Mineral processing by-products characterization and Critical Raw Materials availability of chromite ores from Vourinos mines, Greece

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Abstract

In the present study, mineralogical and chemical characterization of ten samples (X1-X10) was made for chromite ore-hosting ultramafic rock samples collected from the Xerolivado mine of Vourinos. Their characterization is aiming to their evaluation regarding the possibility of upgrading their physicochemical properties using various treatment methods (e.g. thermal) under the frame of the circular economy. Secondary serpentine and primary olivine were the main mineral phases observed in all samples. Other minerals present in the samples in minor amounts are chromite, magnetite, sulphides and metal alloys. All samples have undergone severe alteration and their serpentinization degree is rather high. Chemically, the composition range found for the samples is: SiO_2 36.4-38.29 wt.%, Al_2O_3 0.02-0.05 wt.%, Fe_2O_3 5.69-6.45 wt.%, MnO 0.10-0.11 wt.%, MgO 46.93-49.94 wt.%, CaO 0.11-0.18 wt.%, P_2O_5 0.02-0.04 wt.% and Cr 1695-1993 ppm. K_2O, TiO_2 and Na_2O were found below the detection limit of the method for all samples. These rocks -that are considered the by-products of chromite mining processes- can be potentially transformed into raw materials. For this consideration, they have to be subjected to suitable –thermal- treatment procedures for the upgrade of their physicochemical characteristics. Critical Raw Materials availability in the Vourinos mining district is not yet clarified. Platinum Group Elements and Au along with Ga, V and Co might be considered as possible exploration targets.

Introduction

It is well known that the EU has many and uncharacterized and unexplored deposits; however, the existing economic and regulatory framework, combined with growing land use competition limits the exploitation. Secondary supplies can reduce the demand for primary materials. However, for many materials very little recycling and recovery occurs. In most of the cases, it cannot completely replace primary supply even for materials with high recycling rates. Therefore, much of Europe's industry and economy is reliant on international markets to provide access to essential raw materials.

On this basis, a list of Critical Raw Materials (CRMs) is made by EU since 2011 (updated in 2014 and 2017)[1] taking into account mainly the supply risk and the economic importance of raw materials. Chromium was considered as a CRM in the 2011 and 2014 lists, but, in the 2017 was not reported as a CRM because it marginally did not pass the supply risk threshold (1.0), having a value of ~0.95 (although it is the 3rd most important economic raw material; the economic importance threshold is 2.8, chromium value ~6.8). Nevertheless, its high economic importance for the EU is undoubtable and the supply risk remains high. Additionally, chromite ores are often reported having significant concentrations of Platinum Group Minerals (PGMs) which are reported as CRMs constantly in the EU reports (in 2017 list they easily passed both thresholds: they had economic importance value of ~5.0 and supply risk of ~2.6).

The chief source of chromium is in the mineral chromite. Chromite (Cr-spinel) is found in economic and sub-economic levels in chromitite (~20-70% modal chromite), olivine chromitite (~12-20% modal), and chromitiferous dunite (~6-12% modal chromite). The range of Cr_2O_3 content within chromite varies from levels less than 25% to more than 70%. High levels of Cr_2O_3 in chromite can be processed to metallurgical-grade level (for ferrochrome production) and lower levels for refractory uses. The source rocks of economic or sub-economic chrome ores are ultramafic tectonite hosts within ophiolitic sections or mafic to ultramafic rocks in layered igneous intrusions. Within Europe, ophiolitic hosted ores have been economically exploited in the past from upper mantle host rock (metamorphic tectonite); potential refractory grade ores within layered igneous intrusions occur in Greenland and though low in Cr_2O_3 promise economic exploitation. Chromite itself can be used as a refractory material due to its high melting point, thermal stability and conductivity. The main chromite refining products are metallic chromium, and ferrochrome, used for special steel manufacture, chromite foundry sand, used for foundry casting and chromate, used in the chemical industry.

