

Article

Tsikourasite, $\text{Mo}_3\text{Ni}_2\text{P}_{1+x}$ ($x < 0.25$), a New Phosphide from the Chromitite of the Othrys Ophiolite, Greece

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Abstract: Tsikourasite, $\text{Mo}_3\text{Ni}_2\text{P}_{1+x}$ ($x < 0.25$), is a new phosphide discovered in a mantle-hosted podiform chromitite collected in the abandoned mine of Agios Stefanos (Othrys ophiolite), Central Greece. It forms tiny grains (from a few μm up to about 80 μm) and occurs as isolated grains or associated with other known minerals such as nickelporphide and awaruite, and with undetermined minerals such as Ni-allabogdanite or Ni-barringerite and a V-sulphide. Tsikourasite is brittle and has a metallic luster. In plane-polarized light, tsikourasite is white yellow and it shows no birefractance, anisotropism or pleochroism. Internal reflections were not observed. Reflectance values of tsikourasite in air (R in %) are: 55.7 at 470 nm, 56.8 at 546 nm, 57.5 at 589 nm and 58.5 at 650 nm. Five spot analyses of tsikourasite give the average composition: P 7.97, S 0.67, V 14.13, Fe 14.37, Co 7.59, Ni 23.9, and Mo 44.16, total 99.60 wt%, corresponding to the empirical formula $(\text{Mo}_{1.778}\text{V}_{1.071}\text{Fe}_{0.082}\text{Co}_{0.069})_{\Sigma 3.000}(\text{Ni}_{1.572}\text{Co}_{0.428})_{\Sigma 2.000}(\text{P}_{0.981}\text{S}_{0.079})_{\Sigma 1.060}$, on the basis of $\Sigma(\text{Mo} + \text{V} + \text{Fe} + \text{Co} + \text{Ni}) = 5$ apfu and taking into account the structural results. The simplified formula is $\text{Mo}_3\text{Ni}_2\text{P}_{1+x}$ ($x < 0.25$). The density, which was calculated based on the empirical formula and single-crystal data, is 9.182 g/cm^3 . The mineral is cubic, space group F-43m, with $a = 10.8215(5)$ Å and $Z = 16$. Although tsikourasite is similar in composition to those of monipite (MoNiP), polekhovskiyite (MoNiP_2), and the synthetic compound MoNiP_2 , all these phases are hexagonal and not cubic like tsikourasite. It exhibits the same structure as the cubic $\text{Mo}_3\text{Ni}_2\text{P}_{1.18}$ compound [space group F-43m, $a = 10.846(2)$ Å] synthesized at 1350 °C. The mineral and its name have been approved by the Commission of New Minerals, Nomenclature and Classification of the International Mineralogical Association (No. 2018-156). The mineral honors Professor Basilios Tsikouras of the Universiti Brunei Darussalam.

Keywords: tsikourasite; phosphide; chromitite; Agios Stefanos mine; Othrys; ophiolite; Greece

1. Introduction

Natural phosphides are very uncommon minerals and only 15 phases, listed below in alphabetic order, have been officially approved by the IMA: allabogdanite (Fe,Ni)₂P [1], andreyivanovite Fe(Cr,Fe)P [2], barringerite (Fe,Ni)₂P [3], florenskyite Fe(Ti,Ni)P [4], halamishite Ni₅P₄ [5], melliniite (Ni,Fe)₄P [6], monipite MoNiP [7], murashkoite FeP [8,9], negevite NiP₂ [5], nickelphosphide (Ni,Fe)₃P [10], polekhovskiyite MoNiP₂ [11], schreibersite (Fe,Ni)₃P [12] and references therein, transjordanite Ni₂P [5], and zuktamrurite FeP₂ [13]. Recently, Zaccarini et al. [14] and Sideridis et al. [15], based on microprobe analyses, reported the presence of a new phosphide, characterized by the stoichiometry (Ni,Fe)₅P, in the ophiolitic chromitites of Gerakini-Ormylia, Greece and Alapaevsk, Russia. Ifandi et al. [16] and Zaccarini et al. [17] reported the chemical composition of several new minerals in a heavy concentrate obtained from one chromitite sample collected in the Othrys ophiolite. They were tentatively classified as either Ni-allabogdanite or Ni-barringerite and either V-allabogdanite or V-barringerite and V-sulphide. All the described phosphides in the recent papers [14–17] were too small to be studied by X-ray diffraction.

During the study of the Othrys heavy concentrate, a few Mo-Ni-phosphides were quantitatively analyzed by electron microprobe and one of them was large enough to obtain the mandatory structural data to fully characterize the mineral. The quantitative chemical analysis and crystal structure proved that the studied phase is the natural equivalent of the cubic Mo₃Ni₂P_{1.18} compound [space group F-43m, *a* = 10.846(2) Å] synthesized at 1350 °C [18]. This new mineral was named tsikourasite to honor Basilios Tsikouras (b. 1965), associate professor at the Faculty of Science, Physical and Geological Sciences, Universiti Brunei Darussalam, for his contributions to the ore mineralogy and mineral deposits related to ophiolites. The mineral and its name have been approved by the IMA CNMNC, under the number 2018-156. The type material is deposited in the mineralogical collections of the Museo di Storia Naturale, Università di Firenze, Via La Pira 4, I-50121, Firenze, Italy, catalogue number 3296/I.

2. Geological Background and Occurrence of Tsikourasite

Tsikourasite was found in a heavy mineral concentrate obtained from chromitites from the Othrys ophiolite, central Greece (Figure 1A).

The chromitites were collected in the abandoned mine of Agios Stefanos located about 10 km south of Domokos village (Figure 1B). The studied sample consists of massive chromitite, hosted in strongly serpentinized dunite from a mantle tectonite composed of harzburgite and minor intercalations of plagioclase-bearing lherzolite [19–22]. Mafic rocks, mainly gabbro of the crustal sequence and gabbro dykes, have also been recognized (Figure 1B,C).

