FRAME
FORECASTING AND ASSESSING EUROPE'S STRATEGIC RAW MATERIALS NEEDS

DELIVERABLE D4.2 New mineralogical and geochemical data on samples from phosphate deposits/occurrences

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

Table of Contents

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1. Introduction

This deliverable is devoted to the acquisition of new mineralogical and geochemical data on representative samples from phosphate deposits/occurrences in Europe.

These data are meant to give information about the potential in Critical Raw Materials (CRMs) of phosphate mineralization and the speciation of the CRMs in the studied samples.

2. Methodology

2.1. Samples collection

Phosphate mineralizations are widespread in Europe. They are distributed in rocks from the Archean to the Quaternary. In addition, they belong to various types of deposits, ranging from sedimentary phosphorite to igneous-related phosphate mineralization, comprising also hydrothermal deposits and phosphate concentrations related to elluvial/alluvial deposits.
Therefore, to have the best assessement of their potential regarding CRMs, the samples collected for this task had to be as diverse as possible – i.e. being of different types and different ages – and widely distributed.
Considering the limited number of partners working for this WP, most of the samples have been collected in the collections of the Royal Belgian Institute of Natural Sciences (RBINS), the BGR (Berlin), the Natural History Museum (London), the Museum d'Histoire Naturelle (Paris), the Geological Surveys of Hungary and Serbia. Besides, researchers from the Universities of Madrid, Cadiz (SP), Würzburg (DE), Mons (BE), and Rennes (FR) have provided additional specimens.
Several samples have been collected in the field (Czech Republic, Italy, Belgium) and will be further investigated for D4.3. Preliminary results about a selection of representative samples are nevertheless part of the database produced for D4.2. It is worth mentioning that - overall - the most representative phosphate deposits in Europe are further studied for the deliverable D4.3 "Detailed metallogenic studies of key phosphate deposits".
In total, about ninety samples have been collected (see Annex 1) and investigated regarding their mineralogy and geochemistry. Taken as a whole, this selection of samples illustrates the diversity of phosphate mineralizations in Europe, especially regarding sedimentary phosphate deposits. As such, almost all the European countries are covered, apart from Scandinavia. Deposits located in Norway and Finland will be studied for D4.3. Complementary data about the phosphate mineralizations in Sweden (which are helpful for comparison purposes) will be gathered from the literature later in the course of this project.

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2.2. Mineralogical and geochemical investigations

In order to carry out mineralogical investigations, several analytical techniques were used depending on the needs: petrographic characterizations of the samples were done using scanning electron microscopy (SEM) coupled with energy dispersive spectrometer (EDS) at the RBINS. Raman spectroscopy and X-ray diffraction (XRD) – at the RBINS – were used to give complementary information about the mineralogy of the studied samples. XRD was also helpful to give clues about the abundance of the different minerals constituting the rock. Optical microscopy including cathodoluminescence (performed at the University of Mons, Belgium) was used to further constrain apatite in a few samples.

Figure 1 presents the kind of images and spectra that were obtained on the samples (here, an Ordovician phosphorite from Belgium is given as example). A short petrographic description of the samples and the main mineralogical results (paragenesis observed using the SEM, minerals determined using XRD and peaks identified on Raman spectra) are given in the database presented in Annex 1 and further described here below (in section “3.1. Database”).

Whole rock analyses were carried out (mostly at the University of Brussels, G-Time lab) to obtain precise data about the CRMs content of the samples. A more comprehensive report about mineralogical and geochemical investigations dedicated to occurrences in the Czech Republic is presented in Annex 2.

All these data are also provided in the database (Annex 1) and the most striking results about CRMs are briefly presented in section “First insights into the potential in CRMs of phosphate mineralizations deposits using whole rock chemistry” below.

Figure 1 (next page). Picture illustrating the results obtained on the samples and summarized in the database. Here, the sample Thy1 (occurrence of Ordovician phosphorite in Belgium) is given as example. (A) SEM picture; short petrographic description, as in column O of the database: Conglomerate bed: phosphate nodules (mm-size) with inclusions of garnet in a silty matrix; (B) cathodoluminescence image of a phosphate nodule; (C) XRD pattern of the sample; the semi-quantitative analysis (proportion of minerals in the rock) is reported in column P of the database; (D) Raman spectrum of apatite; the presence of phosphate vibration peaks and fluorescence induced by REE are mentioned in column R of the database.

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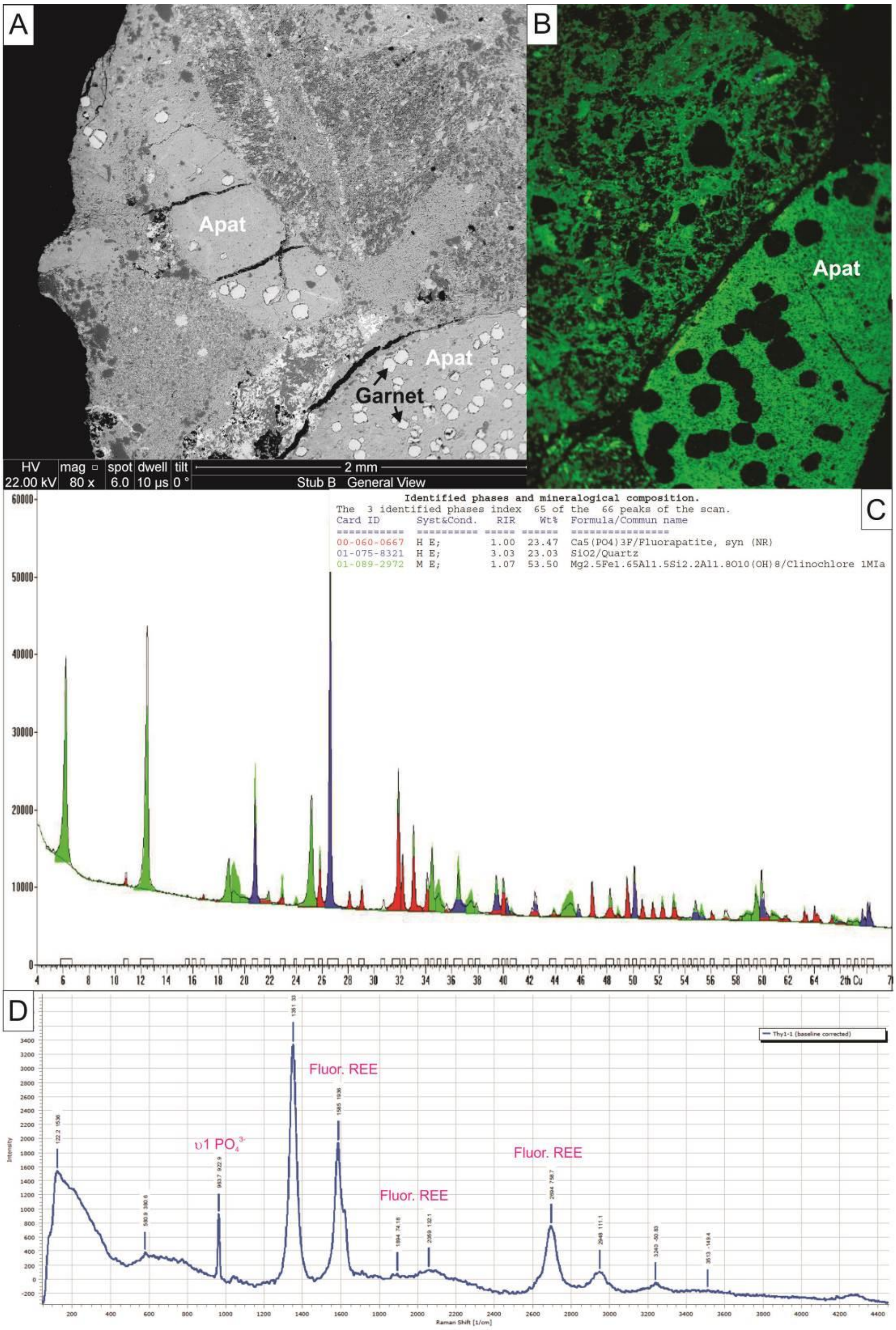

