FIRST OCCURRENCES OF NI-PHOSPHIDES IN CHROMITITES FROM THE OPHIOLITE COMPLEXES OF ALAPAEVSK, RUSSIA AND GERAKINI-ORMYLIA, GREECE

Alkiviadis Sideridis*, Federica Zaccarini,✉, Tassos Grammatikopoulos***, Pavlos Tsitsanis*, Basilios Tsikouras°, Evgeny Pushkarev°°, Giorgio Garuti**** and **Konstantin Hatzipanagiotou***

* *Department of Geology, Section of Earth Materials, University of Patras, Greece.*
** *Department of Applied Geological Sciences and Geophysics, University of Leoben, Austria.*
*** *SGS Canada Inc., Lakefield, Ontario, Canada.*
° *Faculty of Science, Physical and Geological Sciences, Universiti Brunei Darussalam, Gadong, Brunei Darussalam.*
°° *Institute of Geology and Geochemistry, Ural Division of Russian Academy of Sciences, Ekaterinburg, Russia.*
✉ *Corresponding author, email: federica.zaccarini@unileoben.ac.at*

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ABSTRACT

Small grains, approximately 15 μm in size, of a Ni-phosphide, have been discovered in two chromite deposits associated with altered mantle peridotite: (i) in Bakanov Kluch, Alapaesk ophiolite, Russia and (ii) in Agios Dimitrios, Gerakini-Ormylia ophiolite, Greece. On the basis of the chromite composition, both the Bakanov Kluch and the Agios Dimitrios chromitites are classified as Cr-rich chromitites with a boninitic affinity. Under reflected-light optical microscope, the Ni-phosphides are yellow in colour and isotropic. Their calculated stoichiometry, based on the average of 20 electron microprobe analyses, approaches the ideal formula $(Ni,Fe)_5P$. One essential condition for the formation of terrestrial minerals in the Ni-Fe-P system is the presence of a highly reducing local geochemical environment. Serpentinization of oceanic peridotites produces reducing fluids containing dissolved H_2 resulting from the reduction of H_2O. Therefore, we suggest that the $(Ni,Fe)_5P$ from the Alapaevsk and Gerakini-Ormylia were very likely formed after the precipitation of the host chromitites during the serpentinization process at low temperatures. Nickel may have been released during the alteration of olivine and phosphorous may represent an alteration product of apatite. The $(Ni,Fe)_5P$ grains analyzed in the present work contain the highest value of Ni and they are characterized by the highest Ni to P ratio reported so far from similar minerals. Their stoichiometry indicates that the $(Ni,Fe)_5P$ grains found in the Alapaevsk and Gerakini-Ormylia chromitites represent a new mineral species. However, their small size prevents the acquisition of crystallographic data to support this assumption.

INTRODUCTION

Phosphides are uncommon minerals and, up to now, only ten natural phases have been described in the Ni-Fe-P system (Table 1). In particular, five minerals with Fe > Ni, namely allabogdanite $(Fe,Ni)_2P$, barringerite $(Fe,Ni)_2P$, murashkoite FeP, schreibersite $(Fe,Ni)_3P$, and zuktamrurite FeP_2, and five minerals with Ni > Fe, including halamishite Ni_5P_4, melliniite $(Ni,Fe)_4P$, negevite NiP_2, nickelphosphide $(Ni,Fe)_3P$, and transjordanite Ni_2P have been officially accepted by the International Mineralogical Association (IMA) (Buseck, 1969; Britvin et al., 1999; 2002; 2013; 2104; 2015; Skala and Cisarova, 2005; Pratesi et al., 2006). Schreibersite was first described from an iron meteorite in 1847 (Skala and Cisarova, 2005 and references therein). Barringerite and nickelphosphide were discovered in the last century in a nickel-iron meteorite and in an iron meteorite, respectively (Buseck, 1969; Britvin et al., 1999). Subsequently, allabogdanite and melliniite were both documented in an iron meteorite and in an acapulcoite achondrite (Britvin et al., 2002; Pratesi et al., 2006). Only recently, the new minerals murashkoite, zuktamrurite, halamishite, negevite and transjordanite have been described in terrestrial metasedimentary rocks located in the northern Negev Desert, Israel and Transjordan Plateau, Jordan (Britvin et al., 2013; 2014; 2015). Schreibersite was also reported in reduced differentiated lenses in basalts and in hydrothermal replacement in petrified wood (http://mindat.org) and associated with native iron from the Disko Island, Greenland (Pedersen, 1981). Barringerite was documented in a garnet peridotite from China (Hu et al., 2005).

In this paper, we report an additional terrestrial occurrence of Ni-phosphides, which have been found, for the first time, in chromitites associated with mantle peridotites from the Alapaevsk and Gerakini-Ormylia ophiolite complexes, located in Russia and Greece, respectively. The results are used to provide new insights into the origin of this uncommon mineral, associated with mantle-derived rocks.

GEOLOGICAL BACKGROUND AND SAMPLES PROVENANCE

The Paleozoic Alapaevsk ophiolite is located in the Ural Orogen, Russia, east of the Main Uralian Fault, approximately 150 km northeast from Ekaterinburg (Fig. 1A) and 15 km north of the city of Neivo-Shaitanka (Fig. 1B). It consists mainly of harzburgites, and minor lherzolites, dunites, chromitites and gabbros. The Alapaevsk complex is in tectonic contact with an island arc sequence composed of metavolcanic and sedimentary rocks of Devonian-Carboniferous age (Fig. 1B). A Later Paleozoic collisional granite massif intrudes the Proterozoic metamorphic rocks westward of the Alapaevsk massif (Fig. 1B).

More than 80 small chromite deposits were discovered and mined from the end of the 19th century to the second half of the 20th century. The mining activity yielded more than 70 thousand tons of ore. Two types of chromite ore have been reported in the Alapaevsk complex: a Cr-rich and an Al-rich (Shilova et al., 1977; Chashchukhin, et al., 2002; 2012; Zaccarini et al., 2016b). The studied samples were collected from the Bakanov Kluch Cr-rich chromite deposit,

Table 1 - IMA accepted minerals in the Ni-Fe-P system.