The interstitial assemblage of the Agios Stefanos chromitite is pervasively replaced by chlorite and hydrogrossular and minor talc and serpentine. Locally, hydrogarnet fills veins up to 50 μm thick crosscutting magnesiochromite. These veins are presumably associated with the rodingitized gabbro cross-cutting the ore body. Rare titanite, kammererite, pentlandite, and millerite also occur in the hydrogarnet-rich veins. A few fractures are partially filled with calcite and quartz as late alteration products. The chromitite displays a massive and brecciated texture as shown in Figure 2.

The chromitites that were studied, based on electron microprobe analyses of the spinels, were classified as magnesiochromite [16] with Cr₂O₃ (44.96–51.64 wt%), Al₂O₃ (14.18–20.78 wt%), MgO (13.34–16.84 wt%), and FeO (8.3–13.31 wt%). The calculated Fe₂O₃ ranged from 6.72 to 9.26 wt%. The amounts of minor elements MnO (0.33–0.60 wt%), V₂O₃ (0.04–0.30 wt%), ZnO (up to 0.07 wt%) and NiO (0.03–0.24 wt%) exhibit minor variations. The TiO₂ content is low (0.03–0.23 wt%) consistent with most mantle-hosted podiform chromitites. The Cr/(Cr + Al) ratios are lower than those typical of chromites with a boninitic affinity formed in a supra-subduction-zone (SSZ) [16].

Bortolotti et al. [23] recognized, in distinct units of the Othrys ophiolite, three types of basalts characterized by a different geochemical signature: (i) alkaline within-plate (WPB), (ii) normal-type mid-ocean ridge (N-MORB) and (iii) low-K tholeiite (L-KT). The biostratigraphic investigation indicated that radiolarites associated with N-MORB were deposited in the Middle and Late

Triassic. Radiolarites deposited over the L-KT basalts are early Carnian-middle Norian-Late Norian in age [23]. Therefore, based on geochemical and biostratigraphic data, it was suggested that the Othrys ophiolite is characterized by a complex geological evolution [23]. The N-MORB erupted during the Middle-Late Triassic time, related to the initial opening of the Vardar oceanic basin. The L-KT basalts erupted during Middle-Late Triassic time, in part simultaneously with N-MORB, in the ocean-continent transition zone, close to the rifted continental margin. Finally, the alkaline WPB are interpreted to have formed either in oceanic seamounts or in the ocean-continent transition zone adjacent to the rifted continental margin [23].

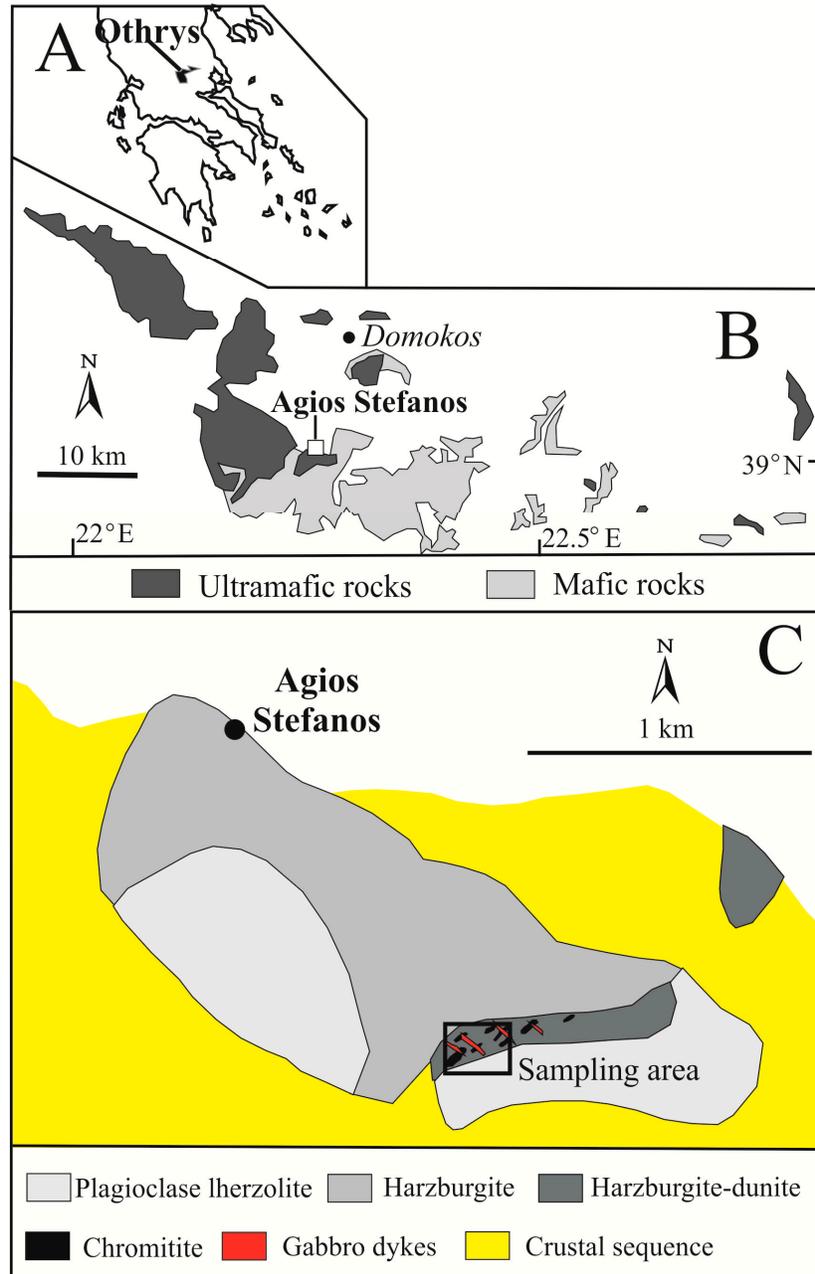


Figure 1. Location of the Othrys complex in Greece (A), general geological map of the Othrys ophiolite showing location of the Agios Stefanos chromium mine (B), and (C) detailed geology of the Agios Stefanos area (modified after [19] and [16]).

In addition to tsikourasite, previous mineralogical studies on specimens from the Agios Stefanos chromium mine revealed the presence of accessory minerals such as the platinum group minerals (PGM) [21,22], which are Ru-Os-Ir-Ni alloys, laurite, erlichmanite, Pd-Sb-Cu alloys, Pd-Cu-Pt alloys, irarsite, platarsite, hollingworthite, merenskyite, and cooperite-braggite.

