







Article

# Grammatikopoulosite, NiVP, a New Phosphide from the Chromitite of the Othrys Ophiolite, Greece

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**Abstract:** Grammatikopoulosite, NiVP, is a new phosphide discovered in the podiform chromitite and hosted in the mantle sequence of the Othrys ophiolite complex, central Greece. The studied samples were collected from the abandoned chromium mine of Agios Stefanos. Grammatikopoulosite forms small crystals (from 5  $\mu\text{m}$  up to about 80  $\mu\text{m}$ ) and occurs as isolated grains. It is associated with nickelporphide, awaruite, tsikourasite, and an undetermined V-sulphide. It is brittle and has a metallic luster. In plane-polarized light, it is creamy-yellow, weakly birefractant, with measurable but not discernible pleochroism and slight anisotropy with indeterminate rotation tints. Internal reflections were not observed. Reflectance values of mineral in air ( $R_1$ ,  $R_2$  in %) are: 48.8–50.30 at 470 nm, 50.5–53.5 at 546 nm, 51.7–55.2 at 589 nm, and 53.2–57.1 at 650 nm. Five spot analyses of grammatikopoulosite give the average composition: P 19.90, S 0.41, Ni 21.81, V 20.85, Co 16.46, Mo 16.39, Fe 3.83, and Si 0.14, total 99.79 wt %. The empirical formula of grammatikopoulosite—based on  $\Sigma(\text{V} + \text{Ni} + \text{Co} + \text{Mo} + \text{Fe} + \text{Si}) = 2$  apfu, and taking into account the structural results—is  $(\text{Ni}_{0.57}\text{Co}_{0.32}\text{Fe}_{0.11})_{\Sigma 1.00}(\text{V}_{0.63}\text{Mo}_{0.26}\text{Co}_{0.11})_{\Sigma 1.00}(\text{P}_{0.98}\text{S}_{0.02})_{\Sigma 1.00}$ . The simplified formula is  $(\text{Ni},\text{Co})(\text{V},\text{Mo})\text{P}$  and the ideal formula is NiVP, which corresponds to Ni 41.74%, V 36.23%, P 22.03%, total 100 wt %. The density, calculated on the basis of the empirical formula and single-crystal data, is 7.085  $\text{g}/\text{cm}^3$ . The mineral is orthorhombic, space group  $Pnma$ , with  $a = 5.8893(8)$ ,  $b = 3.5723(4)$ ,  $c = 6.8146(9)$  Å,  $V = 143.37(3)$  Å<sup>3</sup>, and  $Z = 4$ . The mineral and its name have been approved by the Commission of New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2019-090). The mineral honors Tassos Grammatikopoulos, geoscientist at the SGS Canada Inc., for his contribution to the economic mineralogy and mineral deposits of Greece.

**Keywords:** grammatikopoulosite; phosphide; chromitite; Agios Stefanos mine; Othrys; ophiolite; Greece

## 1. Introduction

Natural phosphides are very rare phases, representing only 3% of the minerals approved by the International Mineralogical Association (IMA) ([1] and references therein). Most of these natural phosphides have been discovered and described in meteorites. Only recently have several new

