoší	Czech Republic	Phosphorite	FR Q3	Quercy	France	eluvial placer	C3	Cursi	Italy	Phosphorite
60A	Česká Třebová	Czech Republic	Phosphorite	FR Q1	Quercy	France	eluvial placer	L10b	Lecce	Italy	Phosphorite
70	Česká Třebová	Czech Republic	Phosphorite	FR Q2	Quercy	France	eluvial placer	C2	Cursi	Italy	eluvial placer
80A	Březinka – Chvalka	Czech Republic	Phosphorite	RB7269	Neuville	France	Phosphorite	It-Si1	Donnalucata, Sicily	Italy	Phosphorite
80B	Březinka – Chvalka	Czech Republic	Phosphorite	DE-FR1	Alzen	France	Phosphorite	It-Si2	Donnalucata, Sicily	Italy	Phosphorite
RB7192	Lahn River, Nassau	Germany	eluvial placer	MNHN1	Sissone-02	France	Phosphorite	DE-PL2	Podkonce	Poland	Phosphorite
RA4065	Nassau	Germany	eluvial placer	MNHN2	Hardivillers-60	France	Phosphorite	DE-PL5	Annopol	Poland	Phosphorite
DE-DE6	Schmirchau, Ronneburg	Germany	Phosphorite	MNHN3	Hem-59	France	eluvial placer	DE-PL1	Annopol	Poland	Phosphorite
RA2332	Eichen (Hanau), Hesse	Germany	eluvial placer?	MNHN4	Hélemmes-59	France	Phosphorite	DE-PL6	Dabrowka-Zablotnia (Radom)	Poland	Phosphorite
DE-DE7	Helmstedt	Germany	Phosphorite	MNHN5	Sassenage-Isère	France	Phosphorite	DE-PL4	Dygowo, Persante	Poland	Phosphorite
DE-DE9	Klein Dahlum	Germany	Phosphorite	MNHN6	Assigny-18	France	Phosphorite		Jakubowice, Weichselufer	Poland	Phosphorite
DE-DE8	Aachen	Germany	oolitic iron / ironsto	MNHN8	Celle-Joyeuse-08	France	Phosphorite				
DE-DE11	Brilon, Hoppeke, Romberg	Germany	Phosphorite	MNHN9	Assigny-18	France	Phosphorite				
*undersaturated and saturated syenitic and alkali igneous rocks and pegmatites											

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Table 2. Bulk rock analyses obtained in the frame of the deliverable D4.3 'Detailed metallogenic studies of key phosphate deposits in Europe'. Analyses from Norwegian rocks are performed at the NGU, the others at the ULB (for the GSB). Note that the data published by Coint et al. (2020) and Decrée et al. (2020) were obtained for the FRAME project

Mineral deposit type/group (INSPIRE compliant)	Deposit/District	Deposit/occurrence considered in the district	Country	References for the analyses (#analyses)
Carbonatite	Siilinjarvi	-	Finland	Decrée et al. (2020) (11)
	Fen	Hydro quarry, Söve mine, Tuftstolen mine, Rauhaug	Norway	Deliverable D4.3 (1)
Unsaturated and saturated syenitic and alkali granitic igneous rocks and pegmatites	Larvik Plutonic Complex	Kodal, Eskedal, Heirønningen, Rånerød	Norway	Deliverable D4.3 (6)
	Raftsund intrusion, Lofoten	Gindvika, Utåker, Sukkertoppen, Fiskebøl	Norway	Coint et al. (2020) (43); Deliverable D4.3 (7)
	Nordre Følstad- Lofoten	-	Norway	Deliverable D4.3 (2)
Phosphorite	Mons Basin	-	Belgium	Deliverable D4.3 (11)
	Salento Peninsula	-	Italy	Deliverable D4.3 (7)
Ironstone	Moncorvo	-	Portugal	Deliverable D4.3 (15)

Table 3. Summary of the LA-ICPMS analyses performed for the deliverable D4.3 'Detailed metallogenic studies of key phosphate deposits in Europe'. Analyses from Norwegian rocks were performed at the NGU, analyses from Finnish rocks were obtained at the ULB (for the GSB). Note that the data published by Coint et al. (2020) and Decrée et al. (2020) were obtained for the FRAME project