Mineral	*Ideal formula*	*Crystal system*	*Host rock*	*Year of discovery*	*References*
Fe-dominant					
Allabogdanite	$(Fe,Ni)_2P$	Orthorhombic	Iron meteorite	2002	Britvin et al., 2002
Barringerite	$(Fe,Ni)_2P$	Hexagonal	Nickel-iron meteorite	1969	Buseck, 1969
Murashkoite	FeP	Orthorhombic	Metasediments	2013	Britvin et al., 2013; 2015
Schreibersite	$(Fe,Ni)_3P$	Tetragonal	Iron meteorite	1847	Skála and Císařová, 2005
Zuktamrurite	FeP_2	Orthorhombic	Metasediments	2014	Britvin et al., 2014; 2015
Ni-dominant					
Halamishite	Ni_5P_4	Hexagonal	Metasediments		Britvin et al., 2013; 2015
Melliniite	$(Ni,Fe)_4P$	Isometric	Acapulcoite achondrite	2006	Pratesi et al., 2006
Negevite	NiP_2	Isometric	Metasediments	2013	Britvin et al., 2013; 2015
Nickelphosphide	$(Ni,Fe)_3P$	Tetragonal	Iron meteorite	1999	Britvin et al., 1999
Transjordanite	Ni_2P	Hexagonal	Metasediments	2014	Britvin et al., 2014; 2015

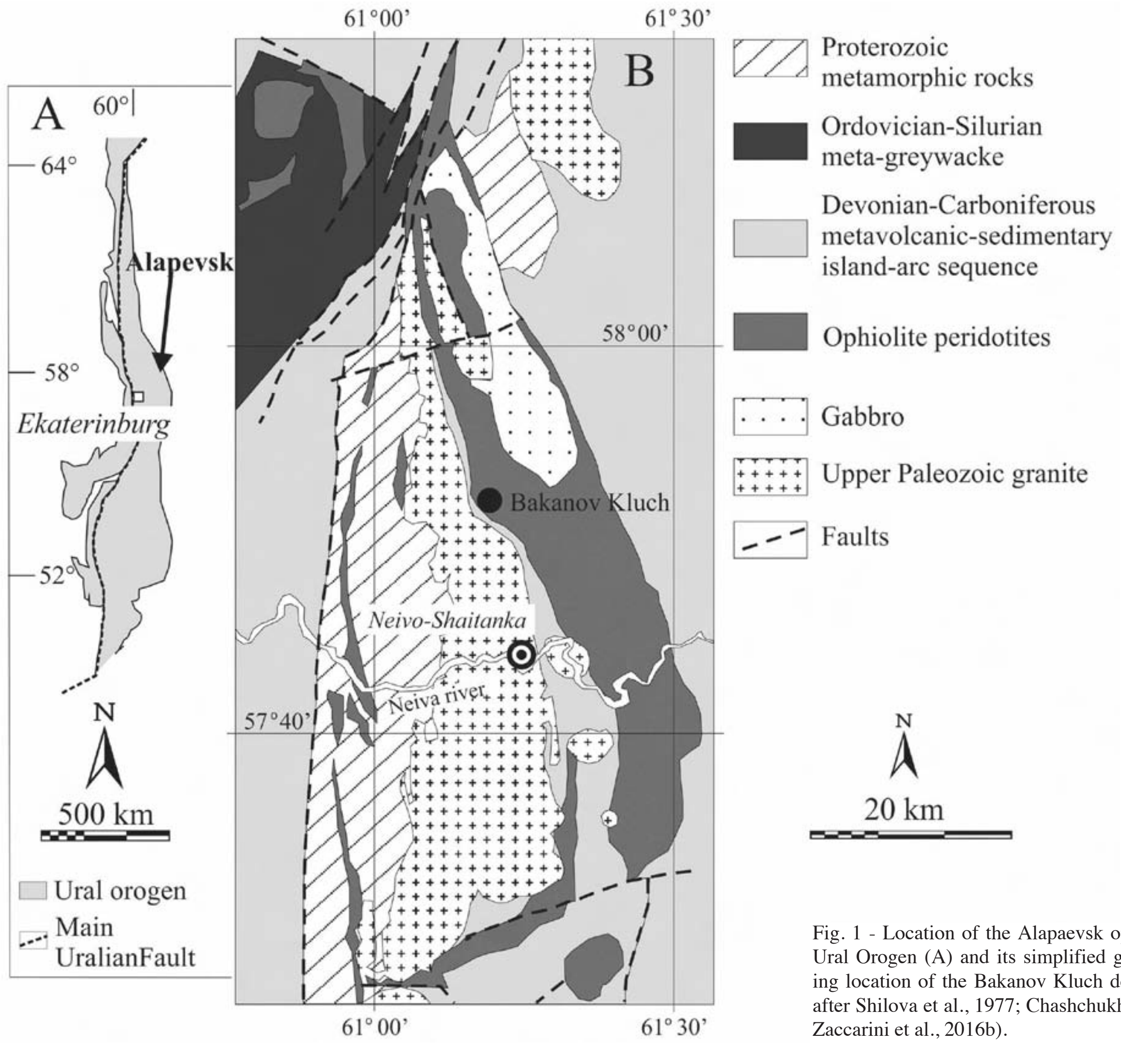

Fig. 1 - Location of the Alapaevsk ophiolite massif in the Ural Orogen (A) and its simplified geological map showing location of the Bakanov Kluch deposit (B). (Modified after Shilova et al., 1977; Chashchukhin et al., 2002; 2012; Zaccarini et al., 2016b).

which is currently mined. It consists of 6 ore bodies about 300 m in length, and with a thickness that varies between 1 up and 4 m and with 300 m dipping. Based on available exploration data, the estimated resource is about 15 thousand tons (Zaccarini et al. 2016b).

The Mesozoic Gerakini-Ormylia ophiolite is part of the supra-subduction zone (SSZ) dismembered ophiolite complex of west Chalkidiki Peninsula in northern Greece (Fig. 2A), north of the Kassandra Gulf (Fig. 2B). The ophiolite consists of massive dunite (hosting podiform chromitites), minor harzburgites, layered pyroxenites and cumulate gabbroic rocks (Gauthier, 1984; Michailidis, 1993; Michailidis and Sklavounos, 1996; Kalitsi et al., 2005). At the NE, the ophiolite is bounded by diorite and quartz diorite as well as metamorphic rocks (marbles and epigneisses) (Fig. 2B). Neogene and Quaternary sedimentary rocks are abundant and partially cover the ophiolite suite.

About 80.000 tons of Cr-rich chromite ore have been mined from these ophiolites (Burgath and Weiser, 1980). The samples of this study were collected from the abandoned mine of Agios Dimitrios, located about 6 km from the town of Gerakini (Fig. 2B).