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3. Outcome

3.1. Database

The database, compiled for this second deliverable, presents new mineralogical and geochemical data obtained on about 90 samples representative of ~75 phosphate occurrences and deposits throughout Europe. The Tables 1 to 4 presented below illustrate the work done for phosphate deposits and occurrences in Germany (the complete database is provided as Annex 1).

The database comprises 65 columns, giving information about:

- The coordinates, sample name, origin of the sample (collection, field,…), reference name of the sample in the collection (if applicable) (columns A to E, see Table 1). The locality and country of the deposit/occurrence are given in columns F to H.
- Deposit type name, deposit group name, lithology and geologic event (according to Inspire) are information provided in columns I to L. Columns M and N aims to relate the sample to a larger deposit or district (and to the importance of the latter), according to the data compiled in the database prepared for the deliverable D4.1.
- A short petrographic description of the sample is provided in column O, while the identification of the minerals constituting the rock using XRD (with a semi-quantitative estimation of the mineral proportions) and SEM are given in columns P and Q, respectively. Further information about the determination of Raman peaks are provided in column R.
- Columns S to BN present the whole rock analysis of the sample. Data are given in percent for the major elements (SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, TiO_2, SO_3, Cr_2O_3, LOI, Total; columns S to AF) and in ppm for trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Cd, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, U, Th, sum REE; columns AG to BN).
- Finally, references used to obtain data about the age and type of deposits are presented in column BO.

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Table 1. Structure of the database - part 1. Data for phosphate deposits and occurrences in Germany

	A	B	C	D	E	F	G	H
1	**Longitude**	**Latitude**	**Sample name**	**Collection/collector**	**Ref name in collection (if applicable)**	**Locality**	**Country**	**Code country**
2	7.815646	50.311522	RB7192	RBINS	RB7192	Lahn River, Nassau	Germany	DE
3	7.815646	50.311522	RA4065	RBINS	RA4065	Nassau	Germany	DE
4	12.168612	50.849022	DE-DE6	BGR		Schmirchau, Ronneburg	Germany	DE
5	7.541157	50.630216	RA2332	RBINS	RA2332	Eichen (Hanau), Hesse	Germany	DE
6	11.02255	52.195136	DE-DE7	BGR		Helmstedt	Germany	DE
7	10.859912	52.121738	DE-DE9	BGR		Klein Dahlum	Germany	DE
8	6.074532	50.740972	DE-DE8	BGR		Aachen	Germany	DE
9	8.643034	51.372664	DE-DE11	BGR		Brilon, Hoppeke, Romberg	Germany	DE
10	14.026534	52.308966	DE-DE12	BGR		Rauen, Windmühlenberg	Germany	DE
11	7.260799	51.363474	DE-DE10	BGR		Sprochkövel	Germany	DE
12	11.874271	49.454317	DE-DE1	BGR		Oberpfalz, Amberg, Bavaria	Germany	DE

Table 2. Structure of the database - part 2. Data for phosphate deposits and occurrences in Germany

	I	J	K	L	M	N	O
1	**Deposit type name**	**Deposit group name**	**Lithology**	**Geologic events**	***Name of the district (according to the database prepared for D4.1)***	***Importance of the district (small, medium, large, very large)***	**Description**
2	eluvial placer	residual/surficial	limestone	Tertiary	Lahn Valley Deposits	Small	Microcrystalline matrix and nodules of apatite, including quartz and iron oxides grains on which micrcrystalline concretions of apatite has grown.
3	eluvial placer	residual/surficial	limestone	Tertiary ?	Lahn Valley Deposits	Small	(>)1mm aggregates of microcrystalline matrix of apatite next to aggregates of feldspar
4	Phosphorite	sedimentary	shale	Ordovician			Vesiculated phosphorite with microcrystalline matrix, 50µm anhedral quartz grains, apatite-filled foraminifera and level of mostly homogeneous quartz on the edge of the sample
5	eluvial placer?	residual/surficial?	limestone?	Tertiary ?			Very homogeneous phosphorite with microgranular to microcrystalline texture.
6	Phosphorite	sedimentary	sandstone	Eocene			Well sorted fine-grained sandstone with anhedral 100µm grains of quartz, feldspar and apatite in a microcrystalline apatitic matrix
7	Phosphorite	sedimentary	sand	Pleistocene			200µm grains of quartz, apatite and biotite supporting a microcrystalline phosphate-rich matrix
8	oolitic iron / ironstone	chemical sediment	limestone	Famennian?			300µm Fe-Mn nodules, grains, aggregates and concretions bound together by an imperfect intergranular fill of apatite.
9	Phosphorite	sedimentary	siltstone	Middle Devonian?			Concretion of quite pure apatite including 10µm rounded grains of oxides and clay minerals
10	Phosphorite	sedimentary	silt	Mio-Pleistocene			Quite homogeneous phosphorite with disseminated 50µm anhedral quartz and clay grains into a micrcrystalline apatitic matrix. Abundant
11	oolitic iron / ironstone	chemical sediment	sandstone	Namurian			Laminated phosphorite, with mm-size feldspar aggregates and deforamted 100µm iron sulfides aggregates
12	Phosphorite	sedimentary	sandstone	Cenomanian	Oberpfälz	Small	Very fractured concretion of apatite on a cm-size feldspar core. Fractures filled by iron oxides,

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Table 3. Structure of the database - part 3. Data for phosphate deposits and occurrences in Germany