Mining and processing of chromite ores in the EU has faced several problems throughout the last decades: relatively low enrichment effectiveness, big cut-off, old tailings handling and production of large amounts of by-products and wastes. Chromite ores are found in ultramafic environments; their separation by-products (gangue) are their host rocks: peridotites. Gangue peridotites are mainly dunites and/or (to a lesser extend) hartzburgites and their mineralogical composition is olivine and pyroxenes + olivine respectively. Olivine is already classified as an industrial mineral with many known uses (e.g. slag conditioner, refractory material, neutralization of acidic waters, building material), and potential for carbon capture. Thus, olivine gangue could potentially become an economic by-product if it wasn't for serpentinization: these ultramafic rocks, have in most cases undergone a series of tectonic and geochemical events and are found altered. The alteration process is called serpentinization and, mineralogical, it means that primary minerals (olivine for dunites and pyroxenes+olivine for hartzburgites) are altered partially -or even totally- to the serpentine group of minerals (antigorite, lizardite, chrysotile). This alteration affects negatively the physiochemical and mechanical properties of the rocks and limits drastically their potentiality for applications and uses and thus, no beneficiation can be made of them.

For the beneficiation of these by-products, thermal treatment (at variable conditions) could be applied in order to achieve recrystallization of serpentine to its primary mineral phase (olivine), thus upgrading the physicochemical properties of the by-products and –depending on the effectiveness of the treatment- leading to the production of a material similar with olivine and its uses. Under this perspective, the scope of this paper is to provide data about the mineralogy and the chemistry of these by-products that could be useful for determining the treatment conditions applied in order to achieve their upgrade. Regarding the availability of Critical Raw Materials of the Vourinos chromite ores, this paper presents data about the potentiality of exploitation of Platinum Group Elements (PGE) and Au.

Experimental procedures

For the current study, ten (10) ultramafic rock samples from the Xerolivado-Skoumtsa chromite mine (Vourinos, Greece) were collected. For the mineralogical investigation of the samples, polished-thin sections were examined under transmitted and reflected light and by means of Scanning Electron Microscopy (SEM). During SEM investigation, back-scattered electron (BSE) images of the samples were acquired.

For the determination of the whole rock chemistry of the samples, chemical characterization by X-Ray Fluorescence (XRF), as well as the determination of the loss on ignition (LOI) was performed. For the application of the XRF method, each sample was crushed and grinded (<73μm) and mixed with a binder. The mixture (~10g) was poured into a pressing die and the samples were pressed at a pressure of 15T.

Results and discussion

The macroscopic examination of the samples showed that samples are serpentinized in high degree (Figures 1 and 2). This observation was confirmed by the microscopic study of samples: optical and electronic microscopy examinations showed that in all samples the alteration of olivine to serpentine was very high and only separate olivine relics could be observed in some parts of the studied thin-polished sections. This result is in good agreement with Filippidis[2] and Tzamos[3] that have reported serpentinization degrees 92-93% and 80-100% respectively for ultramafic samples from the same mine. Their results are presented in Table 1. Secondary serpentine and primary olivine were the main mineral phases observed in all samples. Other minerals present in the samples in minor amounts are chromite, magnetite, sulphides and metal alloys.