METHODOLOGY

Ten polished sections were prepared from the massive chromitites from the Bakanov Kluch deposit, and two polished sections of chromitite concentrates were studied from the Gerakini-Ormylia chromitite. The concentrates were prepared from ten samples, each one weighting ca. 2 kg, from the Agios Dimitrios mine. These samples were subsequently stage crushed to -10 mesh and blended into a homogenous composite sample. The processing and recovery of the PGM was carried out at SGS Mineral Services, Canada. Approximately 500 grams of the composite sample were riffled and stage crushed to a P80 (80% passing) of 75 µm. The sample was subsequently subjected to heavy liquid separation (density of the heavy liquids was 3.1 g/cm^3) to separate the heavy minerals such as chromite, platinum group minerals (PGM) and sulphides from the lighter silicates. The separation produced a heavy and light mineral concentrate. The heavy fraction was further processed with a superpanner. This method is designed for small samples and is closely controlled leading to very effective separation. It consists of a tapering triangular deck with a "V" shape cross section. The table mimics the concentrating action of a gold pan. Initially the sample is swirled to stratify the minerals. Then, the heaviest minerals settle to the bottom and are deposited on the deck surface. In contrast, the less dense material moves towards the top, overlying the heavy minerals. Subsequently, the operation of the deck is then changed to a rapid reciprocal motion, with an appropriate "end-knock" at the up-slope end of the board, and a steady flow of wash water is introduced. The "end-knock" causes the heavy minerals to migrate to the up-slope end of the deck, whereas the wash water carries the light minerals to move to the narrower, down-slope end of the deck. The heaviest fractions were split into the heaviest fraction (tip) followed by a less dense fraction (middling). The "tip" and the "middlings" of the superpanner are the densest fractions and included liberated grains of chromite, sulphides, PGM and the Ni-phosphide, while the lighter tail consists of particle mixture of chromite and silicates. Two polished blocks were prepared from each of the tip and middlings for the mineralogical examination.

The polished blocks and the concentrates were carefully investigated with a reflected-light microscope at 250-800X magnification. Chromite and Ni-phosphide grains were analyzed with an electron microprobe using a Superprobe Jeol JXA 8200 at the Eugen F. Stumpfl Laboratory at the University of Leoben, Austria, equipped with both energy dispersive spectrometer (EDS) and wavelength dispersive spectrometer (WDS). Back scattered electron (BSE) images

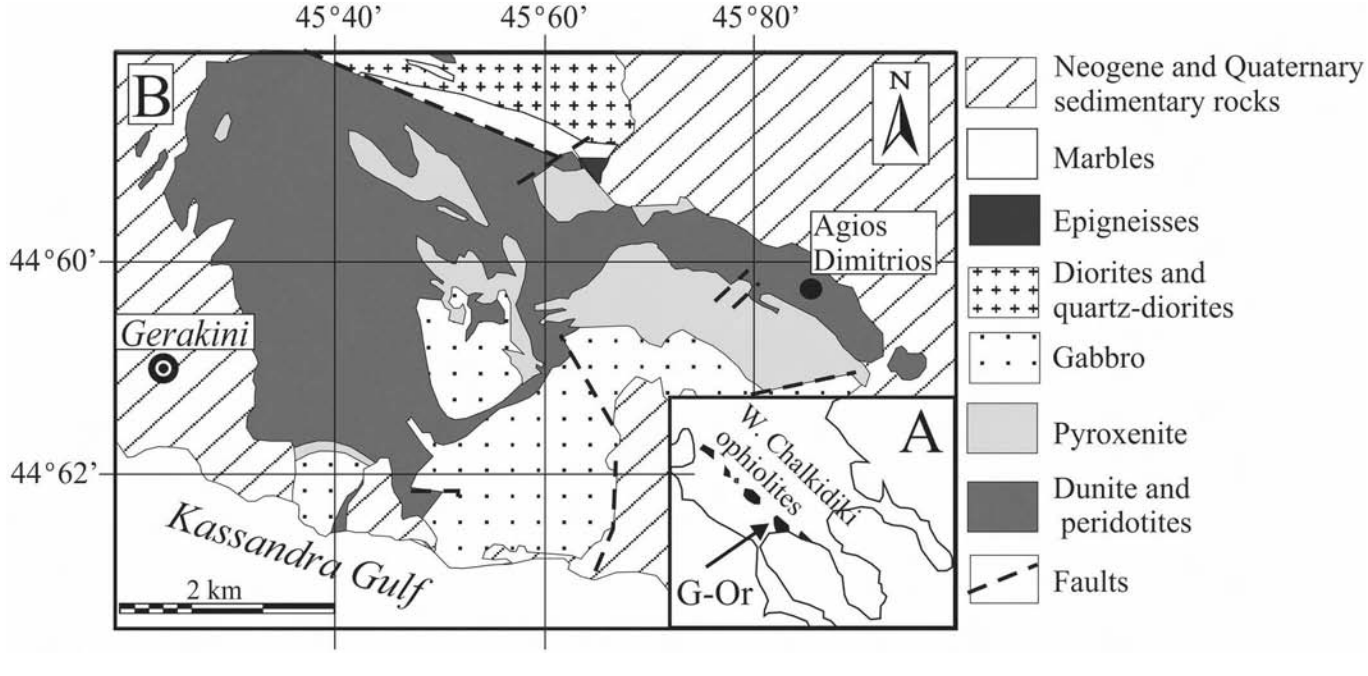

Fig. 2 - Location of the Gerakini-Ormylia ophiolite complex (G-Or) (A) and its geological map, showing the location of the studied deposits (B). (Modified after 'Poliyiros' and 'Arnaea' sheets of the Intistute of Geological and Mining Research).

were also obtained using the microprobe. Chromite analyses with the electron microprobe were conducted in the WDS mode, with an accelerating voltage of 15 kV and a beam current of 10 nA. The analysis of Mg, Al, Si, Ti, V, Cr, Zn, Mn, Fe, and Ni was obtained using the Kα lines, and was calibrated on natural chromite, rhodonite, ilmenite, pentlandite, kaersutite, sphalerite, and metall, and LIFH for Ti, V, Cr, Zn, Mn, Fe, and Ni. Representative analyses of chromite are listed in Table 2.

The Ni-phosphides were quantitatively analyzed in the WDS mode, at 20 kV accelerating voltage and 10 nA beam current, and beam diameter of about 1 micron. The peak and background counting times were 20 and 10s, respectively. The Kα lines were used for Fe, Cr, Ni, and P. The reference materials were chromite and synthetic Ni_3P and Fe_3P. The following diffracting crystals were selected: PETJ for P; and LIFH for Fe, Cr and Ni. The results are presented in Table 3. The natural Ni-phosphides along with the Ni_3P and Fe_3P standards were studied also by Raman spectroscopy, using the procedure described by Vymazalova et al. (2014). However, all the analyzed Ni-phosphides proved to be Raman inactive.

RESULTS

Chromite texture and composition

The studied chromitite from Bakanov Kluch deposit consists of about 60 modal % of medium and coarse-grained chromite crystals (Fig. 3A). Several chromite grains display a pull-apart like texture. The interstitial silicate matrix of the chromitites is completely altered, and is composed of serpentine, talc and chlorite (Fig. 3A). The massive Agios Dimitrios chromitite is coarse-grained (Fig. 3B), brecciated and locally display pull-apart texture. The host dunite of Agios Dimitrios mine is highly altered; carbonate minerals (dolomite and magnesite) and predominantly rusty-colour amorphous silica and quartz, form either polycrystalline masses or veins cross-cutting both the dunite and the chromite ore. There are scarce relics of olivine, pyroxene, serpentine and chlorite.