	P	Q	R
1	**Mineralogy XRD**	**Mineralogy SEM**	**Raman description (only fluorescence : OF, phosphate peak at ~963 cm-1 : v1, or all phosphate peaks + REE-induced fluorescence : REE-F)**
2	Apatite-F 95%, Quartz 4%, Goethite 1%	Apatite, quartz, iron oxides, (manganese oxides)	v1
3	Apatite-F 95%, Muscovite 5%	Apatite, feldspar, iron and titanium oxides	v1
4	Apatite-F 82%, Quartz 14%, Dolomite 5%	Apatite, quartz, iron and copper sulfides	OF, ~v1
5	Apatite-F 97%, Muscovite 3%	Apatite, iron (and titanium) oxides	OF, ~v1
6	Apatite-F 56%, Quartz 44%	Apatite, quartz, feldspar, iron and titanium oxides	OF
7	Apatite-F 62%, Microcline 7% Quartz 22%, Muscovite 9%	Fluorapatite, quartz, biotite, ilmenite, zircon	OF, ~v1
8	Apatite-F 77%, Goethite 23%	Fluorapatite, iron and manganese oxides, rhodochrosite, hornblende, (nepheline)	OF, ~v1
9	Apatite-F 95%, iron oxide 5%	Fluorapatite (+ iron oxides, ilmenite and clay minerals)	OF, v1 ; v1, REE-F
10	Apatite-F 85%, Muscovite 4%, Quartz 11%	Apatite, quartz, clay minerals, iron sulfides	OF
11	Apatite-F 64%, Siderite 36%	Apatite, feldspar, iron sulfides	v1
12	Apatite-F 100%	Apatite, feldspar, iron oxides	~v1

Table 4. Structure of the database - part 4. Data for phosphate deposits and occurrences in Germany

	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	TiO2	SO3	Cr2O3	LOI	total	Sc	V	Cr	Co	Ni	Cu
2	3.94	0.70	1.47	0.17	0.07	51.10	0.00	0.05	39.02	0.05	0.84	0.00	2.72	96.50	1.56	80.56	17.31	2.62	50.70	3.14
3	2.14	1.32	0.35	0.01	0.15	52.06	0.00	0.23	40.71	0.05	0.80	0.00	1.71	97.60	1.42	###	14.06	0.68	47.33	<bdl
4	10.08	0.24	0.34	0.02	0.68	44.09	0.28	0.00	33.82	0.02		0.00	10.40	90.30	5.62	###	10.06	0.91	45.50	###
5	4.25	1.46	0.83	0.09	0.30	48.87	0.01	0.00	36.21	0.05	0.78	0.00	5.18	94.12	2.84	###	54.60	2.90	37.44	4.17
6	30.94	1.49	2.26	0.04	0.47	31.54	0.86	0.49	22.23	0.29		0.00	7.44	67.37	5.94	65.07	66.92	7.78	25.87	<bdl
7	22.29	2.45	4.32	0.06	0.48	34.86	0.45	0.73	23.43	0.15		0.00	9.56	76.73	5.28	101.13	42.33	5.56	34.42	<bdl
8	3.12	1.90	25.54	12.23	0.27	23.20	0.30	0.25	18.01	0.10		0.00	14.37	98.97	3.21	58.20	23.54	###	###	39.00
9	8.63	4.20	9.66	0.44	0.38	40.04	0.22	0.84	28.93	0.44		0.00	6.74	92.06	9.79	###	21.88	11.61	72.45	9.38
10	10.90	2.12	1.68	0.07	0.51	42.11	0.94	0.34	27.46	0.14		0.00	10.51	86.19	3.78	49.72	34.52	12.71	41.78	2.94
11	0.23	0.13	33.46	0.37	1.11	9.15	0.27	0.00	6.87	0.01		0.00	49.70	101.18	0.38	4.71	17.16	9.56	11.93	3.83
12	1.30	0.59	0.67	0.07	0.03	54.45	0.22	0.00	42.20	0.03		0.00	1.87	100.18	1.41	18.72	10.33	6.20	33.78	1.83

	Zn	Rb	Sr	Y	Zr	Nb	Cd	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
2	2124.96	4.64	56.03	9.75	20.52	1.65	4.38	40.38	8.51	11.09	1.69	6.46	1.44	0.31	1.70	0.22	1.34	0.23	0.65
3	989.66	16.93	45.70	5.44	15.29	1.25	0.18	18.98	3.65	7.44	0.98	4.16	0.81	0.12	0.89	0.09	0.58	0.10	0.30
4	28.19	3.39	####	556.14	26.54	0.37	0.00	259.47	208.00	179.48	50.14	236.02	64.69	15.61	76.87	9.96	64.40	13.89	41.95
5	27.28	4.58	483.44	####	20.49	0.82	0.26	164.23	99.73	9.86	21.57	134.34	37.54	14.19	83.52	12.04	90.91	22.13	67.58
6	38.36	29.05	####	25.30	391.81	6.14	0.33	152.22	28.99	71.74	6.27	25.17	4.97	1.11	4.50	0.63	4.10	0.79	2.36
7	29.80	37.92	850.59	118.40	###	2.87	0.08	122.02	116.85	190.01	21.72	87.83	16.86	3.94	19.88	2.55	15.73	3.07	8.76
8	#####	15.94	99.56	27.97	27.04	1.94	###	239.15	16.60	26.75	3.38	12.89	2.42	0.55	2.27	0.34	2.30	0.53	1.56
9	491.49	41.21	94.20	48.09	53.03	6.41	5.53	122.14	29.73	35.10	5.94	26.01	5.47	1.64	6.44	0.88	5.24	1.08	3.03
10	15.38	24.85	####	25.82	48.62	2.57	0.03	172.31	28.83	54.41	4.77	18.96	3.34	0.82	3.93	0.52	3.53	0.67	2.00
11	15.26	0.24	710.44	1.36	1.09	0.12	0.00	145.05	1.09	2.45	0.39	1.41	0.21	0.06	0.21	0.04	0.27	0.04	0.09
12	164.75	3.88	53.21	24.58	7.66	0.50	1.75	30.42	10.87	4.45	1.42	5.43	0.94	0.27	1.52	0.22	1.59	0.37	1.21