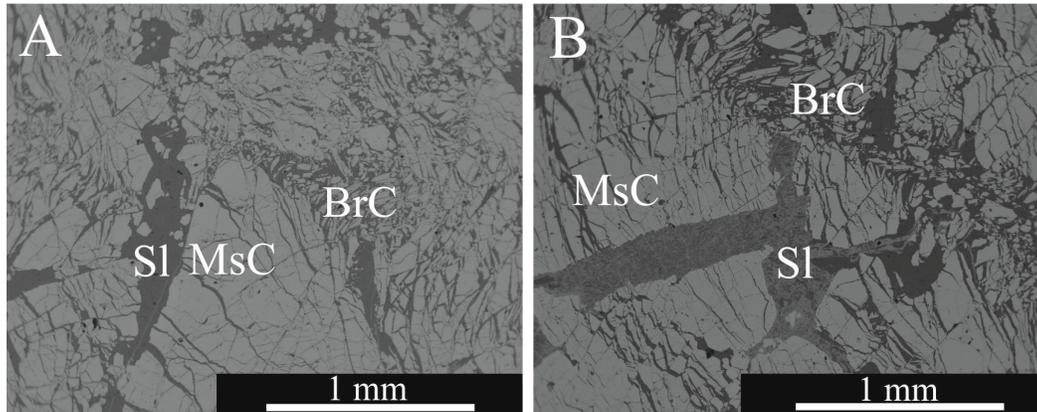


Figure 2. Back-scattered electron images (BSE) of massive and brecciated Othrys chromitite from polished sections (A,B). Abbreviations: Sl = silicates, MsC = massive chromite, BrC = brecciated chromite.

3. Analytical Methods

The processing and recovery of the heavy minerals were carried out by treating about 10 kg of massive chromitite at SGS Mineral Services, Canada, following the procedure described by Tsikouras et al. [23] and Ifandi et al. [16]. The heavy minerals were prepared in epoxy blocks, and then, polished for mineralogical examination. Quantitative chemical analyses of tsikourasite were carried out using a JEOL JXA-8200 electron microprobe, installed in the E. F. Stumpfl laboratory, Leoben University, Austria, operating in WDS (wavelength dispersive spectrometry) mode. Major and minor elements were determined at 20 kV accelerating voltage and 10 nA beam current, with 20 s as counting time for the peak and 10 s for the backgrounds. The beam diameter was about 1 μm in size. For the WDS analyses, the following lines and diffracting crystals were used: P, S = ($K\alpha$, PETJ); V, Fe, Co, Ni, Cr = ($K\alpha$, LIFH); and Mo = ($L\alpha$, PETJ). The following standards were selected: synthetic Ni_3P for Ni and P, molybdenite for S and Mo, synthetic Fe_3P for Fe, synthetic metallic vanadium for V, skutterudite for Co, and chromite for Cr. The ZAF correction method was applied. Automatic corrections were performed for interferences P-Mo, Cr-V, and Mo-S using the same standards selected for quantitative analyses, that is to say, molybdenite that does not contain P and synthetic Fe_3P that does not contain Mo. The detection limits were calculated using the software and expressed as ppm are: P and S = 100; Ni, Fe, V, and Co = 150; Mo and Cr = 200. Representative analyses of tsikourasite are listed in Table 1.

Table 1. Analytical data (wt% of elements) for tsikourasite.

Sample	P	S	V	Fe	Co	Ni	Mo	Total
ot2gr17an4	7.59	0.64	14.19	1.14	7.47	23.78	43.56	98.37
ot2gr17an3	7.96	0.67	14.18	1.18	7.72	23.77	44.04	99.52
ot2gr17an5	8.03	0.65	14.16	1.18	7.53	24.16	44.16	99.87
ot2gr17an2	8.05	0.71	13.98	1.19	7.56	23.86	44.39	99.74
ot2gr17an1	8.20	0.66	14.13	1.20	7.67	23.91	44.65	100.42
average	7.97	0.67	14.13	1.18	7.59	23.90	44.16	99.60

According to the values reported in Table 1, trace amounts of S were also detected even after the interference Mo-S was corrected but this was not conclusive. In most cases, chromium was below detection limit. The same instrument was used to obtain back-scattered electron images.

X-ray powder diffraction data were not collected owing to the small size of the grain and the limited material available. Single-crystal X-ray studies were carried out at the University of Florence using an Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Diffraction CCD detector, with graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) using a hand-picked crystal fragment from the polished section under a reflected light microscope. The crystal (about 80 μm in size) was carefully and repeatedly washed in acetone. It did not show any other visible phase attached to the surface. Single-crystal X-ray diffraction intensity data were integrated and corrected for standard Lorentz polarization factors with the CrysAlis RED package [24]. The program ABSPACK in CrysAlis RED [25] was used for the absorption correction.

The reflectance measurements on tsikourasite were carried out using a WTiC standard and a J & M TIDAS diode array spectrophotometer at the Natural History Museum, London, UK.

Unpolarized micro-Raman spectra on tsikourasite were collected at the University of Pisa, Italy, using a Jobin Yvon Horiba XploRA Plus apparatus equipped with a motorized x-y-stage and an Olympus BX41 microscope with a 100 \times objective. The 532 nm line of a solid-state laser was used. The minimum lateral and depth resolution was set to a few μm . The system was calibrated using the 520.6 cm^{-1} Raman band of silicon before each experimental session. Spectra were collected through multiple acquisitions with single counting times of 120 s, with the laser power filtered at 1%. The backscattered radiation was analyzed with a 1200 mm^{-1} grating monochromator. However, the results suggested that the micro-Raman spectroscopy was not appropriate to study tsikourasite as its spectrum is very similar to those of the associated minerals such as nickelphosphide, Ni-allabogdanite or Ni-barringerite, and V-sulphide, despite the difference in their chemical composition.

4. Physical and Optical Properties

Tsikourasite forms tiny grains (from a few μm up to about 80 μm) and occurs as isolated grains or associated with other known minerals such as nickelphosphide and awaruite, and with new minerals such as Ni-allabogdanite or Ni-barringerite and a V-sulphide (Figure 3).