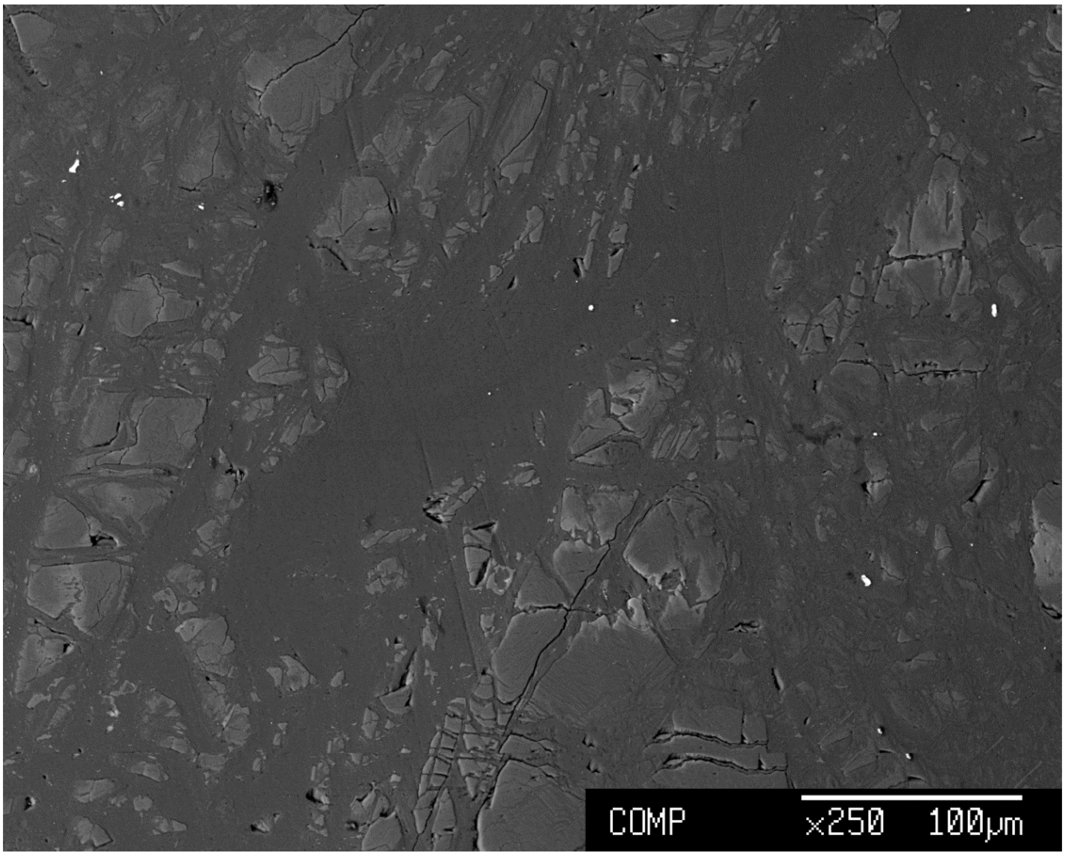

Figure 1. Back-scattered electron image from scanning electron microscope revealing the high degree of serpentinization (sample X3).

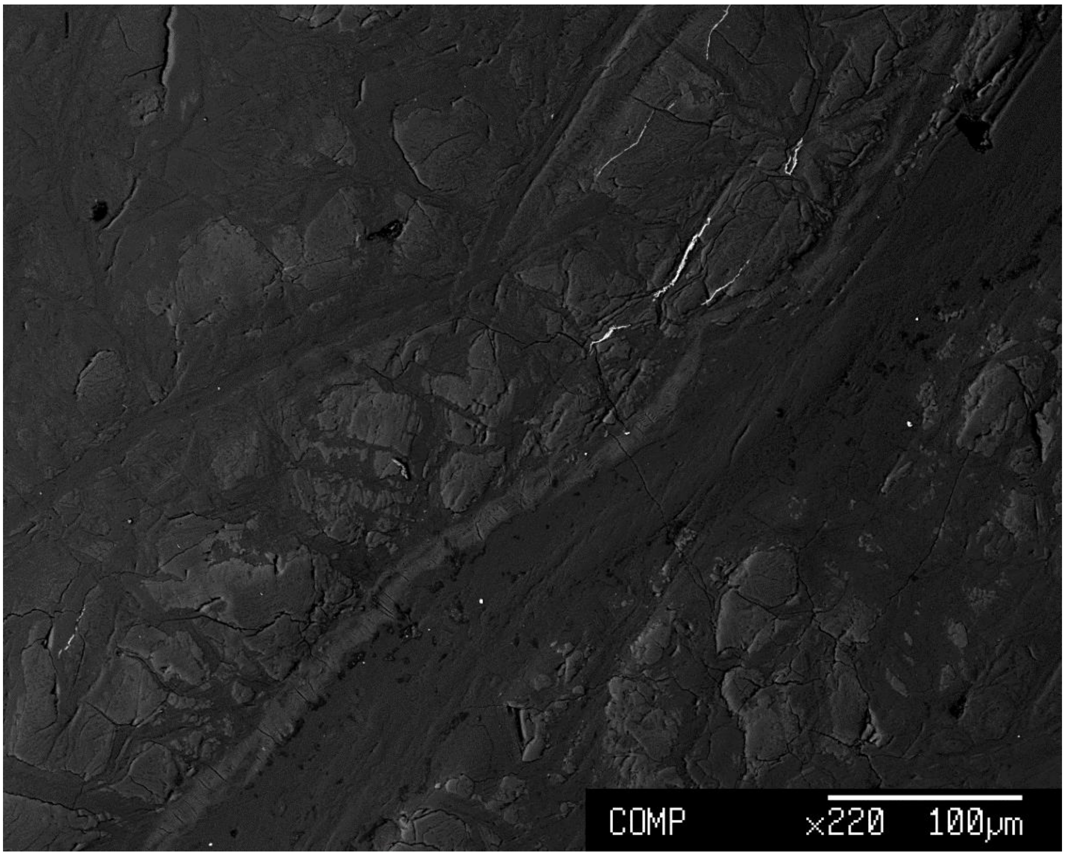

Figure 2. Back-scattered electron image from scanning electron microscope revealing the high degree of serpentinization (sample X5).