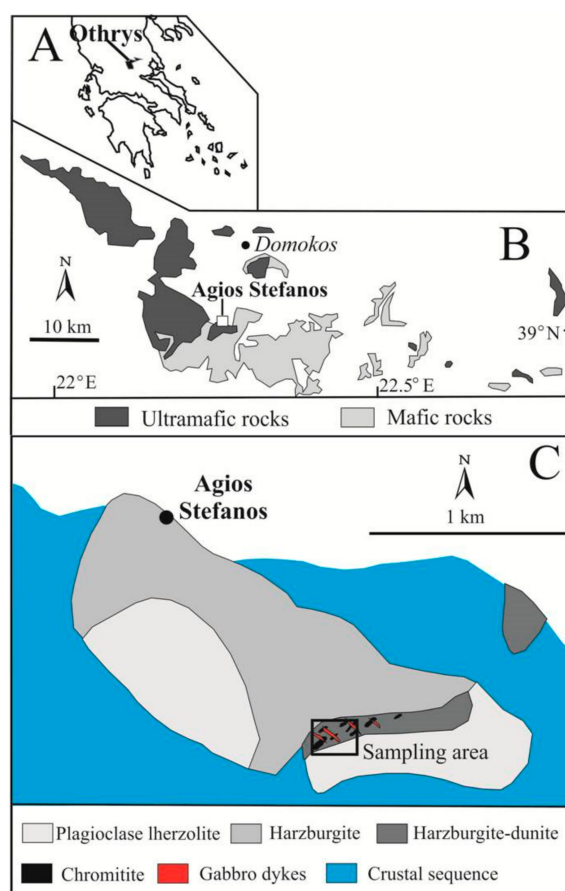
phosphides been discovered in terrestrial rocks, most of which are associated with the pyrometamorphic rocks of the Hatrurim Formation, Southern Levant [2]. Phosphides are documented in podiform chromitites hosted in the mantle sequence of ophiolite complexes of Greece and Russia [3–6] but are very rare. The phosphide found in the Russian chromitite was found in situ, in contact with serpentine of the altered interstitial silicates. The phosphides associated with the Greek chromitite were documented in heavy concentrates. Recently, the new mineral tsikourasite ( $\text{Mo}_3\text{Ni}_2\text{P}_{1+x}$  ( $x < 0.25$ )) was discovered in heavy mineral concentrates from a chromitite from the Othrys ophiolite (Greece) [1]. Further investigation of the same mineral concentrates led to the discovery of a second new mineral. Quantitative chemical analysis and crystal structure proved that the studied phase is a new phosphide, characterized by the simplified formula  $(\text{Ni},\text{Co})(\text{V},\text{Mo})\text{P}$  and by the ideal formula  $\text{NiVP}$ , which corresponds to Ni 41.74%, V 36.23%, P 22.03%, total 100 wt %. The mineral is orthorhombic, space group  $Pnma$ , with  $a = 5.8893(8)$ ,  $b = 3.5723(4)$ ,  $c = 6.8146(9)$  Å, and  $Z = 4$ . The mineral and its name have been approved by the Commission of New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2019-090). The mineral honors Tassos Grammatikopoulos (b. 1966), a geoscientist at the SGS Canada Inc., for his contribution to the investigation of economic mineralogy and mineral deposits of Greece. Holotype material is deposited in the Mineralogical Collection of the Museo di Storia Naturale, Università di Pisa, Via Roma 79, Calci (Pisa, Italy), under catalogue number 19,911.

## 2. Geological Background and Occurrence of Grammatikopoulosite

Grammatikopoulosite was discovered in a heavy mineral concentrate, which was prepared from chromitite specimens hosted in the mantle sequence of the Mesozoic Othrys ophiolite, central Greece (Figure 1A–C).

Othrys ophiolite is a complete but dismembered suite (Mirna Group) and consists of three structural units: the uppermost succession with variably serpentinized peridotites, which is structurally bounded by an ophiolite mélange; the intermediate Kournovon dolerite, including cumulate gabbro and local rhyolite; and the lower Sipetorrema Pillow Lava unit including also basaltic flows, siltstones, and chert. The Mirna Group constituted multiple inverted thrust sheets [7], which were eventually obducted onto the Pelagonian Zone during the Late Jurassic–Early Cretaceous [8–14]. Three types of basalts with different geochemical signatures have been described: (i) alkaline within-plate (WPB), (ii) normal-type mid-ocean ridge (N-MORB), and (iii) low-K tholeiite (L-KT). A 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 [15]. N-MORB erupted during the Middle–Late Triassic period. The L-KT basalts erupted during the Middle–Late Triassic period, 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 in oceanic seamounts or in the ocean–continent transition zone adjacent to the rifted continental margin [15].

Electron microprobe analyses of the assemblages of these chromitites revealed that the studied spinel-supergroup minerals are magnesiochromites [1,5,6]. However, spinel mineral chemistry is rather heterogeneous with  $\text{Cr}_2\text{O}_3$  (44.96–51.64 wt %),  $\text{Al}_2\text{O}_3$  (14.18–20.78 wt %),  $\text{MgO}$  (13.34–16.84 wt %), and  $\text{FeO}$  (8.3–13.31 wt %). The calculated  $\text{Fe}_2\text{O}_3$  ranges from 6.72 to 9.26 wt %. The amounts of  $\text{MnO}$  (0.33–0.60 wt %),  $\text{V}_2\text{O}_3$  (0.04–0.30 wt %),  $\text{ZnO}$  (up to 0.07 wt %), and  $\text{NiO}$  (0.03–0.24 wt %) exhibit minor variations. The  $\text{TiO}_2$  content is low (0.03–0.23 wt %), in agreement with the typical value reported for the mantle-hosted podiform chromites. The  $\text{Cr}/(\text{Cr} + \text{Al})$  ratios of the investigated magnesiochromite are lower than those of chromites formed in the supra-subduction zone (SSZ) and those related to boninitic melt [1,5,6].