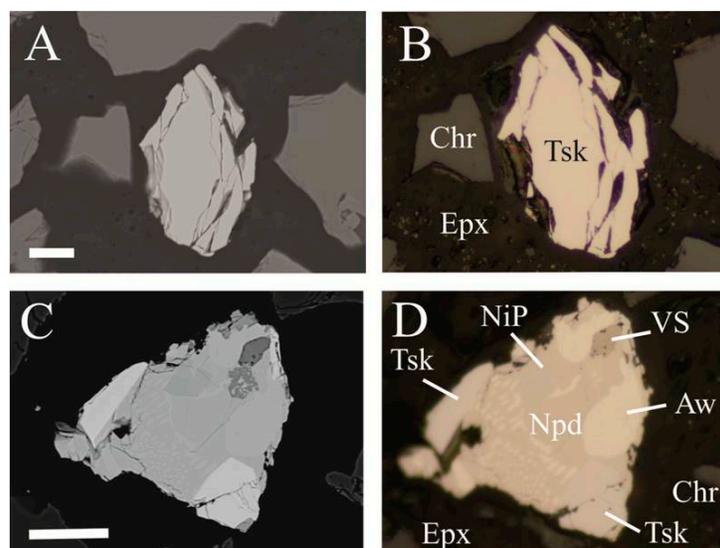


Figure 3. Back-scattered electron images (BSE) (A,C) and digital image in reflected plane polarized light (B,D) showing tsikourasite from the chromitite of Agios Stefanos. Abbreviations: Tsk = tsikourasite, Epx = epoxy, Chr = chromite, NiP = Ni-allabogdanite or Ni-barringerite, VS = V-sulphide, Aw = awaruite, Npd = nickelphosphide. Scale bar = 10 μm .

The hardness and density were not measured because of the small grain size. However, the density of tsikourasite is $9.182 \text{ g}\cdot\text{cm}^{-3}$ and it was calculated based on the ideal chemical formula and unit-cell volume from the single-crystal X-ray data. Tsikourasite is brittle and has a metallic luster. In plane-polarized light, the mineral is white yellow and shows no birefractance, anisotropism or pleochroism. Internal reflections were not observed. Reflectance values of tsikourasite in air (R in %) are reported in Table 2.

Table 2. Reflectance values for tsikourasite.

λ (nm)	R	λ (nm)	R
400	54.6	560	57.0
420	54.9	589	57.5
440	55.2	580	57.3
460	55.5	600	57.6
470	55.7	620	58.0
480	55.8	640	58.3
500	56.1	650	58.5
520	56.4	660	58.6
546	56.8	680	58.9
540	56.7	700	59.2

Note: The values required by the Commission on Ore Mineralogy are given in bold.

5. Chemical Composition and X-ray Crystallography

Electron microprobe analyses and X-ray data reveal that the empirical formula of tsikourasite, based on $\Sigma(\text{Mo} + \text{V} + \text{Fe} + \text{Co} + \text{Ni}) = 5$ apfu coupled with the structural results (see below) is $(\text{Mo}_{1.778}\text{V}_{1.071}\text{Fe}_{0.082}\text{Co}_{0.069})_{\Sigma 3.000}(\text{Ni}_{1.572}\text{Co}_{0.428})_{\Sigma 2.000}(\text{P}_{0.981}\text{S}_{0.079})_{\Sigma 1.060}$ and the simplified formula is $\text{Mo}_3\text{Ni}_2\text{P}_{1+x}$.

A total of 2548 unique X-ray reflections were collected. Noteworthy, 59 reflections did not belong to the tsikourasite structure. The indexation of these reflections led to a cubic cell of $\approx 8.3 \text{ \AA}$ with a F lattice, likely corresponding to a very minor amount of a spinel-group mineral (e.g., magnesiochromite) finely intergrown in the selected crystal. Systematic absences, the statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.785$) that indicated the absence of an inversion center and the similarity of the unit-cell parameter (and chemical composition) with the synthetic $\text{Mo}_3\text{Ni}_2\text{P}_{1.16}$ compound [17], led to the choice of the space group F-43m. The structure was thus refined starting from the atom coordinates of the $\text{Mo}_3\text{Ni}_2\text{P}_{1.16}$ compound [18], using the program Shelx-97 [26]. The site occupation factor (s.o.f.) at the structural sites was permitted to vary (Mo vs. \square , Ni vs. \square and P vs. \square) using scattering curves for neutral atoms taken from the International Tables for Crystallography [27]. The Ni sites were found fully occupied by nickel and then fixed in the subsequent refinement cycles. One of the phosphorous positions (P1) was found to be fully occupied, whereas P2 was found partially occupied (20%), as it occurs in the synthetic equivalent of tsikourasite [18]. The two Mo positions showed a mean electron number of 32.84 and 36.04, and were thought to be occupied by Mo, V, and minor Fe and Co. Given the large number of metals with similar site scattering it is difficult to report a definitive site distribution for tsikourasite. However, the mean electron numbers refined at the two Mo sites clearly indicate that Mo (the species with the higher electron number) is there and that it is replaced by a lighter element. In analogy with natural and synthetic compounds we chose V as the main species present at the Mo sites responsible for the lowering of the mean electron numbers. In this way, the following two site populations were derived for the Mo1 and Mo2 sites:



The Ni sites were thought to be filled by Ni and the remaining Co.

Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 3, whereas selected bond distances are shown in Table 4. The X-ray powder diffraction data obtained using the atom coordinates shown in in Table 3 are shown in Table 5. The crystallographic Information File is available as Supplementary Material (tsikourasite.CIF).

Table 3. Atoms, Wyckoff positions, atom coordinates, and isotropic displacement parameters (\AA^2) for tsikourasite.