Mineral deposit type/group (INSPIRE compliant)	Deposit/District	Deposit/occurrence considered in the district	Country	References for the analyses (#analyses)
Carbonatite	Siilinjarvi	-	Finland	Decrée et al. (2020) (41)
	Fen	Söve mine	Norway	Deliverable D4.3 (20)
Unsaturated and saturated syenitic and alkali granitic igneous rocks and pegmatites	Larvik Plutonic Complex	Kodal (Vestfold), Bisjord, Eskedal, Kroken	Norway	Deliverable D4.3 (90, of which 7 EPMA)
	Raftsund Intrusion	Utåker, Sukkertoppen, Fiskebøl, Grindvika	Norway	Coint et al. (2020) (65, of which 30 EPMA)

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3.2.2. Test on a potential standard: apatite from Phalaborwa (South Africa)

The Phalaborwa world-class phosphate deposit (Kaapval Craton, South Africa, Figure 2a) is hosted by a Paleoproterozoic alkaline complex. It contains, among others, apatite-rich pegmatoid dikes and veins (Figure 2b). A study achieved out of the frame of this project showed that apatite forming these veins is exceptionnaly homogeneous regarding its O and Sr isotope compositions (Decrée et al. 2020b). Moreover, these samples are available in large quantity, an important criterium for a standard.

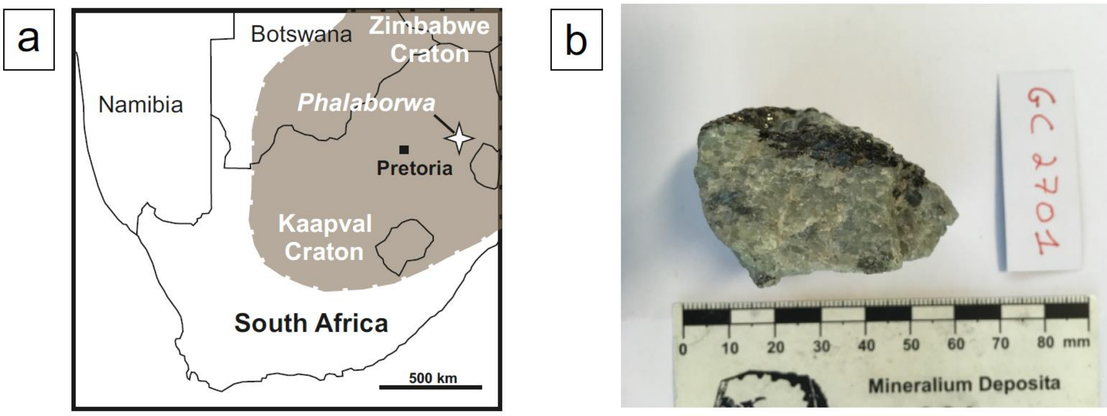

Figure 2. a) Location of the Phalaborwa deposit in the Kaapval Craton (from Decrée et al. 2020b) and b) macrophotograph of the apatite vein from Phalaborwa (sample GC 2701)

It was therefore decided to test one of these apatite veins (the sample GC 2701, provided by Grant Cawthorn, retired professor of the Wits University) to check whether the in-situ signature of apatite regarding the REE and a few other trace elements is reproductible and similar from one laboratory to the other.

Twenty-two analyses were performed at the University of Lorraine (France) for the GSB (Table 4) and 60 analyses were performed at the NGU. The focus was on a limited selection of elements including the REE and V, which are CRM, Y and Sr that are typically measured on apatite, and Pb, Th and U that are pollutants for the processing of apatite. The main features about these data are the following:

- the errors obtained are more important for the dataset obtained at the NGU (RSD: 13-35%) than for the one gathered by the GSB (2 RSD: 6-21%). This is likely due to a more important variability of the sample provided at the NGU;

- the highest errors are observed for U and Th (2 RSD: 18-21% for GSB data and 31-35% for NGU data) and the lowest for Sr (2 RSD= 6% for the GSB data and 13% for the NGU data);