**Figure 1.** Location of the Othrys complex in Greece: (A) general geological map of the Othrys ophiolite showing the location of the Agios Stefanos chromium mine; (B) and (C) detailed geological setting of the Agios Stefanos area (modified after [5,10,16,17]).

### 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 several authors [1,5,6,18]. Approximately 10 kg of chromitite were collected in the abandoned mine of Agios Stefanos. Subsequently, they were crushed and blended to generate a homogenous composite sample. About 500 g of the composite sample were riffled and stage crushed to a P80 (80% passing) of 75  $\mu\text{m}$ . After, the sample was treated with heavy liquid (the density of the heavy liquids was 3.1  $\text{g}/\text{cm}^3$ ) to separate the heavy minerals. This procedure produced a heavy and light mineral concentrate. The heavy fraction was selected and processed with a superpanner. This method is designed for small amounts of sample and is closely controlled, leading to very effective separation. It consists of a tapering triangular deck with a “V” shape cross section. The table reproduces 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. The less dense material moves towards the top, overlying the heavy minerals. 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” forces the heavy minerals to migrate to the up-slope end of the deck. 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, alloys, and phosphides, while the lighter tail consisted of a particle mixture of chromite and silicates. No source of contamination is likely during

sample collection and subsequent treatment. The heavy minerals were prepared in epoxy blocks, and then polished for mineralogical examination. Quantitative chemical analyses and acquisition of back-scattered electron images of grammatikopoulosite were performed with a JEOL JXA-8200 electron microprobe, installed in the E. F. Stumpfl laboratory, Leoben University, Austria, operating in Wavelength Dispersive Spectrometry (WDS) mode. Major and minor elements were determined at a 20 kV accelerating voltage and a 10 nA beam current, with 20 s as the counting time for the peak and 10 s for the backgrounds. The beam diameter was about 1  $\mu\text{m}$  in size. For the WDS analyses, the following lines and diffracting crystals were used: P, S, Si = ( $K\alpha$ , PETJ), V, Fe, Co, Ni = ( $K\alpha$ , LIFH), and Mo = ( $L\alpha$ , PETJ). The following standards were selected: synthetic  $\text{Ni}_3\text{P}$  for Ni and P, molybdenite for S and Mo, synthetic  $\text{Fe}_3\text{P}$  for Fe, synthetic metallic vanadium for V, skutterudite for Co, quartz for Si, and chromite for Cr. The ZAF correction method was applied. Automatic corrections were performed for interferences P-Mo, Cr-V, and Mo-S. Representative analyses of grammatikopoulosite are listed in Table 1.

**Table 1.** Chemical data (wt % of elements) for grammatikopoulosite.

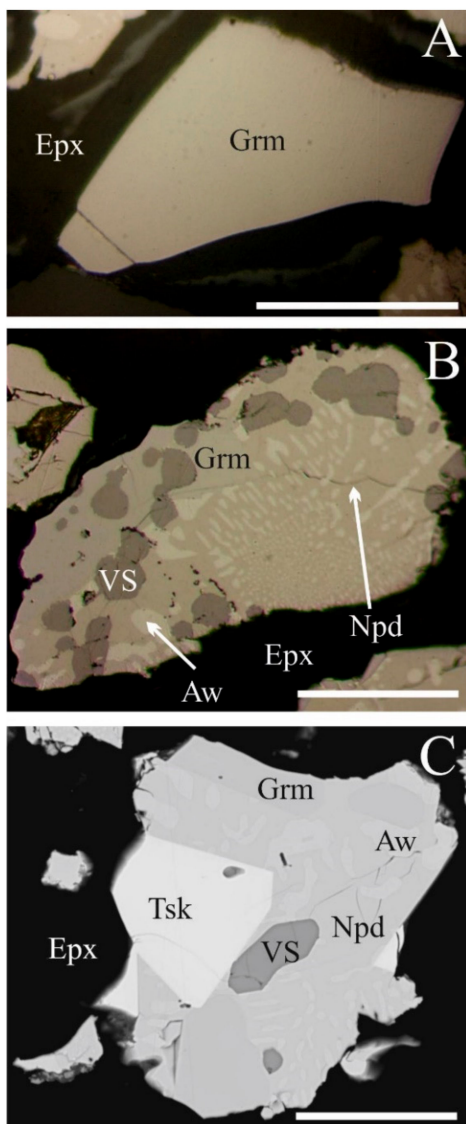
Sample	P	S	Ni	V	Co	Mo	Fe	Si	Total
VP40-1	20.38	0.41	21.98	21.02	16.33	16.72	3.82	0.14	100.79
VP40-2	19.83	0.42	21.70	20.48	16.66	16.36	3.83	0.14	99.41
VP40-3	19.65	0.39	21.72	20.73	16.51	16.35	3.86	0.13	99.33
VP40-4	19.65	0.40	21.95	21.05	16.37	16.31	3.85	0.13	99.71
VP40-5	20.01	0.41	21.69	20.98	16.45	16.20	3.78	0.16	99.67
average	19.90	0.41	21.81	20.85	16.46	16.39	3.83	0.14	99.79