Atom	Wyckoff	x/a	y/b	z/c	U_{iso}
Mo1	24f	0.1941(2)	0	0	0.0162(8)
Mo2	24g	0.4437(2)	$\frac{1}{4}$	$\frac{1}{4}$	0.0169(8)
Ni1	16e	0.8319(2)	0.8319(2)	0.8319(2)	0.0189(7)
Ni2	16e	0.4186(2)	0.4186(2)	0.4186(2)	0.0151(7)
P1	16e	0.6231(9)	0.6231(9)	0.6231(9)	0.0288(6)
P2	4a	0	0	0	0.056(17)

As shown in Figure 4, the crystal is similar in structure to $\text{Mn}_3\text{Ni}_2\text{Si}$, which is a superstructure of the NiTi_2 type [28]. The difference in the unit-cell parameters between tsikourasite [$10.8215(5) \text{\AA}$] and its synthetic equivalent [$10.846(2) \text{\AA}$] is related to the presence of V and Co contents, which exhibit a smaller metallic radius with respect to that of Mo. The tsikourasite structure shows numerous metal–metal bonds (Ni–Ni, Mo–Ni, and Mo–Mo) in contrast to Mo–P and Ni–P bonds. Indeed, the metal atoms are connected to only two or three P atoms while 12 or six metal atoms surround the P1 and P2 atoms, respectively.

Table 4. Selected bond distances (\AA) for tsikourasite.

Mo1–P2	2.100(2)	Ni2–P1 ($\times 3$)	2.303(11)
Mo1–Ni1 ($\times 2$)	2.588(2)	Ni2–Ni2 ($\times 3$)	2.492(5)
Mo1–Ni2 ($\times 2$)	2.730(2)	Ni2–Mo2 ($\times 3$)	2.594(2)
Mo1–P1 ($\times 2$)	2.732(2)	Ni2–Mo1 ($\times 3$)	2.730(2)
Mo1–Mo2 ($\times 4$)	2.8384(2)	P1–Ni2 ($\times 3$)	2.303(11)
Mo1–Mo1	2.970(3)	P1–Ni1 ($\times 3$)	2.362(11)
Mo2–Ni2 ($\times 2$)	2.594(2)	P1–Mo1 ($\times 3$)	2.732(2)
Mo2–Ni1 ($\times 2$)	2.733(2)	P1–Mo2 ($\times 3$)	2.746(3)
Mo2–P1 ($\times 2$)	2.746(3)	P2–Mo1 ($\times 6$)	2.100(2)
Mo2–Mo1 ($\times 4$)	2.8384(2)		
Mo2–Mo2 ($\times 2$)	2.964(3)		
Ni1–P1 ($\times 3$)	2.362(11)		
Ni1–Ni1 ($\times 3$)	2.507(5)		
Ni1–Mo1 ($\times 3$)	2.588(2)		
Ni1–Mo2 ($\times 3$)	2.733(2)		

The main feature of the structure results from the arrangement of Mo atoms, which generate $[\text{PMo}_6]$ -octahedra in a diamond-like network, with intra Mo–Mo distances of 2.97\AA . Half of the octahedra, which are built by Mo2 atoms, are empty, while the second half formed by Mo1 atoms are occupied by P2, which shows partial occupancy (20%). According to Oryshchyn et al. [18], these occupied octahedra are displayed in an fcc array.

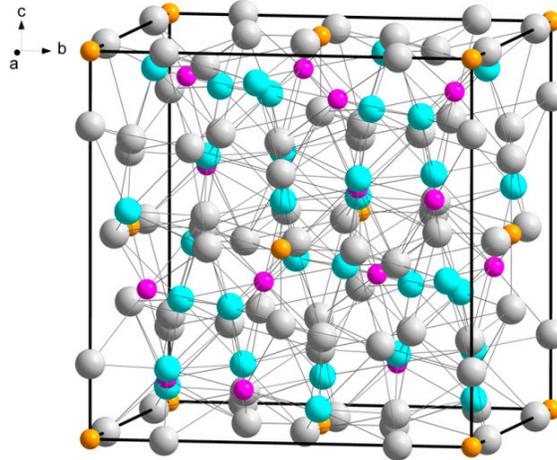


Figure 4. The crystal structure of tsikourasite. Grey and light blue circles refer to Mo and Ni atoms, respectively. Violet circles refer to the P1 position whereas orange spheres indicate the partially occupied P2 position. The unit cell and the orientation of the structure are outlined.

Table 5. Calculated X-ray powder diffraction pattern for tsikourasite ($\text{CuK}\alpha$). The strongest reflections are given in bold.

<i>h</i>	<i>k</i>	<i>l</i>	d_{calc}	I_{calc}
2	2	2	3.1239	5
4	0	0	2.7054	13
3	3	1	2.4826	12
4	2	2	2.2089	42
5	1	1	2.0826	65
3	3	3	2.0826	35
4	4	0	1.9130	21
4	4	2	1.8036	8
5	5	1	1.5153	5
7	3	1	1.4088	5
7	3	3	1.3221	6
6	6	0	1.2753	14
8	2	2	1.2753	17
5	5	5	1.2496	7
9	3	3	1.0876	8
8	8	4	0.9018	5
11	5	1	0.8925	8

6. Relation to Other Species

Tsikourasite does not correspond to any valid or invalid unnamed mineral [29]. According to the calculated formula, tsikourasite could represent the Mo equivalent of the grains recently found in chromitites of the Alapaevsk and Gerakini-Ormylia ophiolites, located in Russia and Greece, respectively, characterized by the formula $(\text{Ni,Fe})_5\text{P}$ [14,15]. Although tsikourasite is similar in composition to monipite (MoNiP) [7], to the recently discovered polekhovskiyite (MoNiP_2) [11], and to the synthetic material MoNiP_2 [30], these phases are hexagonal and not cubic like tsikourasite.