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- by comparison, the errors for the REE, Y and V and intermediate (2 RSD: 12-15% for GSB data and 22-27% for NGU data);

- the chondrite-normalized REE patterns are similar for the analyses performed at the NGU and by the GSB (Figure 3). The field corresponding to the GSB data is narrower. These differences in terms of errors are also highlighted in the box plots presented in Figure 4. Despite the discrepancies about the accuracy of the data between the GSB and NGU datasets, the average and median values are commonly very close to each other (Figure 4 and Tables 4 and 5). This means that the sample GC 2701 from Phalaborwa could constitute a suitable standard for in-situ analyses of REE, Sr, Y and V on apatite. Of course, this study is the first step of a protocole that should involve a large numbers of laboratories to test and validate the data.

Table 4. LA-ICPMS analyses (and related statistics) obtained on the potential apatite standard (apatite from Phalaborwa GC 2701). Analyses done by the GSB at the University of Lorraine (France)

(ppm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sr	Pb	Th	U	V
*Norm. Chond.**	*0.349*	*0.904*	*0.137*	*0.674*	*0.219*	*0.083*	*0.293*	*0.053*	*0.363*	*0.081*	*0.236*	*0.036*	*0.237*	*0.036*						
phal23-2	1683	3675	421	1864	334	63	213	19	76	9	17	1.5	6.1	0.7	239	5963	27	133	9	19
phal23-3	1763	4025	465	2124	392	74	250	23	90	11	19	1.7	7.3	0.8	272	6029	30	149	12	19
phal23-4	1682	3710	420	1893	352	65	221	20	79	10	17	1.4	6.3	0.7	244	5913	26	134	10	19
phal23-5	1427	3363	386	1753	324	61	207	19	73	9	16	1.4	5.7	0.6	229	5838	22	107	8	15
phal23-6	1755	3906	438	1942	351	67	220	20	79	10	17	1.5	6.6	0.7	250	6060	26	125	9	17
phal23-7	1768	4017	464	2075	386	73	246	23	88	11	20	1.7	6.9	0.8	276	6017	26	128	10	18
phal23-8	1547	3525	406	1844	338	64	216	20	75	9	17	1.4	5.9	0.6	237	6036	25	125	9	15
phal23-9	1575	3632	417	1904	353	66	223	20	79	10	17	1.4	6.2	0.7	248	5976	27	136	10	18
phal23-10	1747	4058	473	2141	393	74	248	23	88	11	20	1.7	6.9	0.8	283	5853	30	146	11	19
phal23-11	1834	4101	462	2053	375	70	232	21	83	10	18	1.6	7.0	0.7	266	5989	26	126	9	19
phal23-12	1781	4141	471	2153	395	74	250	23	90	11	19	1.8	7.4	0.8	282	5742	29	144	11	18
phal23-13	1637	3949	457	2057	379	72	243	22	87	11	19	1.7	7.0	0.7	275	5905	25	120	9	18
phal23-14	1837	4259	493	2237	416	79	265	24	92	11	21	1.7	7.3	0.8	296	6027	31	151	11	19
phal23-15	1773	4020	461	2094	379	71	241	22	85	11	19	1.6	6.8	0.8	273	5891	27	136	10	18
phal23-17	1831	4202	473	2133	392	72	246	22	87	11	19	1.6	7.4	0.7	274	6315	28	144	10	19
phal23-18	1838	4207	473	2131	395	73	254	22	89	11	19	1.6	7.4	0.7	280	6248	28	135	10	20
phal23-19	1731	3948	451	2021	384	72	243	22	86	11	18	1.7	7.1	0.7	269	6259	27	135	10	18
phal23-20	1743	4034	460	2067	385	71	247	22	87	11	19	1.6	7.2	0.8	273	6337	30	142	10	19
phal23-21	1574	3716	424	1933	366	67	235	21	83	10	18	1.6	6.6	0.7	256	6162	24	113	8	17
phal23-22	1731	3948	451	2021	384	72	243	22	86	11	18	1.7	7.1	0.7						
phal23-23	1743	4034	460	2067	385	71	247	22	87	11	19	1.6	7.2	0.8						
phal23-24	1574	3716	424	1933	366	67	235	21	83	10	18	1.6	6.6	0.7						
N=22 for the REEs N=19 for Y, Sr, Pb, Th, U	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sr	Pb	Th	U	V
Average	1708	3918	448	2020	374	70	237	21	84	10	18	1.6	6.8	0.7	264	6029	27	133	10	18
2 RSD (%)	13	12	12	12	12	12	13	13	13	12	14	14	15	14	14	6	17	18	21	15
Median	1743	3983	458	2055	382	71	243	22	86	11	19	1.6	6.9	0.7	272	6017	27	135	10	18
5th percentile	1548	3530	407	1845	335	63	213	19	75	9.4	17	1.4	5.9	0.6	236	5828	23	112	8.1	15
25th percentile	1637	3716	424	1933	366	67	232	21	83	10	18	1.6	6.6	0.7	252	5907	26	126	8.9	18
75th percentile	1775	4069	466	2103	387	72	247	22	87	11	19	1.7	7.2	0.8	276	6162	28	142	10	19
95th percentile	1837	4212	475	2161	397	75	255	23	90	11	20	1.7	7.4	0.8	286	6321	30	147	11	20