	Tm	Yb	Lu	Hf	Ta	W	Pb	Th	U	References
2	0.07	0.55	0.07	1.27	0.09	0.28	3.79	0.51	2.10	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
3	0.03	0.29	0.05	0.50	0.10	0.06	2.28	0.99	2.17	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
4	5.46	###	5.01	0.41	0.02	<bdl	8.58	11.31	###	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
5	8.29	###	7.97	0.64	0.08	0.65	0.71	0.15	25.61	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
6	0.33	2.40	0.34	2.35	0.47	<bdl	12.76	3.99	24.46	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
7	1.16	7.04	1.05	3.82	0.17	<bdl	13.86	2.98	28.09	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
8	0.20	1.22	0.21	0.63	0.13	<bdl	####	1.53	6.16	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
9	0.35	2.40	0.33	1.20	0.39	2.03	9.63	1.36	11.86	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
10	0.28	1.89	0.27	1.14	0.16	<bdl	3.60	1.82	32.88	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
11	0.01	0.09	0.01	0.03	<bdl	<bdl	1.73	0.28	0.15	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D
12	0.14	0.97	0.15	0.18	0.02	<bdl	3.46	0.43	24.65	Geological map of Germany (https://geoviewer.bgr.de/); Notholt AJG, Highley D

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3.2. First insights into the potential in CRMs of phosphate mineralizations deposits using whole rock chemistry

The petrographic observations have shown that - apart in three monazite concentrates (lines 18-20) – there are very few mineral phases bearing massively REEs in the samples investigated. One can therefore consider that a large part of the REE content analysed through whole rock chemistry is contained in apatite, where these elements substitute for Ca in the lattice (e.g., Jarvis et al. 1994[1]; Ihlen et al. 2014[2]).

The first results and preliminary conclusions presented here below only aim to show the main trends observed regarding the chemistry of the samples of interest. It is however necessary to keep in mind that there is still a problem of representativeness of the studied samples (most often, only one or two samples from a single deposit or occurrence were analyzed).

The P and REE contents vary significantly among the samples analyzed. A part of these discrepancies is related to a bias in sample collection (for instance, host-rock containing a few small apatite nodules/grains vs. a "pure" phosphatic nodule or an apatite pegmatitic vein). Taken as a whole, the P content ranges from a few % to a few tens of %, while the REE content doesn't exceed 0.3% (with two notable exceptions, a Jurassic phosphorite in Hungary and an apatite deposit related to lamproites in Spain, showing REE contents up to 7000 ppm). Interesting concentrations of some critical elements are detected in new Early Turonian phosphate occurrences from the Bohemian Cretaceous Basin (Czech Republic), reaching up to ~1500 ppm REE and ~400 ppm Y, related to apatite-rich hardgrounds with monazite inclusions.

Within the group of the sedimentary phosphate mineralizations, which encloses phosphorite, oolitic iron, alluvial and eluvial placers, differences in terms of REE content are observed and can be correlated - to some extent - to the age of the mineralization, as already noted by Emsbo et al. (2015)[3] for the phosphorites in the U.S. The corresponding REE patterns obtained are shown in Figure 2 and the data are presented in Annex 1. Regarding their contents in REEs, phosphorites dated from the Ediacaran, Cambrian, Ordovician are the most interesting, with a total amount of REE being usually above 500 ppm. Same observations can be made for most of the Jurassic sedimentary phosphate deposits. Alluvial and eluvial placers are other mineralizations that show a particular enrichment in phosphate and locally in REEs compared to the primary deposit from which they derive (see Figure 2H for a placer formed during the Quaternary on a phosphorite dated from the Cretaceous in the Mons Basin: 11% P_2O_5 and

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[2] 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

[3] Emsbo P, McLaughlin PI, Breit GN et al. (2015) Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis? Gondwana Res 27, 776-785

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~1800 ppm REE in the alluvial placer vs. 0.8-6.7% P_2O_5 and ~70-500 ppm REE in the primary phosphorite). As expected, the three monazite placers investigated show high P and REE contents (up to 18% P_2O_5 and 35% REE oxides), which are consistent with those observed in other "grey" monazite placers in Europe (e.g., Donnot et al. 1973 [4]; Burnotte et al. 1989[5]).

Regarding igneous-related phosphate mineralizations, P and REE contents vary significantly from one type to another (see Figure 2I for the REE patterns). P mineralization associated with exotic alkaline rocks in Spain is clearly enriched in P and REE, with contents reaching 19% P_2O_5 and 6800 ppm REE, respectively. The rocks from the alkaline complex of Loch Borralan is also quite enriched in REE (288-1046 ppm); however, its P_2O_5 content hardly reaches 2% in the samples investigated. Finally, the granite/pegmatite-related P deposits of the Caceres-Logrosan zone in Spain are particularly poor in REE (7-61 ppm), though being enriched in P (25-41 % P_2O_5).

Another CRM that could be recovered from phosphate mineralization is vanadium. In western USA, a V_2O_5 concentration reaching 0.2% has been documented in phosphate rocks. Through dedicated extraction processes a recovery of 85% of the vanadium is obtainable (Notholt et al. 1979[6]; Notholt 1980[7]).
In our samples, V content is usually low, though its content can reach a few hundred ppm in a few mineralizations (more commonly, the lower Paleozoic and Jurassic phosphate deposits/occurrences).

Of course, the potential in REEs and other CRMs also depends on the size (in terms of tonnes of reserves/resources) of the deposits, which must furthermore be (re-)assessed. More information about the potential in REE, F and V (and possible issues regarding the processing of apatite linked to their U and Th contents) will be investigated in the course of the project thanks to electron microprobe and LA-ICPMS analyses.

[4] Donnot M, Guigues J, Lulzac Y, Magnien A, Parfenoff A, Picot P (1973) Un nouveau type de gisement d'europium: la monazite grise à europium en nodules dans les schistes paléozoïques de Bretagne. Mineralium Deposita 8, 7-18

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[7] Notholt AJG (1980) Economic phosphatic sediments: mode of occurrence and stratigraphical distribution. J Geol Soc London 137, 793-805