According to the data presented in this contribution and those reported by Zaccarini et al. (2016b), the Bakanov Kluch chromite is compositionally homogenous and the overall variation ranges of major oxides (wt%) in the unaltered cores of chromite grains are Cr_2O_3 (57.49-58.93 wt%), Al_2O_3 (9.42-9.76 wt%), MgO (12.67-13.61 wt%) and FeO (12.4-13.95 wt%). The TiO_2 contents ranges from 0.12 wt% to 0.21 wt%, the calculated amount of Fe_2O_3 from 4.78 to 6.00 wt% and MnO from 0.19 to 0.28 wt%. SiO_2, NiO, ZnO and V_2O_3 contents are very low and in most cases are below the detection limits (Table 2).

The Gerakini-Ormylia chromite displays little variation and the major oxides (wt%) show the following ranges Cr_2O_3 (55.36-60.05 wt%), Al_2O_3 (10.84-14.10 wt%), MgO (10.96-12.76 wt%) and FeO (14.21-17.06 wt%). The TiO_2 amounts are low (0.15-0.22 wt%), the Fe_2O_3 is up to 2.83 wt%, while MnO vary between 0.25 and 0.35 wt%. Similarly to the Bakanov Kluch chromite, the SiO_2, NiO, ZnO and V_2O_3 concentrations are negligible and even below detection limit (Table 2). The chromites analyzed from both localities show very high Cr# (= Cr/(Cr+Al) atomic ratio) ranging from 0.70 to 0.85, values which are comparable to those spinels occurring in boninitic formations (Fig. 4A), as it has also been suggested by Garuti et al. (2012). The Cr, Al, Ti and Fe contents of the analyzed chromites also verify their podiform nature (Fig. 4B-D).

The Ni-phosphides

Ni-phosphides from both localities form small grains, about 10 microns in size. In the Bakanov Kluch chromitite, they occur in the interstitial to chromite serpentine matrix (Fig. 5A), whereas for the Gerakini-Ormylia chromitites the exact textural relationships cannot be ascertain due to the fact that Ni-phosphide was discovered in the concentrates (Fig. 5B). Under reflected-light microscope, they show a yellow colour and they are isotropic, potentially implying

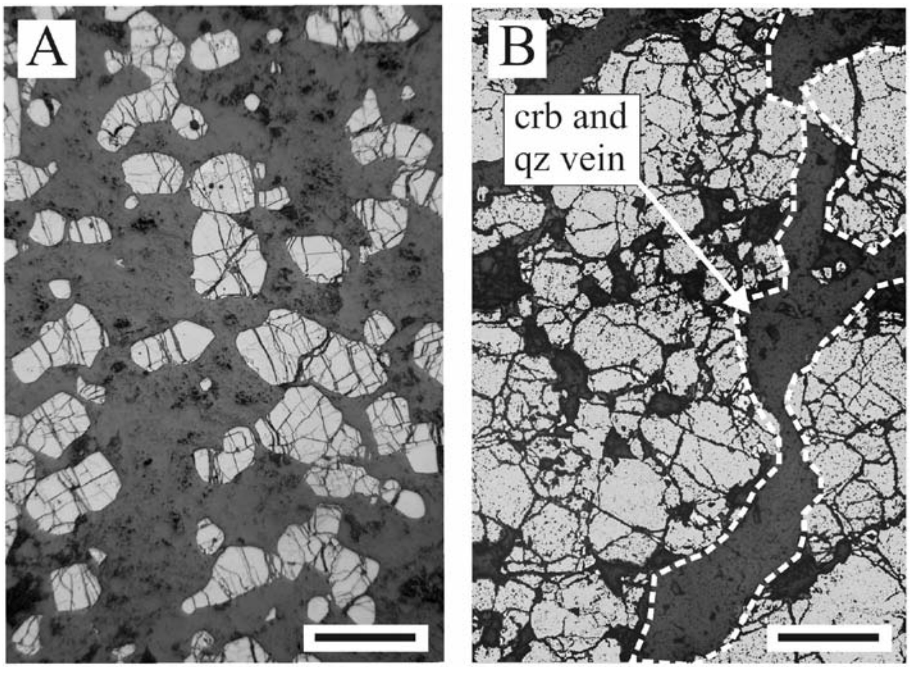

Fig. 3 - Reflected-light image showing the texture of the chromitites of Alapaevsk (A) and Gerakini-Ormylia (B). Light grey minerals = chromite, dark grey minerals = altered silicates, crb = carbonate minerals, qz = quartz. Scale bar is 1 millimetre.

Table 2 - Representative electron microprobe analyses (wt %) of chromite from chromitites of Alapaevsk and Gerakini-Ormylia.