** McDonough WF, Sun SS (1995) The composition of the Earth. Chem Geol 120, 223-253*

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Table 5. LA-ICPMS analyses (and related statistics) obtained on the potential apatite standard (apatite from Phalaborwa GC 701). Analyses done by and at the NGU

(ppm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sr	Pb	Th	U	V
*Norm. Chond.**	*0.349*	*0.904*	*0.137*	*0.674*	*0.219*	*0.083*	*0.293*	*0.053*	*0.363*	*0.081*	*0.236*	*0.036*	*0.237*	*0.036*						
A_GC2701	1889	4390	573	2413	446	84	283	27	99	13	23	1.9	8.2	0.9	326	5855	22	145	11	-
A_GC2701	1839	4470	573	2371	441	84	291	27	100	13	21	2.0	8.4	0.9	322	5993	22	143	11	-
A_GC2701	1850	4350	550	2312	427	82	285	26	100	12	21	1.8	7.8	0.9	311	6087	20	133	11	-
A_GC2701	1970	4704	595	2499	456	88	299	28	104	13	23	1.9	8.4	0.8	336	5999	22	144	11	-
A_GC2701	1910	4601	577	2438	444	85	296	28	102	12	22	1.8	8.4	0.9	327	6145	22	150	11	-
A_GC2701	1844	4503	570	2405	440	84	307	28	101	13	22	1.8	8.7	0.9	325	5912	22	146	11	-
A_GC2701	1646	3936	517	2216	407	76	264	24	91	12	19	1.7	7.0	0.8	282	5934	19	138	11	-
A_GC2701	1446	3592	464	1964	363	68	237	22	82	10	17	1.5	6.3	0.7	262	6030	17	112	9	-
A_GC2701	1822	4315	560	2348	436	81	281	26	98	12	21	1.8	7.8	0.9	316	5970	21	143	11	-
A_GC2701	1873	4436	606	2539	467	89	298	27	103	13	23	1.9	8.4	0.9	332	6109	21	151	11	-
A_GC2701	1674	4053	530	2134	406	79	270	25	91	12	20	1.7	7.7	0.8	284	5948	20	138	11	-
A_GC2701	1698	4140	545	2216	403	80	278	25	95	12	20	1.7	7.7	0.8	299	5977	21	150	12	-
A_GC2701	1300	3161	400	1689	310	60	214	19	70	9	15	1.3	5.4	0.6	222	6198	15	91	7	13
A_GC2701	1348	3314	422	1786	335	66	220	21	76	10	16	1.4	6.1	0.7	235	6283	15	96	7	13
A_GC2701	1358	3295	418	1744	323	62	216	20	71	9	15	1.3	6.1	0.6	230	6223	14	86	6	14
A_GC2701	1380	3447	435	1804	337	65	232	21	76	10	16	1.4	5.8	0.6	247	6336	16	108	8	15
A_GC2701	1334	3223	405	1715	317	60	210	19	71	9	15	1.2	5.8	0.6	224	6326	15	100	7	13
A_GC2701	1438	3495	443	1827	346	68	233	21	77	10	17	1.5	6.0	0.7	251	6316	15	95	7	15