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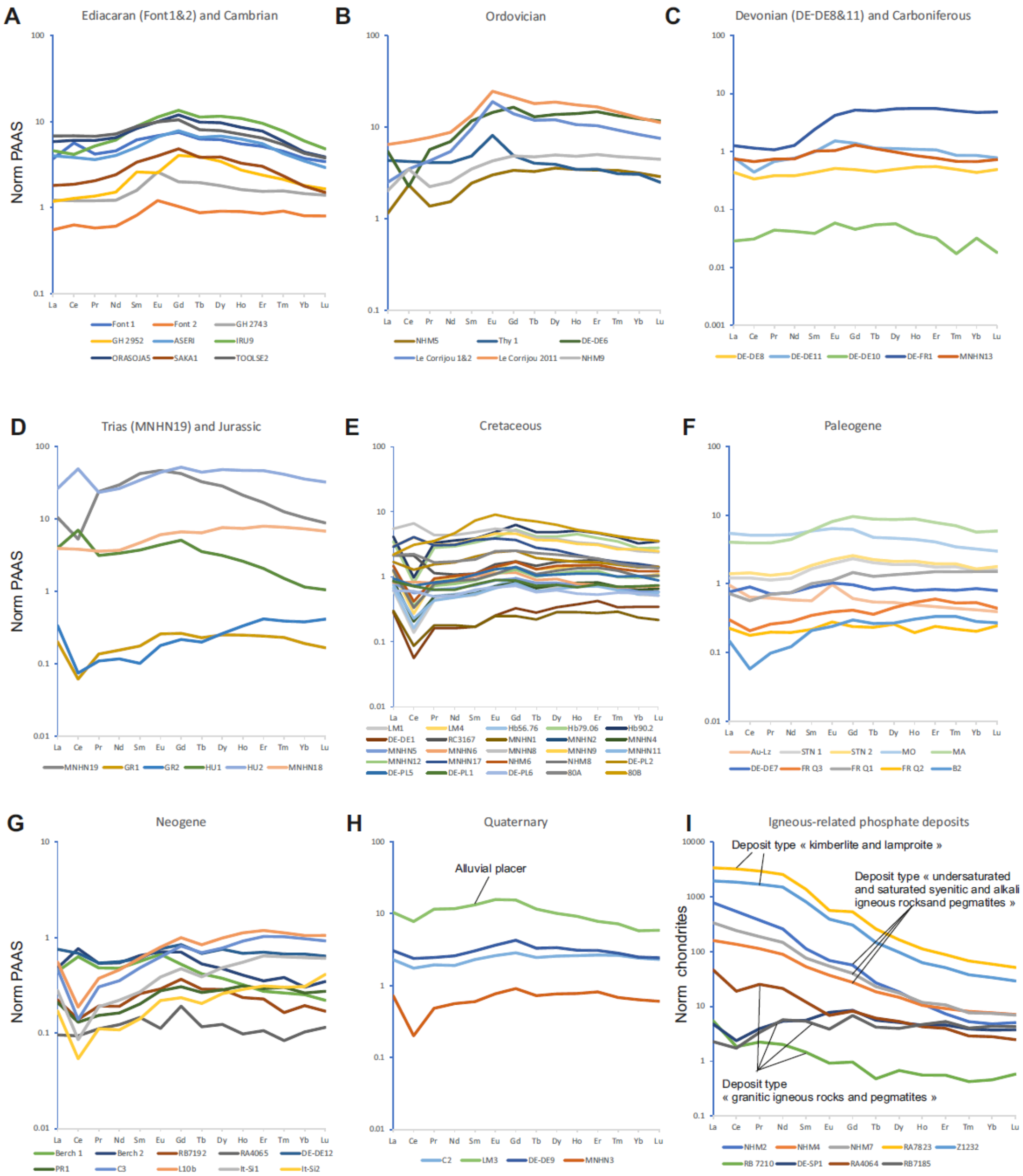

Figure 2. REE patterns of the samples investigated and presented according to their ages/types. (A) to (H): Phosphorites; (I) Igneous-related phosphate deposits/occurrences. Normalized to the Post Archean Australian Shales (Taylor and McLennan, 1985[8]) for the phosphorites, and to chondrites (McDonough and Sun, 1995[9]) for the igneous-related mineralizations. Note the change of scale from one diagram to the other.

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[8] Taylor SR & McLennan SM (1985) The continental crust: its composition and evolution

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3.3. Maps

Five maps have been drawn to illustrate the data presented in the database. The first one (Figure 3) shows the location and the mineral deposit types (according to Inspire) of the phosphate deposits and occurrences studied for this deliverable. This map shows the metallogenic provinces and the genetic type of the phosphate mineralization, which has an incidence on the potential in CRMs of the deposit.

The second map (Figure 4) discriminates the deposits/occurrences investigated for deliverable D4.2 according to their age.

The third map (Figure 5) illustrates the enrichment in REE of the phosphate deposits and occurrences investigated for deliverable D4.2, according to their importance (depicted as an empty circle at the back). Enrichment in REE is considered as follows: High (>X) 1,000; Moderate (>X) 500; Low (>X) 100 ppm; Very low (<X) 100 ppm.

The last two maps (Figures 6 and 7; draft versions of the final maps to prepare for deliverable D4.5) show the mineral deposit type and the age of the phosphate mineralizations presented in the databases provided for deliverables D4.1 and D4.2.

The maps drawn after the database constitute an added value to the database itself, since they allow visualizing at a glance the most striking features concerning phosphate mineralization in Europe. For instance, the maps showing the deposits/occurrences according to their age (Figures 4 and 7) allow considering the regions where important phosphogenetic event occurred. This information can be combined with the new data about enrichment in REE of the sedimentary phosphate mineralization according to its age (Figures 2 and 5).

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[9] McDonough WF and Sun SS (1995) The composition of The Earth. Chem Geol 120: 223-253

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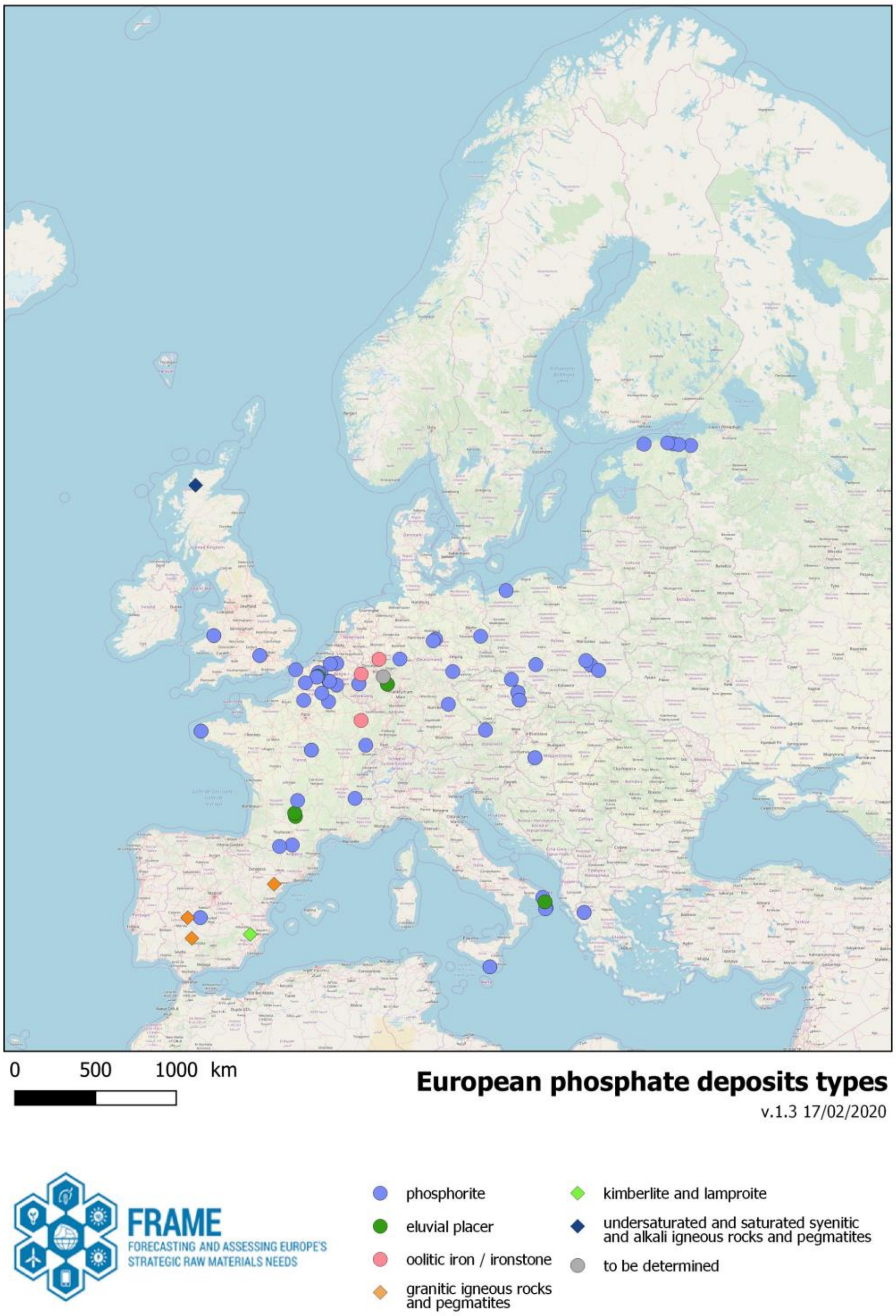