7. Discussion

The investigation of rare accessory minerals in rocks and ores is usually limited by the scarcity and small grain size of the target minerals. Many studies rely on the investigation of only a few

mineral grains found using in situ technique. On the contrary, the study of mineral concentrates provides a greater bulk and more extensive range of minerals than petrographic thin sections and, as consequently, a better characterization of the heavy-mineral assemblage and a better statistical basis for mineralogical and petrological conclusions can be achieved (e.g., [22,31–33]). Using this technique, several new minerals have been discovered in recent years. However, the main disadvantages of a study of minerals concentrates are: (1) lack of in situ textural information, and (2) some of the phases occurring in the concentrates can be contaminants (introduced in the separation process). In this respect, the finding of base metals alloys, diamonds, corundum, and carbides, which are compounds that are widely used during sample collection and preparation, has generated justified skepticism among the mineralogical research community. Therefore, aware of the facts described above, all the sample preparation procedures were carefully checked. The laboratory uses a grinder manufactured by TM Engineering with media Alloy 1 composed of Cr and Mo. This material is very hard and is recognized to be the best for applications where abrasion and impact is the norm. The grinder used to obtain our concentrate does not consist of a superalloy of Ni and Fe with a phosphide filler. In addition, during the sampling in the Agios Stefanos mine, only a steel hammer was used. Taking into consideration the procedure and the materials used, we discarded the possibility of contamination a priori. Furthermore, tsikourasite exhibits complex chemical compositions, which includes a great number of elements, such as P, S, Fe, Ni, Co, V, and Mo. We tested the Alloy 1 used during the preparation of the studied concentrates and found that it was composed of Cr and Mo only. Previously, other chromitite samples, obtained with the same technique in the same laboratory, had been carefully studied, however, no phosphides had been recovered [22,32,33]. The finding, by X-ray examination of a very minor amount of a spinel-group mineral (e.g., magnesiochromite) finely intergrown with tsikourasite, represents strong proof against possible anthropogenic contamination. Furthermore, we found direct-contact intergrowths of minerals, such as Ni and V phosphides and awaruite that occur associated with tsikourasite (Figure 2), with the host magnesiochromite and other natural phases as illustrated in Figure 5. This finding is further evidence that tsikourasite and the other phosphides found in the Othrys chromitite belong to a natural mineralogical assemblage.

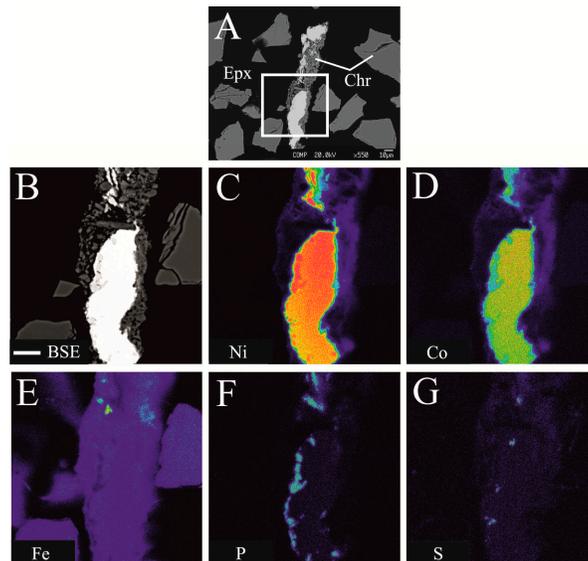


Figure 5. BSE images from heavy concentrate of the Othrys chromitite showing a brecciated texture in a similar way to those reported in Figure 2A. Enlargement of the grain of Figure 5A, displaying the brecciated chromite in contact with awaruite containing small blebs of pentlandite and associated with a Ni-phosphide (B). X-ray elemental distribution map for Ni (C), Co (D), Fe (E), P (F), S (G). Abbreviations: Epx = epoxy, Chr = chromite. Scale bar in Figure B is 10 μ m.

8. Genetic Models for the Precipitation of Tsikourasite

Although interpretation of the origin of tsikourasite is still speculative and it embraces numerous possible processes, its composition and paragenetic assemblage indicates, unequivocally, that it was crystallized in a local reducing geochemical environment. Reducing conditions have been described during the serpentinization of peridotites [34]. These observations allowed us to postulate that the phosphides and the associated minerals found in the ophiolitic chromitites of Othrys and Gerakini-Ormylia (Greece), and Alapaevsk (Russia) may have crystallized during the serpentinization process at a low temperature [14–16]. This assumption was supported by the discovery of the Ni equivalent of tsikourasite in situ and was associated with the serpentine rich matrix of the Alapaevsk chromitite of Russia [14]. In a recent paper, Etiope et al. [35] demonstrated, among several rocks of ophiolites in Greece, i.e., serpentinite, peridotite, chromitite, gabbro, rodingite, and basalt, that only chromitites, including those of the Othrys complex, hosted considerable amounts of abiogenic methane. These authors hypothesized that the CH₄ formation occurred at temperatures below 150 °C via the Sabatier reaction during the serpentinization process, which provides further evidence that reducing conditions can be achieved at a low temperature during the alteration of mantle derived rocks.

However, Xiong et al. [36] suggested that reducing conditions in mantle-derived rocks can be achieved locally due to the interaction of mantle-derived fluids enriched in CH₄ and H₂ with basaltic magmas in the shallow lithosphere. Xiong et al. [36] reported on the presence of carbides, nitrides, silicides, and native metals as an ultra-reduced mantle mineralogical assemblage, however, phosphides were not described in this mineralogical assemblage. Natural phosphides have been reported in the mineralogical assemblages described in a few fulgurites [37] as well as being very common in meteorites. However, the probability of intercepting a fragment of a meteorite or a fulgurite in the Othrys ophiolite during the sampling of the studied chromitite, seems very unlikely, because of the lack of high-pressure minerals in our assemblage, which would have formed during any impact [38]. Therefore, we argue that tsikourasite is natural and terrestrial in origin, and was crystallized in mantle derived rocks in a local reducing environment, perhaps during the serpentinization process at low temperature. However, because the synthetic equivalent of tsikourasite was obtained at a temperature of 1350 °C [18] and considering the complex internal textures of tsikourasite with other phases (Figure 3C,D), we cannot exclude the possibility that tsikourasite formed in the mantle itself prior to its oceanic alteration. Analogously to monipite [7], which was found in a calcium-aluminum inclusion of the Allende meteorite, we hypothesize a local melting of reduced portions in the mantle, to temperatures of the order of 1400 °C. During this melting event, Mo, P, Fe, V, Co, and Ni formed immiscible metallic melts within their host. During cooling, either tsikourasite crystallized from the metallic melt (or a P-rich immiscible melt within the alloy melt), or it exsolved at lower temperatures from a Mo-P enriched crystalline alloy.

Supplementary Materials: The following are available online at www.mdpi.com/link, CIF: tsikourasite.