Sample	$C_{r2}O_3$	Al_2O_3	Fe_2O_3	MgO	FeO	TiO_2	SiO_2	MnO	NiO	ZnO	V_2O_3	Total
Alapaevsk												
PE-1	57.49	9.57	5.94	13.42	12.73	0.19	0.00	0.22	0.06	0.00	0.00	99.62
PE-2	57.94	9.62	5.32	13.10	13.21	0.16	0.00	0.23	0.03	0.02	0.00	99.64
PE-3	58.56	9.62	4.78	13.21	13.26	0.19	0.05	0.19	0.03	0.06	0.05	100.01
PE-4	57.75	9.52	6.00	13.58	12.49	0.12	0.01	0.19	0.03	0.03	0.00	99.72
PE-5	58.73	9.42	5.07	13.04	13.44	0.15	0.02	0.23	0.08	0.00	0.00	100.17
PE-6	57.62	9.60	5.50	13.58	12.40	0.21	0.02	0.22	0.07	0.00	0.01	99.23
PE-7	57.88	9.59	5.23	12.67	13.95	0.18	0.01	0.23	0.00	0.09	0.03	99.86
PE-8	58.93	9.49	5.09	13.22	13.31	0.15	0.06	0.25	0.01	0.10	0.01	100.62
PE-9	57.92	9.74	5.38	13.16	13.20	0.14	0.00	0.22	0.03	0.00	0.01	99.80
PE-10	58.36	9.74	5.28	13.44	12.80	0.13	0.00	0.22	0.08	0.00	0.00	100.05
PE-11	57.84	9.59	5.84	13.15	13.15	0.15	0.01	0.28	0.10	0.08	0.02	100.22
PE-12	57.99	9.69	5.53	13.61	12.58	0.17	0.05	0.23	0.06	0.00	0.00	99.90
PE-13	58.15	9.64	5.54	13.57	12.68	0.17	0.04	0.22	0.07	0.00	0.02	100.10
PE-14	58.76	9.76	5.01	13.51	12.92	0.13	0.04	0.23	0.00	0.02	0.00	100.38
PE-15	58.37	9.52	5.22	13.12	13.40	0.19	0.01	0.19	0.05	0.00	0.05	100.12
Gerakini-Ormylia												
GR1	55.98	13.37	1.79	12.41	14.64	0.22	0.01	0.28	0.08	0.00	0.07	98.84
GR2	55.93	13.17	2.52	11.28	16.68	0.18	0.00	0.32	0.07	0.03	0.05	100.22
GR3	55.73	13.30	2.45	11.42	16.46	0.18	0.00	0.31	0.05	0.00	0.11	100.01
GR4	58.96	10.90	2.38	12.36	14.59	0.17	0.00	0.26	0.05	0.00	0.02	99.69
GR5	58.02	11.20	2.34	12.28	14.42	0.18	0.00	0.30	0.05	0.06	0.05	98.91
GR6	55.89	13.24	2.25	11.33	16.52	0.15	0.02	0.29	0.05	0.09	0.08	99.91
GR7	55.83	12.91	2.83	11.45	16.42	0.19	0.04	0.30	0.02	0.07	0.07	100.12
GR8	60.05	11.87	0.00	12.03	15.09	0.20	0.02	0.25	0.11	0.07	0.13	99.82
GR9	56.08	13.61	1.82	12.42	14.88	0.22	0.01	0.28	0.06	0.00	0.08	99.47
GR10	55.91	13.76	1.02	11.18	16.65	0.19	0.00	0.28	0.06	0.06	0.09	99.21
GR11	55.36	13.58	2.58	12.76	14.21	0.18	0.02	0.29	0.07	0.00	0.08	99.14
GR12	59.65	10.84	0.80	10.69	17.06	0.21	0.00	0.35	0.06	0.08	0.07	99.81
GR13	55.79	13.71	1.38	11.36	16.35	0.19	0.02	0.33	0.09	0.09	0.10	99.41
GR14	58.92	11.65	0.28	11.31	15.98	0.19	0.00	0.31	0.09	0.02	0.06	98.81
GR15	55.45	14.10	1.83	11.58	16.25	0.18	0.00	0.29	0.08	0.09	0.09	99.94

Fe_2O_3 = calculated assuming the ideal spinel stoichiometry.

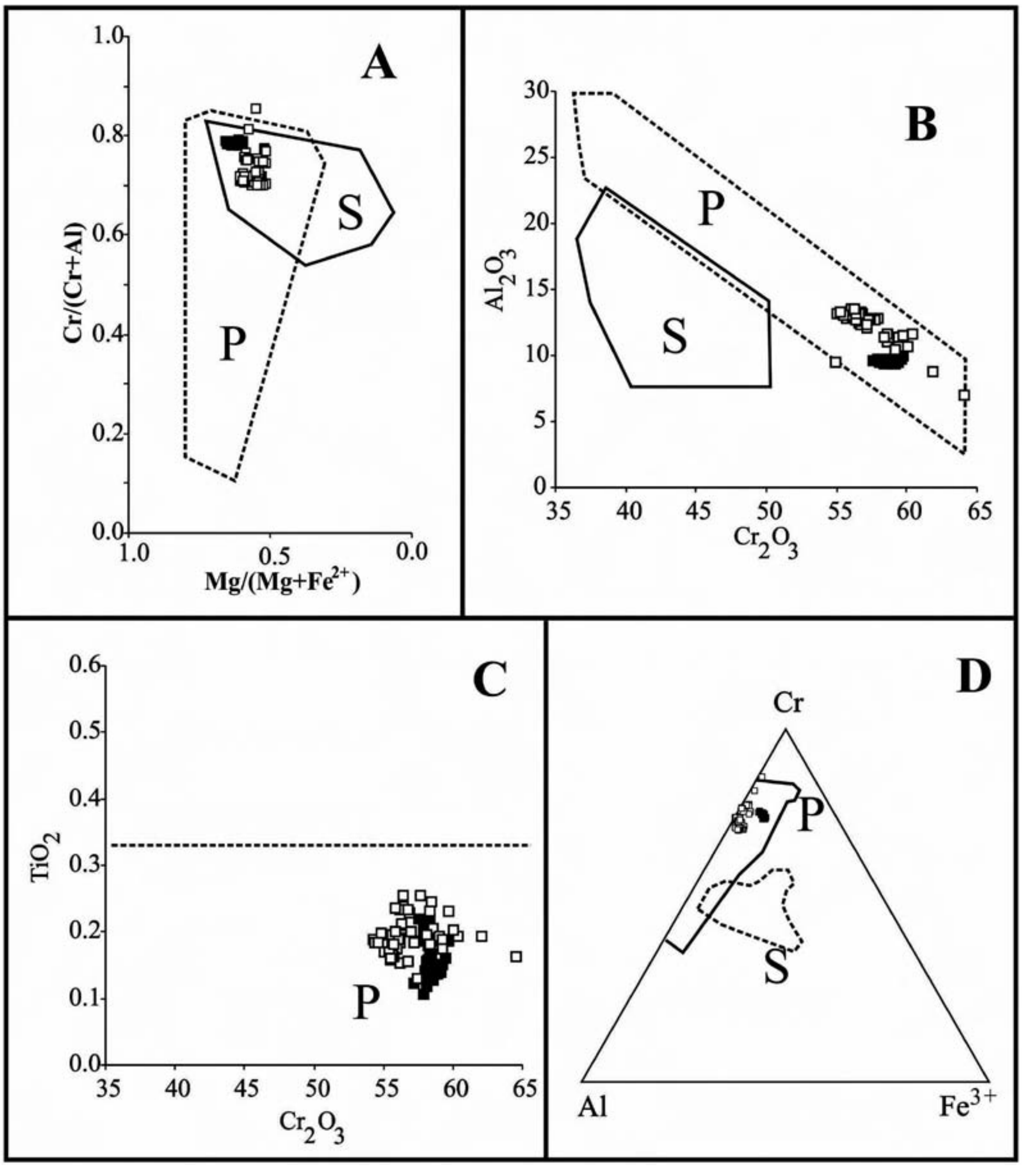

Fig. 4 - Composition of unaltered chromite from the studied chromitites from Alapaevsk (black square) and Gerakini-Ormylia (white square). (A) Variation of Cr/(Cr + Al) and Mg/(Mg + Fe^2); (B) correlation of Al_2O_3 versus Cr_2O_3; (C) variation of Cr_2O_3 and TiO_2 P = field of podiform chromitites; (D) Cr-Al-Fe^{3+} atomic ratios. S = field of stratiform chromitites. Compositional fields after Thayer (1970), Mussalam et al. (1981), Ferrario and Garuti (1988), Arai (1992), Proenza et al. (2007).