Figure 3. Map illustrating the phosphate deposit types investigated for deliverable D4.2

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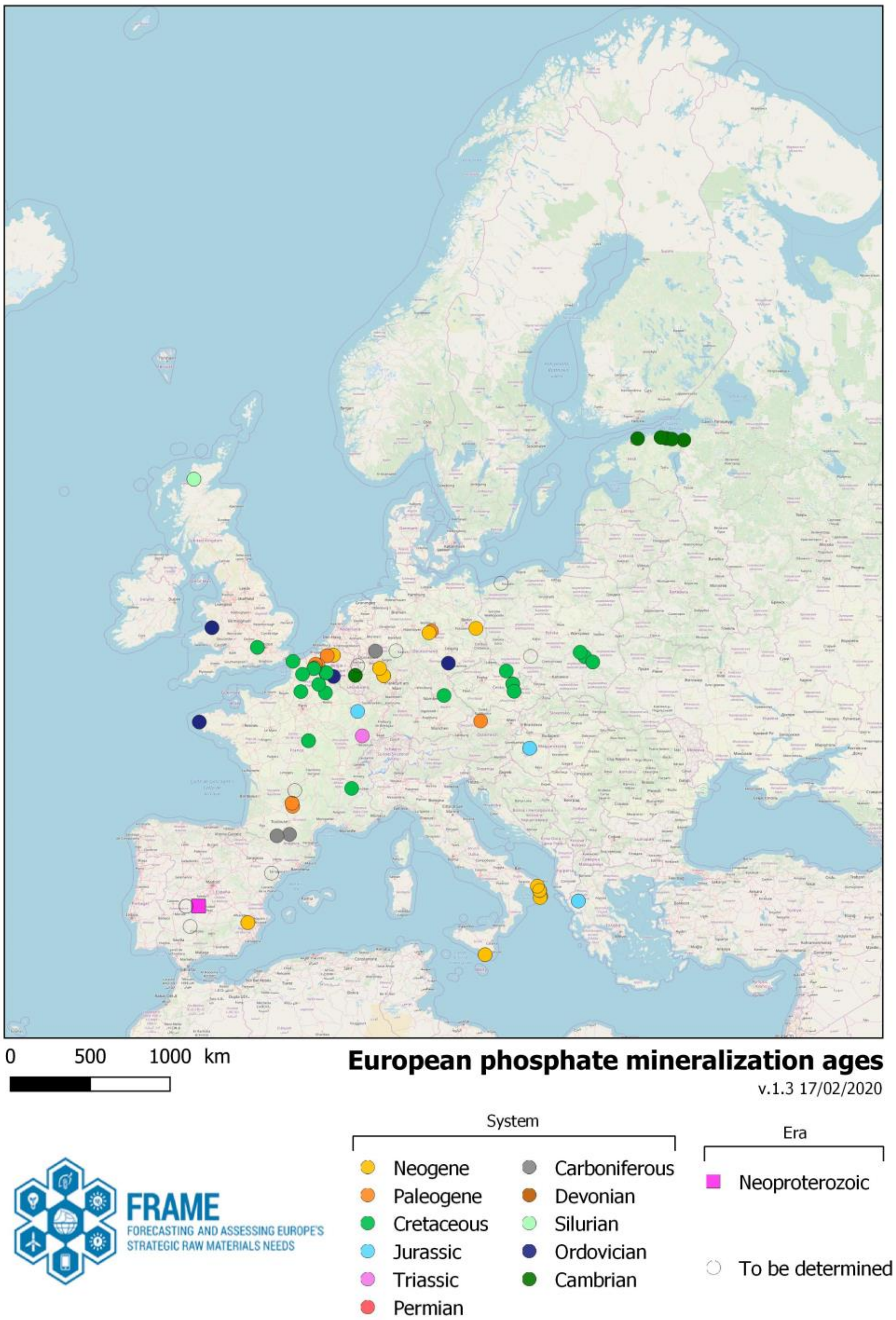

Figure 4. Map illustrating the phosphate deposits/occurrences investigated for deliverable D4.2 according to their age (System/Period for Phanerozoic mineralization, Era for Proterozoic mineralization, and Eon for Archean mineralization)