Author Contributions: F.Z. and L.B. wrote the manuscript; F.Z. and L.B. performed the chemical analyses and the diffraction experiments, respectively; E.I. provided information on the sample provenance and petrography of Othrys chromitite; T.G. have performed the concentrate sample; G.G. discussed the chemical data and C.S. obtained the reflectance data. D.M. studied the sample by Raman. All the authors provided support in the data interpretation and revised the manuscript.

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References

1. Britvin, S.N.; Rudashevskii, N.S.; Krivovichev, S.V.; Burns, P.C.; Polekhovskiy, Y.S. Allabogdanite, $(\text{Fe,Ni})_2\text{P}$, a new mineral from the Onello meteorite: The occurrence and crystal structure. *Am. Mineral.* **2002**, *87*, 1245–1249.
2. Zolensky, M.; Gounelle, M.; Mikouchi, T.; Ohsumi, K.; Le, L.; Hagiya, K.; Tachikawa, O. Andreyivanovite: A second new phosphide from the Kaidun meteorite. *Am. Mineral.* **2008**, *93*, 1295–1299.
3. Buseck, P.R. Phosphide from meteorites: Barringerite, a new iron-nickel mineral. *Science* **1969**, *165*, 169–171.
4. Ivanov, A.V.; Zolensky, M.E.; Saito, A.; Ohsumi, K.; Yang, S.V.; Kononkova, N.N.; Mikouchi, T. Florenskyite, FeTiP , a new phosphide from the Kaidun meteorite. *Am. Mineral.* **2000**, *85*, 1082–1086.
5. Britvin, S.N.; Murashko, M.N.; Vapnik, Y.; Polekhovskiy, Y.S.; Krivovichev, S.V. Negevite, IMA 2013-104, Halamishite, IMA 2013-105, Transjordanite, IMA 2013-106, Zuktamrurite, IMA 2013-107. CNMNC Newsletter No. 19, February 2014. *Mineral. Mag.* **2014**, *78*, 165–170.
6. Pratesi, G.; Bindi, L.; Moggi-Cecchi, V. Icosahedral coordination of phosphorus in the crystal structure of melliniite, a new phosphide mineral from the Northwest Africa 1054 acapulcoite. *Am. Mineral.* **2006**, *91*, 451–454.
7. Ma, C.; Beckett, J.R.; Rossman, G.R. Monipite, MoNiP , a new phosphide mineral in a Ca-Al-rich inclusion from the Allende meteorite. *Am. Mineral.* **2014**, *99*, 198–205.
8. Britvin, S.N.; Vapnik, Y.; Polekhovskiy, Y.S.; Krivovichev, S.V. Murashkoite, IMA 2012-071. CNMNC Newsletter No. 15, February 2013. *Mineral. Mag.* **2013**, *77*, 1–12.
9. Britvin, S.N.; Vapnik, Y.; Polekhovskiy, Y.S.; Krivovichev, S.V.; Krzhizhanovskaya, M.G.; Gorelova, L.A.; Vereshchagin, O.S.; Shilovskikh, V.V.; Zaitsev, A.N. Murashkoite, FeP , a new terrestrial phosphide from pyrometamorphic rocks of the Hatrurim Formation, South Levant. *Mineral. Petrol.* **2019**, *113*, 237–248.
10. Britvin, S.N.; Kolomensky, V.D.; Boldyreva, M.M.; Bogdanova, A.N.; Krester, Y.L.; Boldyreva, O.N.; Rudashevskiy, N.S. Nickelphosphide $(\text{Ni,Fe})_3\text{P}$ —The nickel analogue of schreibersite. *Zap. Vseross. Mineral. Obsh.* **1999**, *128*, 64–72.
11. Britvin, S.N.; Murashko, M.N.; Vereshchagin, O.S.; Vapnik, Y.; Shilovskikh, V.V.; Vlasenko, N.S. Polekhovskiyite, IMA 2018-147. CNMNC Newsletter No. 48, April 2019. *Mineral. Mag.* **2019**, *83*, in press.
12. Skala, R.; Cisarova, I. Crystal structure of meteoritic schreibersites: determination of absolute structure. *Phys. Chem. Miner.* **2005**, *31*, 721–732.
13. Britvin, S.N.; Murashko, M.N.; Vapnik, Y.; Polekhovskiy, Y.S.; Krivovichev, S.V.; Vereshchagin, O.S.; Vlasenko, N.S.; Shilovskikh, V.V.; Zaitsev, A.N. Zuktamrurite, FeP_2 , a new mineral, the phosphide analogue of löllingite, FeAs_2 . *Phys. Chem. Mineral.* **2019**, *46*, 361–369.
14. Zaccarini, F.; Pushkarev, E.; Garuti, G.; Kazakov, I. Platinum-Group Minerals and other accessory phases in chromite deposits of the Alapaevsk ophiolite, Central Urals, Russia. *Minerals* **2016**, *6*, 108.
15. Sideridis, A.; Zaccarini, F.; Grammatikopoulos, T.; Tsitsanis, P.; Tsikouras, B.; Pushkarev, E.; Garuti, G.; Hatzipanagiotou, K. First occurrences of Ni-phosphides in chromitites from the ophiolite complexes of Alapaevsk, Russia and GerakiniOrmylia, Greece. *Ophioliti* **2018**, *43*, 75–84.
16. Ifandi, E.; Zaccarini, F.; Tsikouras, B.; Grammatikopoulos, T.; Garuti, G.; Karipi, S.; Hatzipanagiotou, K. First occurrences of Ni-V-Co phosphides in chromitite of Agios Stefanos mine, Othrys ophiolite, Greece. *Ophioliti* **2018**, *43*, 131–145.
17. Zaccarini, F.; Ifandi, E.; Tsikouras, B.; Grammatikopoulos, T.; Garuti, G.; Mauro, D.; Bindi, L.; Stanley, C. Occurrences of new phosphides and sulfide of Ni, Co, V, and Mo from chromitite of the Othrys ophiolite complex (Central Greece). *Per. Ital. Mineral.* **2019**, in press.
18. Oryshchyn, S.V.; Le Sénéchal, C.; Députier, S.; Bauer, J.; Guerin, R.; Akselrud, L.G. New Ternary Phases in the Mo–Ni–P System: Synthesis and Crystal Structures. *J. Solid State Chem.* **2001**, *160*, 156–166.
19. Rassios, A.; Smith, A.G. Constraints on the formation and emplacement age of western Greek ophiolites (Vourinos, Pindos, and Othris) inferred from deformation structures in peridotites. In *Ophiolites and Oceanic Crust: New Insights from Field Studies and the Ocean Drilling Program*; Dilek, Y., Moores, E., Elthon, D., Nicolas, A. (Eds.); Geological Society of America: Boulder, CO, USA, 2000; pp. 473–484.
20. Economou, M.; Dimou, E.; Economou, G.; Migiros, G.; Vacondios, I.; Grivas, E.; Rassios, A.; Dabitzias, S. Chromite deposits of Greece. In *Chromites, UNESCO's IGCP197 Project Metallogeny of Ophiolites*;