GC2701	1736	3954	496	2104	367	71	252	24	87	11	19	1.6	7.3	0.9	278	6151	19	132	9	16
GC2701	1768	3861	491	2039	373	72	251	23	87	11	19	1.6	7.0	0.8	281	6113	18	126	9	17
GC2701	1834	3932	496	2054	371	74	247	23	88	11	19	1.6	7.0	0.8	279	6116	18	129	9	17
GC2701	1689	3772	476	2012	374	69	246	23	88	11	19	1.5	7.3	0.7	275	6281	18	135	9	16
GC2701	1648	3727	465	1935	361	69	255	23	84	11	18	1.6	6.7	0.7	268	5952	18	132	9	15
GC2701	1689	3749	474	1964	349	68	244	22	82	11	18	1.5	6.5	0.7	268	6046	17	121	8	16
GC2701	1677	3767	462	1978	363	69	253	23	84	11	18	1.5	6.5	0.8	266	6145	19	133	9	15
GC2701	1720	4046	501	2016	378	71	270	25	87	12	21	1.7	7.7	0.8	302	6668	19	123	8	16
GC2701	1860	4542	545	2232	405	82	282	28	104	13	23	1.8	7.8	0.9	317	6134	20	136	9	20
GC2701	2023	4607	579	2404	420	83	302	31	115	15	23	2.0	8.9	0.9	340	6856	21	140	10	19
GC2701	2052	4670	561	2289	410	78	289	29	108	14	23	2.0	8.4	1.0	350	7129	21	135	9	20
GC2701	1974	4578	558	2258	431	85	317	31	103	14	23	1.8	8.0	0.9	345	6661	21	144	10	21
GC2701	1652	3905	494	2130	395	75	250	24	90	11	19	1.6	6.9	0.7	272	5877	19	133	9	17
GC2701	1745	4192	517	2127	384	76	271	25	94	12	20	1.7	7.2	0.8	292	6240	19	132	9	17
GC2701	1574	3836	483	1970	379	72	255	23	86	11	19	1.7	6.5	0.7	267	6071	18	126	9	17
GC2701	1533	3707	458	1927	368	70	245	22	83	11	18	1.5	6.6	0.7	263	6099	17	116	8	16
GC2701	1495	3497	438	1919	353	68	231	22	79	10	17	1.4	6.6	0.6	252	5754	18	119	9	15
GC2701	1394	3233	417	1758	317	61	211	20	77	10	16	1.4	6.1	0.6	240	6668	15	94	7	13
GC2701	1433	3348	413	1761	326	63	217	20	78	10	18	1.5	6.3	0.6	246	6663	15	100	7	13
GC2701	1719	3943	490	2092	387	77	261	25	94	12	22	1.9	7.7	0.8	304	6878	19	130	10	17
GC2701	1423	3302	412	1675	304	63	220	20	76	9	17	1.4	5.8	0.6	244	6994	14	87	6	13
GC2701	1390	3154	385	1687	313	60	206	20	75	9	17	1.4	6.0	0.6	245	6774	14	89	7	13
GC2701	1491	3472	448	1875	350	66	240	23	85	11	19	1.6	6.7	0.7	271	6835	17	108	8	15
GC2701	1535	3546	437	1797	329	64	237	22	84	11	19	1.6	6.5	0.7	267	6977	17	110	7	15
GC2701	1504	3439	436	1808	342	67	237	22	82	10	18	1.5	6.6	0.7	264	6711	16	101	7	15