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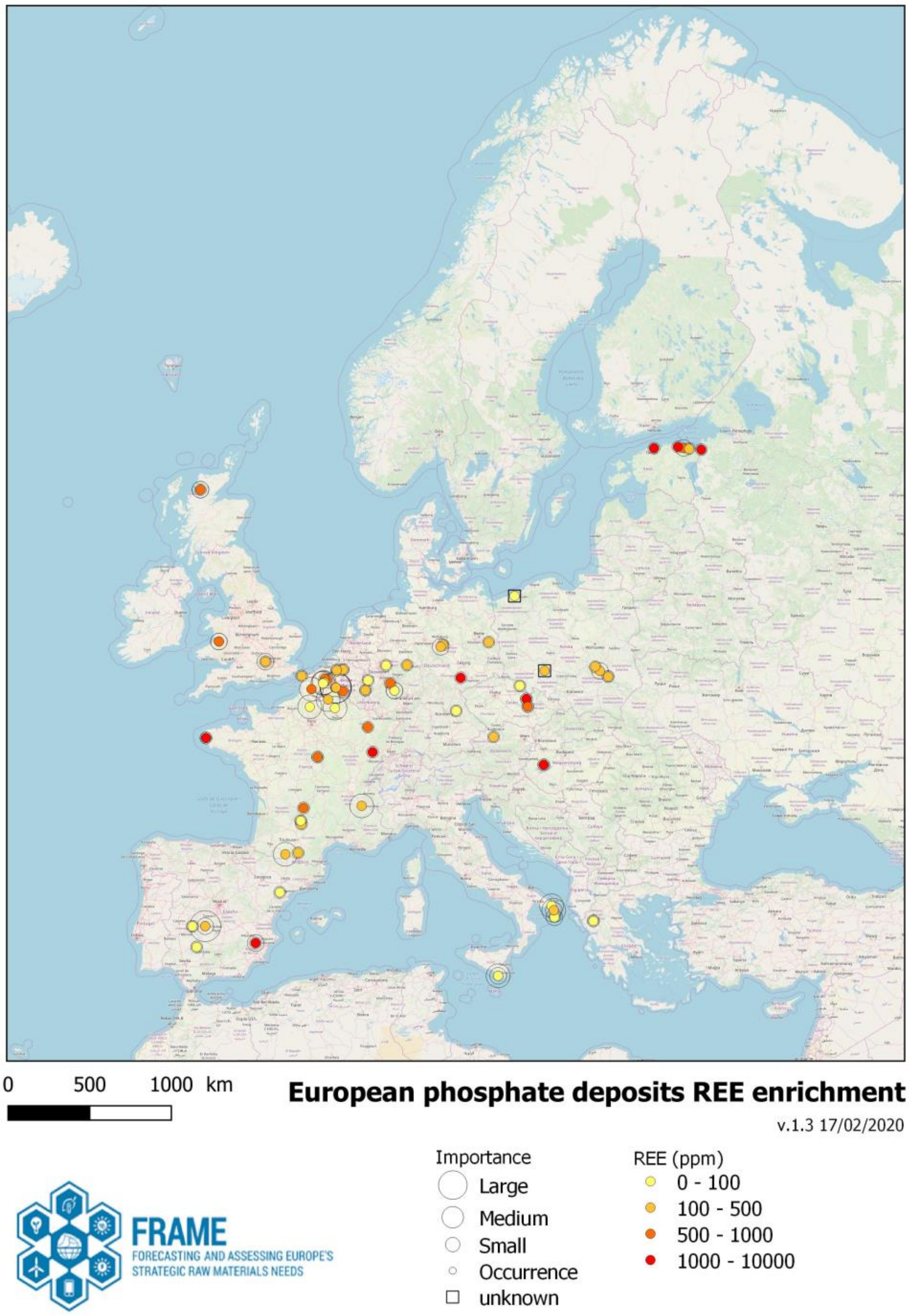

Figure 5. Map illustrating the enrichment in REE of the samples investigated for deliverable D4.2 according to the importance of the phosphate deposit/occurrence it comes from. An average content is considered when several samples come from a single deposit. Enrichment in REE: High (>X) 1,000; Moderate (>X) 500; Low (>X) 100 ppm; Very low (<X) 100 ppm. Deposit importance is indicated by circles of increasing size at the back: Small (>X) 2,000,000; Medium (>X): 20,000,000; Large (>X): 200,000,000; Very large (>X): 2,000,000,000 tonnes

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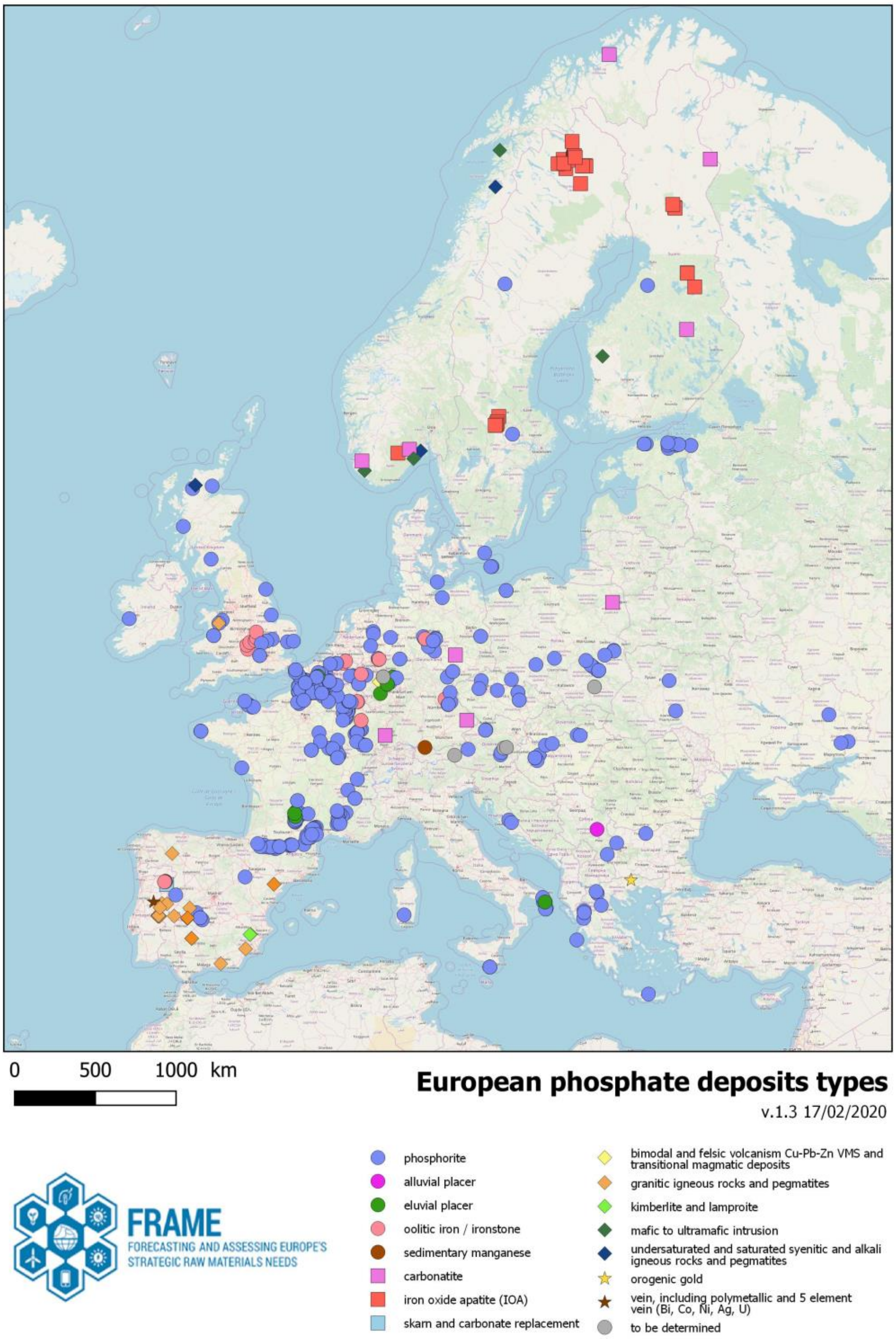