- Petrascheck, W.; Karamata, S.; Kravchenko, G.G.; Johan, Z.; Economou M.; Engin, T. (Eds.); Theophrastus Publications S.A.: Athens, Greece, 1986; pp. 129–159.
21. Garuti, G.; Zaccarini, F.; Economou-Eliopoulos, M. Paragenesis and composition of laurite from chromitites of Othrys (Greece): Implications for Os-Ru fractionation in ophiolite upper mantle of the Balkan Peninsula. *Mineral. Deposita* **1999**, *34*, 312–319.
 22. Tsikouras, B.; Ifandi, E.; Karipi, S.; Grammatikopoulos, T.A.; Hatzipanagiotou, K. Investigation of Platinum-Group Minerals (PGM) from Othrys chromitites (Greece) using superpanning concentrates. *Minerals* **2016**, *6*, 94.
 23. Bortolotti, V.; Chiari, M.; Marcucci, M.; Photiades, A.; Principi, G.; Saccani E. New geochemical and age data on the ophiolites from the Othrys area (Greece): Implication for the Triassic evolution of the Vardar ocean. *Ophioliti* **2008**, *33*, 135–151.
 24. Oxford Diffraction Ltd. *CrysAlis RED*; Oxford Diffraction Ltd.: Abingdon, UK, 2006.
 25. Oxford Diffraction Ltd. *ABSPACK in CrysAlis RED*; Oxford Diffraction Ltd.: Abingdon, UK, 2006.
 26. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
 27. Wilson, A.J.C. *International Tables for Crystallography: Mathematical, Physical, and Chemical Tables*; International Union of Crystallography: Chester, UK, 1992; Volume 3.
 28. Mueller, M.H.; Knott, H.W. The crystal structures of Ti_2Cu , Ti_2Ni , Ti_4Ni_2O , and Ti_4Cu_2O . *Trans. Met. Soc. AIME* **1963**, *227*, 674–678.
 29. Smith, D.G.W.; Nickel, E.H. A system for codification for unnamed minerals: report of the Subcommittee for Unnamed Minerals of the IMA Commission on New Minerals, Nomenclature and Classification. *Can. Mineral.* **2007**, *45*, 983–1055.
 30. Guérin, R.; Sergent, M. Nouveaux phosphures ternaires: $NiMoP_2$, $NiWP_2$, $CoMoP_2$ et $CoWP_2$. *J. Solid State Chem.* **1976**, *18*, 317–323.
 31. Rudashevsky, N.S.; Garuti, G.; Andersen, J.C.Ø; Kretser, Yu.L.; Rudashevsky, V.N.; Zaccarini, F. Separation of accessory minerals from rocks and ores by hydroseparation (HS) technology: Method and application to CHR-2 chromitite, Niquelândia intrusion, Brazil. *Trans. Inst. Mining Metall.* **2002**, *111*, B87–B94.
 32. Kapsiotis, A.; Grammatikopoulos, T.A.; Tsikouras, B.; Hatzipanagiotou, K. Platinum-group mineral characterization in concentrates from high-grade PGE Al-rich chromitites of Korydallos area in the Pindos ophiolite complex (NW Greece). *Resource Geol.* **2010**, *60*, 178–191.
 33. Grammatikopoulos, T.A.; Kapsiotis, A.; Tsikouras, B.; Hatzipanagiotou, K.; Zaccarini, F.; Garuti G. Spinell composition, PGE geochemistry and mineralogy of the chromitites from the Vourinos ophiolite complex, northwestern Greece. *Can. Mineral.* **2011**, *49*, 1571–1598.
 34. Malvoisin, B.; Chopin, C.; Brunet, F.; Matthieu, E.; Galvez, M.E. Low-temperature Wollastonite formed by carbonate reduction: a marker of serpentinite redox conditions. *J. Petrol.* **2012**, *53*, 159–176.
 35. Etiope, G.; Ifandi, E.; Nazzari, M.; Procesi, M.; Tsikouras, B.; Ventura, G.; Steele, A.; Tardini, R.; Szatmari, P. Widespread abiotic methane in chromitites. *Sci. Rep.* **2018**, *8*, 8728.
 36. Xiong, Q.; Griffin, W.L.; Huang, J.X.; Gain, S.E.M.; Toledo, V.; Pearson, N.J.; O'Reilly, S.Y. Super-reduced mineral assemblages in “ophiolitic” chromitites and peridotites: the view from Mount Carmel. *Eur. J. Mineral.* **2017**, *29*, 557–570.
 37. Pasek, M.A.; Hammeijer, J.P.; Buick, R.; Gull, M.; Atlas, Z. Evidence for reactive reduced phosphorus species in the early Archean ocean. *Proc. Natural Acad. Sci. U.S.A.* **2013**, *110*, 100089–100094.
 38. Ballhaus, C.; Wirth, R.; Fonseca, R.O.C.; Blanchard, H.; Pröll, W.; Bragagni, A.; Nagel, T.; Schreiber, A.; Dittrich, S.; Thome, V.; Hezel, D.C.; Below, R.; Cieszynski, H. Ultra-high pressure and ultra-reduced minerals in ophiolites may form by lightning strikes. *Geochem. Perspec. Lett.* **2017**, *5*, 42–46.