their crystallization in the cubic system (Fig. 5C). Electron microprobe analyses showed that the analyzed grains from the Uralian and Greek chromitites have similar Ni and P compositions (Table 3). Nickel is the dominant element and varies between 86.44 and 87.76 wt% and 88.05 and 89.89 wt% in the Bakanov Kluch and Agios Dimitrios grains, respectively. Phosphorus contents range from 9.64 to 10.19 wt%, whereas iron is higher in the Agios Dimitrios Ni-phosphide (2.43-2.58 wt%) than that in the Bakanov Kluch (1.13-1.24 wt%) (Table 3). Chromium was analyzed only in the grain from Agios Dimitrios Ni-phosphide, and it ranges from 1.22 to 1.30 wt% (Table 3). The calculated stoichiometry, based on the average of 20 analyses, approaches the ideal formula $(Ni,Fe)_5P$ (Table 3). The average composition of the analyzed grains is plotted on a P vs. Ni+Fe diagram along with the five Ni-phosphides that have officially been accepted by IMA as mineral species so far (Fig. 6). These minerals include nickelphosphide (Britvin et al., 1999; Skala and Drabek, 2003), melliniite (Pratesi et al., 2006) halamishite, negevite and transjordanite (Britvin et al., 2014). The average composition of the analyzed minerals is relatively poor in P having similar contents to transjordanite, nickelphosphide and melliniite, but it is richer in Ni (and Fe) than the rest of the species. The terrestrial Ni-phosphides, which have been analyzed up to date show higher P contents than those crystals that have been discovered in few meteorites (Fig. 7; Britvin et al., 2015). The analyzed $(Ni,Fe)_5P$ mineral from this study contains the highest reported Ni and the lowest P values, thus having the highest Ni/P ratio reported so far.

DISCUSSION AND CONCLUSION

In the terrestrial occurrences, the phosphides are generally enriched in phosphorous compared to those reported in meteorites. The $(Ni,Fe)_5P$ from the Alapaevsk and Gerakini-Ormylia represents the first occurrence of a Ni phosphide in chromitites. Its chemical composition reveals that it is the most Ni-rich phase among the minerals known in the Ni-Fe-P system, despite of its terrestrial nature. Recently, Britvin et al. (2015) reported the Ni-dominant phases transjordanite, halamishite and negevite from pyrometamorphic rocks of the Hatrurim Formation, located in Israel and Jordan, suggesting that the terrestrial phosphides are Fe-dominant. Hu et al. (2005) found two grains of barringerite Fe_2P in

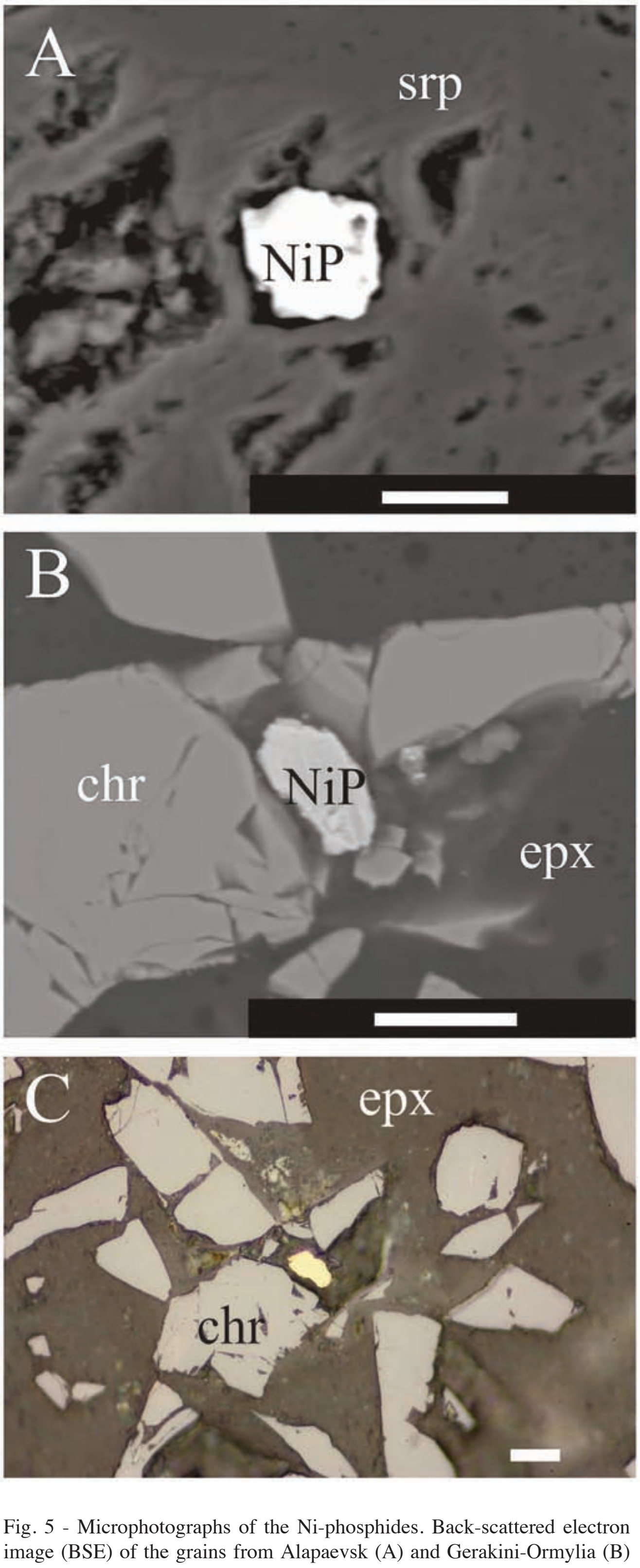

Fig. 5 - Microphotographs of the Ni-phosphides. Back-scattered electron image (BSE) of the grains from Alapaevsk (A) and Gerakini-Ormylia (B) chromitites. (C) Reflected-light image of the Ni-phosphide (yellow in colour) from Gerakini-Ormylia. Scale bar is 10 microns. Abbreviation: NiP = Ni-phosphide, srp = serpentine, chr = chromite, epx = epoxy.

Table 3 - Electron microprobe analyses (wt %, at%, and apfu) of the Ni-phosphide from chromitites of Alapaevsk and Gerakini-Ormylia.