Figure 6. Map illustrating the mineral deposit type of phosphate mineralizations presented in the databases provided for deliverables D4.1 and D4.2. Draft version of the final map to provide for deliverable D4.5

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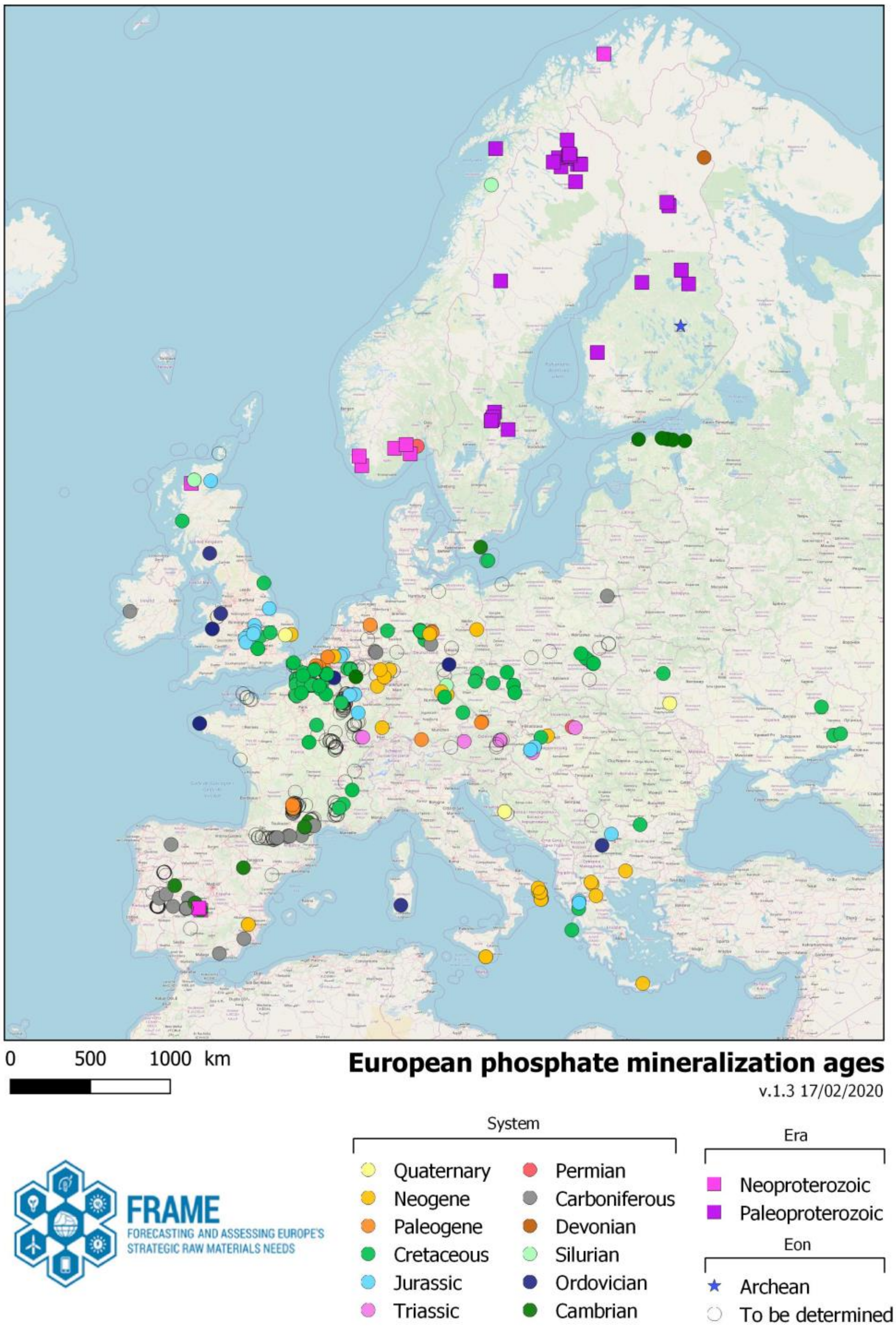

Figure 7. Map illustrating the phosphate mineralizations presented in the databases provided for deliverables D4.1 and D4.2 according to their age (System/Period for Phanerozoic mineralization, Era for Proterozoic mineralization, and Eon for Archean mineralization). Draft version of the final map to provide for deliverable D4.5

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3.4. Conclusions

The potential in REE of sedimentary phosphate deposits is highly dependent on their age and the environment/settings in which they formed (Emsbo et al. 2015 [3]). The study here (Figure 2) suggests that Lower Palaeozoic sedimentary phosphorites (and probably the Jurassic ones, to be confirmed) are the most promising targets regarding their REE content. New areas of interest for CRMs could be regions hosting phosphorites of this age (as shown in maps presented in figures 4 and 7). Of course, such data must be coupled to information about the size of the deposit (when available) to have a more accurate idea of the real potential of the mineralization. At a first glance, the Estonian phosphorites appears as the most promising regarding that issue.
Igneous-related phosphate mineralizations, enriched in REEs compared to the phosphorites, contain an amount of REEs that is highly variable.. From the few results presented in this deliverable, it seems that phosphate mineralizations associated with alkaline magmatism (in a broad sense) are – by far – more interesting regarding the REEs than the granite/pegmatite-related phosphate occurrences/deposits. However, one must highlight the fact that the latter type is more important regarding the potential in P.

In conclusion, the data gathered for this deliverable and the new maps drawn help at identifying new areas of interest for CRMs and constraining the potential of the deposits. The new geochemical data (electron microprobe and LA-ICPMS data) to acquire in the course of this project will help to better constrain these zones.

This project definitely helps in a better understanding of mineralogy, geochemistry and potential of European phosphates for CRM, in addition to paving the way for discovering new phosphate occurrences not reported before (e.g., in Czech Republic).

4. Prospects

In the future, acquisition of LA-ICPMS data will allow investigating apatite chemistry. This will undoubtedly lead to a better understanding of the CRMs distribution and enrichment within phosphate deposits.
The combination of these new data with the dataset issued from deliverable D4.3 “Detailed metallogenic studies of key phosphate deposits” will help to highlight the potential of these deposits regarding the CRMs.
Finally, these data will be integrated into existing databases, such as Minerals4EU, the European Union Raw Materials Knowledge Base (EURMKB), SRT RM1, and the GeoERA Information Platform.

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