Table 1. Mineralogical content and serpentinization degree of samples from Xerolivado, Vourinos.

Sample	Mineralogical composition (v/v %)			Serpentinization degree (%)
	Serpentine	Olivine	Chromite	
D1/717*	92.40	6.20	1.40	93.71
D2/719*	81.50	0.00	18.50	100.00
D2-3/717A*	96.40	0.00	3.60	100.00
D3/717A*	83.00	1.00	16.00	98.81
D3-4/717A*	96.00	0.80	3.20	99.17
D4/717A*	97.00	0.80	2.20	99.18
D4-5/717A*	95.40	0.60	4.00	99.38
D5/717*	94.00	2.60	3.40	97.31
D5-6/717*	81.40	14.80	3.80	84.62
D6/717*	78.40	19.60	2.00	80.00
D7/880**	86.45	12.69	0.86	87.20
D7-8/880**	91.87	7.05	1.08	92.87
D8-9/885**	91.96	7.22	0.81	92.72
D9-10/885**	91.41	7.90	0.69	92.05
D10-11/885**	91.99	6.69	1.32	93.22
D11-12/885**	91.20	7.81	0.99	92.11
D12-13/885**	91.30	6.88	1.82	93.00

*from Tzamos[3]
**from Filippidis[2]

The chemical composition of the samples is presented in Table 2. For the elements analysed, the following range was determined: SiO_2 36.4-38.29 wt.%, Al_2O_3 0.02-0.05 wt.%, Fe_2O_3 5.69-6.45 wt.%, MnO 0.10-0.11 wt.%, MgO 46.93-49.94 wt.%, CaO 0.11-0.18 wt.%, P_2O_5 0.02-0.04 wt.% and Cr 1695-1993 ppm. K_2O, TiO_2 and Na_2O were found below the detection limit of the method for all samples. The loss on ignition of the samples ranges from 5.98 to 9.83% by weight, while this value in serpentine minerals range from 12-13.5% by weight[4], thus, the chemical analyses agree with the mineralogical observations.

In Table 3, the range of chemical compositions of ultramafic rocks from various areas of Vourinos (Voidolakkos, Konivos, Chromion, Rizo and Xerolivado) is presented (data from Tzamos[3] and references therein). Samples from all areas are hartzburgites (primary mineralogical composition of olivine and pyroxenes) except from the Xerolivado locality (dunite). Results presented in this paper are in good agreement with results from Table 3 and more particularly the results from the same sampling area. Hartzburgites –as expected- present a higher content in silica. Also, the loss on ignition results from hartzburgites is significantly lower than that of dunites, implying lower alteration degrees.

For the evaluation of the PGE potential of the Vourinos mining district, we collected data from published papers which is presented in Table 4. The ΣPGE+Au concentrations of the Vourinos mining district localities range between 66.35 (Aetoraches) and 200.75 ppb (Koursoumia).

Table 2. Chemical composition of major and minor elements for the studied samples.

Sample		X1	X2	X3	X4	X5	X6	X7	X8	X9	X10
SiO_2	(wt.%)	37.51	36.40	37.92	37.07	36.98	38.29	37.38	37.12	37.90	37.57
TiO_2	(wt.%)	bdl*	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al_2O_3	(wt.%)	0.05	0.02	0.02	0.05	0.02	0.02	0.04	0.02	0.03	0.04
Fe_2O_3	(wt.%)	5.69	6.21	6.36	5.78	6.3	6.45	5.9	6.19	6.18	5.93
MnO	(wt.%)	0.10	0.11	0.11	0.10	0.11	0.11	0.10	0.11	0.10	0.10
MgO	(wt.%)	49.34	47.04	47.02	49.93	46.93	47.73	48.56	47.60	48.07	48.81
CaO	(wt.%)	0.11	0.15	0.18	0.11	0.14	0.17	0.12	0.15	0.16	0.12
Na_2O	(wt.%)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K_2O	(wt.%)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
P_2O_5	(wt.%)	0.02	0.03	0.04	0.02	0.03	0.04	0.02	0.03	0.03	0.03
LOI**	(wt.%)	6.89	9.83	8.19	5.98	8.98	7.82	7.35	9.01	6.93	7.18
Total	(wt.%)	99.61	99.79	99.84	98.94	99.49	100.63	99.37	100.23	99.30	99.68
Cr	ppm	1964	1695	1731	1993	1718	1903	1885	1750	1889	1701

*bdl=below detection limit
**LOI=loss on ignition

Table 3. Range of chemical composition of major and minor elements from ultramafic rocks of Vourinos.