Sample	P	Ni	Fe	Cr	Total
		wt%			
Alapaevsk					
PE1870-1*	10.16	88.05	1.3	n.a.	99.51
PE1870-2*	10.15	89.12	1.26	n.a.	100.53
PE1870-3*	10.17	89.29	1.19	n.a.	100.64
PE1870-4*	10.15	88.14	1.19	n.a.	99.48
PE1870-5*	9.41	89.89	1.18	n.a.	100.47
PE1870-6*	10.13	88.33	1.23	n.a.	99.69
PE1870-7*	10.09	88.17	1.24	n.a.	99.49
PE1870-8*	10.18	89.45	1.18	n.a.	100.81
PE1870-9*	10.11	88.57	1.18	n.a.	99.86
PE1870-10*	10.19	89.17	1.13	n.a.	100.49
Gerakini-Ormylia					
NiPGr1	10.03	87.50	2.58	1.30	101.42
NiPGr2	10.01	86.95	2.44	1.24	100.64
NiPGr3	10.06	87.76	2.48	1.26	101.57
NiPGr4	9.88	87.37	2.57	1.30	101.11
NiPGr5	9.65	86.95	2.44	1.23	100.28
NiPGr6	9.71	87.15	2.43	1.22	100.51
NiPGr7	9.64	86.44	2.34	1.23	99.65
NiPGr8	9.69	86.46	2.46	1.29	99.90
NiPGr9	9.64	86.90	2.43	1.25	100.23
NiPGr10	9.66	87.10	2.48	1.25	100.49
		at%			
Alapaevsk					
PE1870-1	17.72	81.02	1.26	n.a.	
PE1870-2	17.54	81.25	1.21	n.a.	
PE1870-3	17.55	81.31	1.14	n.a.	
PE1870-4	17.71	81.14	1.15	n.a.	
PE1870-5	16.37	82.5	1.13	n.a.	
PE1870-6	17.64	81.17	1.19	n.a.	
PE1870-7	17.61	81.2	1.2	n.a.	
PE1870-8	17.54	81.33	1.13	n.a.	
PE1870-9	17.59	81.28	1.14	n.a.	
PE1870-10	17.61	81.3	1.08	n.a.	
Gerakini-Ormylia					
NiPGr1	17.16	78.97	1.24	2.63	
NiPGr2	17.25	79.06	1.18	2.51	
NiPGr3	17.18	79.09	1.20	2.53	
NiPGr4	16.96	79.18	1.24	2.63	
NiPGr5	16.73	79.56	1.19	2.52	
NiPGr6	16.79	79.54	1.17	2.51	
NiPGr7	16.82	79.56	1.19	2.43	
NiPGr8	16.86	79.35	1.24	2.55	
NiPGr9	16.72	79.56	1.20	2.51	
NiPGr10	16.71	79.53	1.20	2.56	
		apfu			
Alapaevsk					
PE1870-1	1.06	4.86	0.08	n.a.	
PE1870-2	1.05	4.88	0.07	n.a.	
PE1870-3	1.05	4.88	0.07	n.a.	
PE1870-4	1.06	4.87	0.07	n.a.	
PE1870-5	0.98	4.95	0.07	n.a.	
PE1870-6	1.06	4.87	0.07	n.a.	
PE1870-7	1.06	4.87	0.07	n.a.	
PE1870-8	1.05	4.88	0.07	n.a.	
PE1870-9	1.06	4.88	0.07	n.a.	
PE1870-10	1.06	4.88	0.06	n.a.	
Gerakini-Ormylia					
NiPGr1	1.03	4.74	0.07	0.16	
NiPGr2	1.04	4.74	0.07	0.15	
NiPGr3	1.03	4.75	0.07	0.15	
NiPGr4	1.02	4.75	0.07	0.16	
NiPGr5	1.00	4.77	0.07	0.15	
NiPGr6	1.01	4.77	0.07	0.15	
NiPGr7	1.01	4.77	0.07	0.15	
NiPGr8	1.01	4.76	0.07	0.15	
NiPGr9	1.00	4.77	0.07	0.15	
NiPGr10	1.00	4.77	0.07	0.15	

n.a. = not analyzed, * = data from Zaccarini et al., 2016.

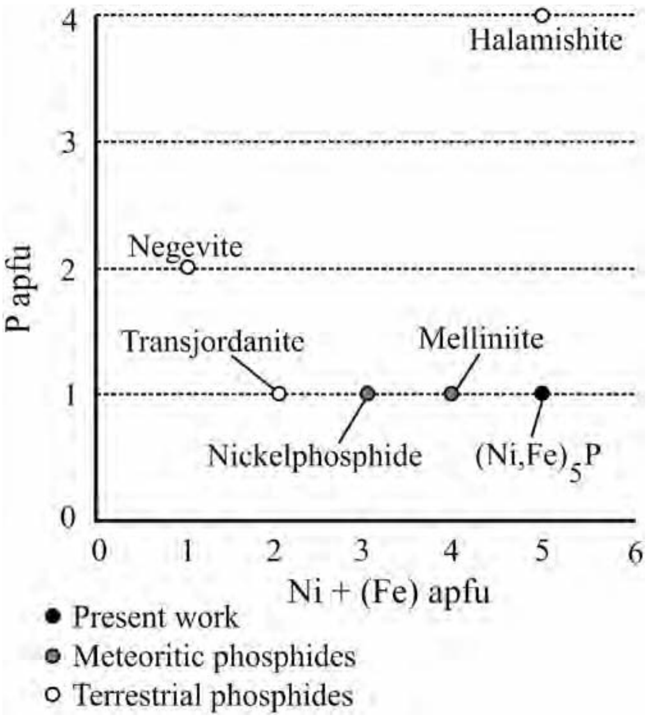

Fig. 6 - Binary diagram of P versus Ni + (Fe), apfu, showing the composition of the Ni-phosphide found in the chromitites from Alapaevsk and Gerakini-Ormylia ophiolites, compared with those of the minerals with Ni > Fe described in the system Ni-Fe-P. (Modified after Zaccarini et al., 2016b).