GC2701	1694	3884	478	2027	370	71	255	24	91	12	21	1.7	7.7	0.8	292	7151	18	127	8	17
GC2701	1757	4006	482	2004	378	69	261	24	91	12	21	1.7	7.3	0.7	299	7648	19	126	8	18
GC2701	1689	3920	469	2028	376	69	256	24	90	11	20	1.7	7.0	0.7	292	7146	18	121	8	17
GC2701	1552	3580	436	1888	357	66	245	22	85	11	19	1.6	6.3	0.8	274	6796	17	112	8	16
GC2701	1825	4034	493	2021	363	75	259	23	87	12	19	1.7	7.7	0.8	287	6618	19	125	9	18
GC2701	1583	3568	422	1750	314	65	227	22	79	10	18	1.4	6.3	0.7	252	6664	16	100	7	19
GC2701	1854	4266	514	2143	390	77	272	26	96	12	20	1.8	7.7	0.9	305	6566	20	138	10	18
GC2701	1684	3833	455	1923	361	71	243	23	86	11	19	1.6	6.9	0.7	280	6703	17	112	8	19
GC2701	1534	3411	413	1709	311	63	224	21	79	10	18	1.4	6.8	0.7	247	6845	16	99	8	18
GC2701	1478	3232	402	1652	293	59	210	20	74	9	17	1.4	6.1	0.6	237	6764	15	95	7	17
GC2701	1548	3445	420	1751	321	62	214	21	78	10	17	1.5	6.3	0.6	251	6786	16	99	7	17
GC2701	1457	3282	399	1701	308	62	218	20	76	10	17	1.4	5.8	0.6	243	6875	16	96	7	17
GC2701	1871	4189	510	2045	374	73	253	24	86	11	19	1.6	7.4	0.8	270	6121	18	127	9	17
GC2701	1707	3966	483	1929	367	70	242	22	82	11	18	1.5	6.9	0.7	260	6092	18	119	9	17
GC2701	1702	4022	495	2005	369	73	250	23	84	11	19	1.6	6.7	0.7	266	6103	19	135	9	16
GC2701	1724	4041	502	2125	378	74	249	23	84	11	19	1.5	6.9	0.8	272	6044	20	135	10	16
GC2701	1750	4036	500	2100	382	75	249	23	88	11	19	1.6	6.4	0.7	270	6164	19	134	9	16
N=60 (N=48 for V)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Sr	Pb	Th	U	V
Average	1660	3865	483	2017	371	72	252	24	87	11	19	1.6	7.0	0.7	279	6392	18	122	8.8	16
2 RSD (%)	23	23	24	23	23	22	22	24	23	23	23	23	24	27	23	13	26	31	35	24
Median	1689	3894	482	2008	369	71	250	23	86	11	19	1.6	6.9	0.7	272	6232	18	126	8.9	16
5th percentile	1358	3232	402	1689	310	60	211	20	74	9	16	1.4	5.8	0.6	235	5910	15	91	6.6	13
25th percentile	1502	3489	436	1807	341	66	232	22	79	10	18	1.5	6.3	0.7	252	6083	16	106	7.6	15
75th percentile	1823	4152	517	2136	397	77	271	25	94	12	21	1.7	7.7	0.8	300	6724	20	135	10	17
95th percentile	1970	4601	577	2415	444	85	299	28	104	13	23	1.9	8.4	0.9	336	7130	22	146	11	20