Locality (samples analysed) Lithotype		Voidolakkos (20) Hartzburgites		Konivos (5) Hartzburgites		Chromion (10) Hartzburgites		Rizo (12) Hartzburgites		Xerolivado (5) Dunites	
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
SiO_2	(wt.%)	43.47	46.01	41.71	44.92	40.64	42.78	38.51	42.78	36.05	38.10
TiO_2	(wt.%)	0.003	0.009	0.010	0.010	0.010	0.010	0.010	0.010	0.000	0.080
Al_2O_3	(wt.%)	0.00	0.27	0.38	0.57	0.19	0.57	0.38	0.57	0.02	0.31
Fe_2O_3	(wt.%)			8.00	8.58	8.29	8.72	8.00	8.29	5.75	8.33
FeO	(wt.%)	8.21	9.93								
MnO	(wt.%)	0.12	0.15	0.13	0.14	0.09	0.12	0.12	0.13	0.08	0.11
MgO	(wt.%)	42.53	46.66	43.11	44.76	43.52	46.42	43.11	46.42	46.50	49.84
CaO	(wt.%)	0.29	1.16	0.56	0.98	0.56	1.32	0.28	0.84	0.11	0.18
Na_2O	(wt.%)	0.00	0.01	0.03	0.03	0.01	0.04	0.01	0.03	0.00	0.00
K_2O	(wt.%)	0.00	0.01	0.00	0.01	0.01	0.02	0.00	0.02	0.00	0.00
P_2O_5	(wt.%)	0.00	0.01	n/a**	n/a	n/a	n/a	n/a	n/a	0.02	0.04
LOI*	(wt.%)	n/a	n/a	1.16	2.80	1.21	3.09	2.14	3.91	1.29	9.93
Cr	ppm	1964	1695	1731	1993	1718	1903	1885	1750	1889	1701

*LOI=loss on ignition
**n/a=not analysed

Table 4. PGE+Au average concentrations from various localities of Vourinos mining district (values in ppb).

Locality	Os	Ir	Ru	Rh	Pt	Pd	Au	ΣPGE+Au
Xerolivado*	29	31	56	15	3.5	1.2	2.2	137.90
Xerolivado**	20	19.9	57	4.6	2.5	1	0.25	105.25
Xerolivado***	1.7	22.98	59	5.21	8.3	9.8	14.95	121.94
Southern Vourinos*	30	18	52	9	10.4	3.5	3	125.90
Aetoraches**	5	13.2	41	3.4	2.5	1	0.25	66.35
Rizo**	5	7.5	57	7.5	10	1	0.25	88.25
Koursoumia**	5	10.5	171	10.5	2.5	1	0.25	200.75
Voidolakkos**	20	16.2	115	5.77	2.5	21	0.25	180.72
Voidolakkos*	23	16	75	11	5.5	6.1	3.4	140.00
Northern Vourinos*	11	11	50	12	4.2	2.2	2.2	92.6

*from Konstantopoulou and Economou-Eliopoulos[5]
**from Kapsiotis[6]
***from Tzamos et al.[7]

Conclusions

The conclusions of the present study can be summarized to the following:

- The mineralogical and chemical composition of the samples reveal that they have undergone severe alteration (serpentinization) which resulted to the recrystallization of primary minerals (mainly olivine) into the secondary mineral serpentine.

- Based on the mineralogical observations, the most possible serpentinization chemical reaction that took place during ocean floor metamorphism was:

$$2\ Mg_2SiO_4\ \text{(forsterite)} + 3\ H_2O \rightarrow Mg_3Si_2O_5(OH)_4\ \text{(serpentine)} + Mg(OH)_2\ \text{(brucite)}$$

- Considering that ultramafic rocks are the by-products of the chromite ore extraction and mineral processing, for the upgrade of their physicochemical characteristics in order to reconsider them as useful raw materials and increase their circularity in the economy, thermal treatment should be applied. Thermal treatment is expected to lead to the decomposing of serpentine and to the forming of "second generation" olivine, thus upgrading the properties of this material.

- The potential of Critical Raw Materials of the Vourinos mining district is not yet clarified. Data regarding the PGE+Au concentrations in the area is limited and mainly acquired for scientific reasons rather than for exploration-production reasons. Other potential CRMs of the area include Ga, V and Co, with ongoing research on these elements having started rather recently (Tzamos[3]).

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