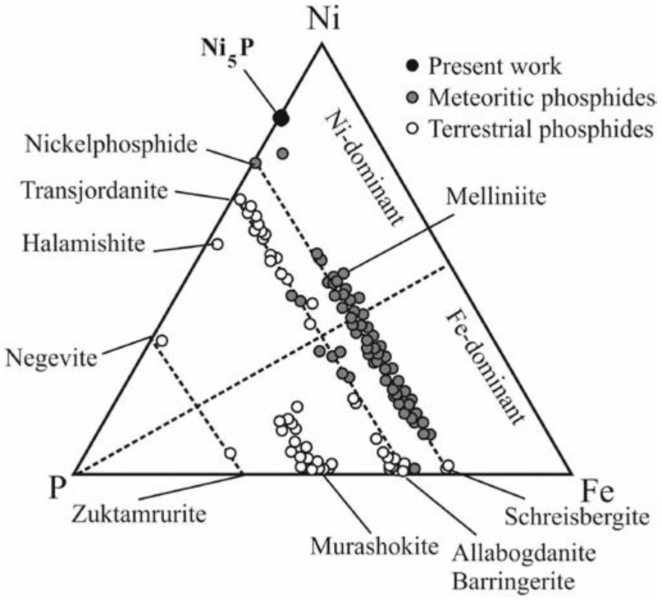

Fig. 7 - Plot (atom %) of the compositions of the minerals in the system Ni-Fe-P. (Modified after Britvin et al., 2015).

ultra high pressure (UHP) garnet peridotites from China. Schreibersite has been reported in reduced differentiated lenses in basalts, in hydrothermal replacement in a petrified wood (http://mindat.org) and in association with native iron in an andesite from the Disko Island, Greenland (Pedersen, 1981). Schreibersite has also been identified in Archean marine sediments (Pasek et al., 2013).

Pasek et al. (2012) investigated the geochemical behaviour of P in selected fulgurites from North America, Africa and Australia, most of which contain reduced phosphorus, mainly in the form of phosphite. The authors suggested that lightning can account for the local reduction of phosphates to produce phosphides. Pratesi et al. (2006), based on the investigation of the crystal structure of selected minerals in the Ni-Fe-P system, suggested that some of these phases are characterized by high symmetry and atomic coordination and may crystallize in a high-pressure environment, such as the core of the Earth. Britvin et al. (2014) depict a reducing environment at temperatures higher than 1,050 °C combined with low pressures (~100 kPa), for the phosphides occurring in the Hatrurim Formation. In the case of the Chinese barringerite found at Donghai, part of the UHP Sulu terrane, the conditions were more extreme. The terrane reached the eclogite facies, more specifically the coesite/diamond stability field, characterized by temperatures between 800-700 °C and pressures > 2.8 GPa (Cong et al., 1994; Ernst and Liou, 1999; Zheng et al., 2005; Schmidt et al., 2008). Pedersen (1981) calculated the formation temperature of schreibersite hosted in andesite to be 1,080 °C using the plagioclase-ground mass thermometer and 1,110-1,150 °C with the orthopyroxene-ilmenite thermometer. The pressures of equilibration for the Disko rocks range from 100 kPa to 0.15 GPa. In summary, the above literature data show that the terrestrial phosphides may crystallize at temperatures between 700 and 1,150 °C. Temperatures around 1,000 °C are consistent with those occurring during the precipitation of the chromitite that hosts the $(Ni,Fe)_5P$ from the Alapaevsk and Gerakini-Ormylia. The data presented by Chashchukhin et al. (2002; 2012) and Garuti et al. (2012) favour the crystallization of the Cr-rich chromitites of the Urals, including those of Alapaevsk complex, under relatively high oxygen activity and above the fayalite-magnetite-quartz (FMQ) buffer. This fact precludes the possibility that the detected phosphide is of primary origin, as it has been discussed above that reducing conditions are essential for the formation of terrestrial minerals in the Ni-Fe-P system. Typically, serpentinization of peridotites produces highly reducing fluids containing dissolved H_2 resulting from the reduction of H_2O (Berndt et al., 1996; Charlou, 2002; Seyfried et al., 2007; Klein et al., 2009; Marcaillou et al., 2011). Consequently, peridotites have a strong reducing potential (Malvoisin et al. 2012).

Therefore, we suggest that the $(Ni,Fe)_5P$ from the Alapaevsk and Gerakini-Ormylia were most likely formed during the serpentinization of the host peridotites at low temperatures. Nickel may have been released during the alteration of olivine and phosphorous from apatite alteration. To understand the origin of P in the studied chromitites is a big challenge. Apatite is the most common natural phosphate, which occasionally occurs as accessory phase also in ultramafic rocks and chromitites (Mücke and Younessi, 1994; Garuti et al., 2002; Morishita et al., 2003; Zaccarini et al., 2004; Li et al., 2005; Zaccarini et al., 2016a). The experimental work of Prins and Bussel (2012) has shown that reduction of phosphate minerals induced by hydrogen may start at temperatures around 400 °C, similar to the temperature of serpentinization. Economou-Eliopoulos (2003) reported the occurrences of apatite from Ni-laterite from Greece. Apatite was found as small grains (< 10 to 50 μm) in the contact between chromite core and magnetite rim and as inclusions in magnetite suggesting that these minerals precipitated concomitantly. Apatite was observed in association with Fe-chlorite and magnetite indicating that they crystallized during the diagenesis-metadiagenesis stage. A gradual dissolution of apatite in the Ni-laterite was also observed, suggesting that this mineral was unstable during a subsequent stage of its formation (Economou-Eliopoulos, 2003).

Another probable source of P could be olivine. Generally silicates could carry P in their lattice. P is as an incompatible element (Cyrena, 1984; Agrell et al., 1998; Mallmann et al., 2009) thus, small quantities can be found in olivine.

Olivine could potentially act as a P host (Brunet and Chazot, 2001), during its crystallization in dunites. Lower degree of polymerization of SiO_4 tetrahedra, is translated to higher P incorporation (Koritnig, 1965), and of course olivine is the least polymerized among other silicates. There are also cases of phosphoran olivines (Cyrena, 1984; Agrell et al., 1998). In most cases olivine is enriched in P after a metasomatic event. In the studied rocks, the incompatible P could have been incorporated in olivine after the reaction of dunite with boninitic melts. Therefore, olivine alteration could have provided trace amounts of P needed for the formation of micrometric and rare $(Ni,Fe)_5P$ grains.

Although we cannot exclude that P was supplied by an external source, there is no field evidence supporting the interaction between the chromitite-peridotite assemblages and their country rocks.

Generally, ultramafic rocks contain more nickel and less phosphorus. Thus, this is probably the reason why the $(Ni,Fe)_5P$ minerals from the Alapaevsk and Gerakini-Ormylia are enriched in Ni.

According to their stoichiometry the $(Ni,Fe)_5P$ grains, analyzed in the Alapaevsk and Gerakini-Ormylia chromitites, represent a new mineral species. However, their small size renders difficult the acquisition of crystallographic data to support this assumption. The discovered grains very likely formed at low temperature. However, this observation cannot be confirmed because of the lack of experimental work on the stability of Ni-phosphides with this composition.

The data presented in this contribution indicate that the $(Ni,Fe)_5P$ minerals occur as very tiny grains and as very rare phases. To recognize them proved to be extremely difficult and required a careful and consuming-time investigation of the samples by reflected-light microscopy and electron microprobe. Therefore, we cannot exclude that Ni-Fe phosphides may occur also in other serpentinized rocks, although they have not been found yet.

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