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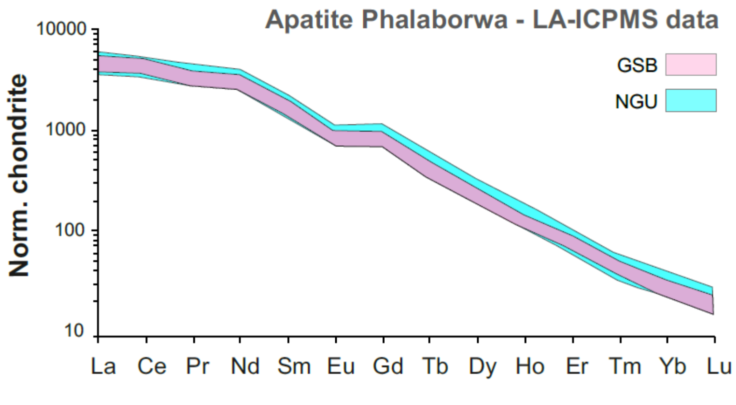

Figure 3. REE patterns corresponding to the LA-ICPMS data obtained at the SGB and the NGU on the potential apatite standard GC 2701 from Phalaborwa. Normalization to the chondrites (McDonough and Sun 1995)

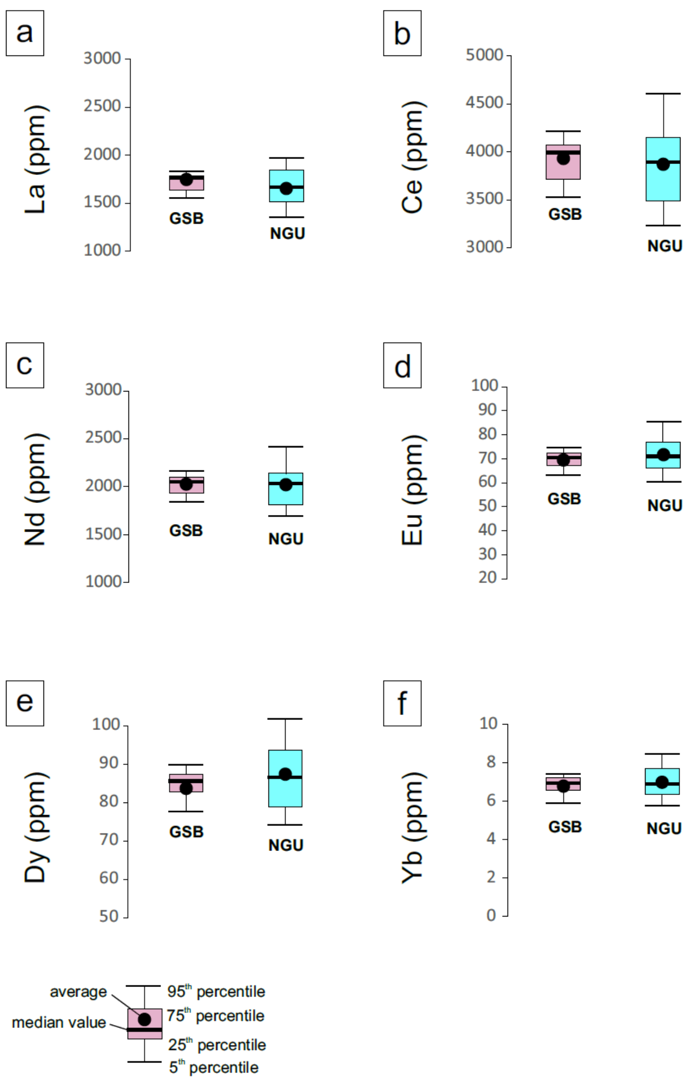

Figure 4. Box plots showing variation of selected REE (LA-ICPMS analyses) for apatite analyzed via the GSB and at the NGU: La content (a); Ce content (b); Nd content (c); Eu content (d); Dy content (e); Yb content (f)

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4. Conclusions and prospects

The studies carried out for this task "Development of a procedure to prepare and analyze phosphate deposits to provide internally consistent geochemical data at a European level" resulted in the production of rather homogeneous sets of data for a single type of analysis, since these analyses were performed in a very limited number of laboratories. These data, obtained on both sedimentary and igneous-related phosphate mineralizations, were provided to WP8 (Annex 1 of the deliverable D4.2 and Annex 8 of the deliverable D4.3) to be integrated into the GeoERA Information Platform.

The work done for this deliverable also emphasized the interest of using the standard BCR-032 for major element analyses of phosphate rocks.

The procedure proposed to harmonize data – considering the present state of knowledge and the availability of standards – is:

- To limit the number of laboratories where the analyses are performed in order to produce large and homogenized datasets
- To stick as much as possible to the list of elements defined for each type of analyses, as described in section 2.1
- To use the standard BCR-032 for bulk rock analyses in order to get reliable data about P and F, which are CRM

The persons involved in this study understand that this constitutes a modest first step to ensure analytical homogeneity and comparability of the data of the phosphate rocks and there is still much work ahead regarding the use of reliable standards. Unfortunately, the infrastructure available for this WP was not sufficient to organize an extensive testing of the potential standard proposed here (apatite from Phalaborwa CG 2701). In the future, well-tested phosphate standards could be more efficiently prepared/obtained to ensure the homogeneity of data. This also applies for bulk rock analyses, considering that the BCR-032 standard does not help for trace elements, which are yet crucial to obtain information about CRM present as traces in phosphate mineralization.

5. References

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