Single-crystal and powder X-ray diffraction data were collected at the University of Florence using a Bruker D8 Venture equipped with a Photon II CCD detector, with graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using a crystal fragment hand-picked from the polished section under a reflected light microscope (cif file, see Supplementary Materials). The crystal (about 80  $\mu\text{m}$  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 software package *Apex3* [19,20].

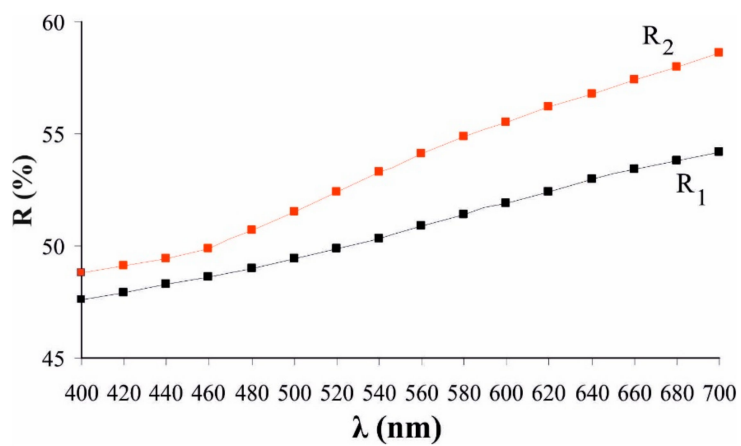
The reflectance measurements on grammatikopoulosite were carried out using a WTiC standard and a J&M TIDAS diode array spectrophotometer at the Natural History Museum of London, UK.

#### 4. Physical and Optical Properties

More than 30 grains of grammatikopoulosite were found in the studied polished sections. Grammatikopoulosite occurs as anhedral to subhedral grains. Most of them were less than 10  $\mu\text{m}$  in size and only two of them were up to about 80  $\mu\text{m}$ . Grammatikopoulosite consists of single (Figure 2A) or poly-phase grains associated with other minerals, such as tsikourasite, nickelphosphide, awaruite, and a V-sulphide, which likely represents another new mineral (Figure 2B,C). Compositions of these minerals have been reported in previous papers [5,6]. In plane-polarized light, grammatikopoulosite is creamy-yellow, weakly bireflectant, with measurable but not discernible pleochroism and slight anisotropy with indeterminate rotation tints. Internal reflections were not observed. Reflectance values of the mineral in air ( $R$  in %) are reported in Table 2 and in Figure 3. Density was not measured because of the small amount of available material and the presence of fine intergrowths with awaruite. The calculated density is equal to  $7.085 \text{ g}\cdot\text{cm}^{-3}$ , based on the empirical composition and unit-cell volume refined from single-crystal XRD data.



**Figure 2.** Digital image in reflected plane-polarized light (A,B) and a back-scattered electron image (C) showing grammatikopouosite from the chromitite of Agios Stefanos. Abbreviations: Grm = grammatikopouosite, Tsk = tsikourasite, VS = V-sulphide, Aw = awaruite, Npd = nickelphosphide, Epx = epoxy. Scale bar = 50 microns.



**Figure 3.** Reflectance data for grammatikopouosite.

**Table 2.** Reflectance values for grammatikopouosite. The values required by the Commission on Ore Mineralogy are given in bold.

$\lambda$ nm	$R_1$	$\lambda$ nm	$R_2$
400	47.6	400	48.8
420	47.9	420	49.1
440	48.3	440	49.4
460	48.6	470	49.9
<b>470</b>	<b>48.8</b>	<b>470</b>	<b>50.3</b>
480	49.0	480	50.7
500	49.4	500	51.5
520	49.9	520	52.4
540	50.3	540	53.3
<b>546</b>	<b>50.5</b>	<b>546</b>	<b>53.5</b>
560	50.9	560	54.1
580	51.4	580	54.9
<b>589</b>	<b>51.7</b>	<b>589</b>	<b>55.2</b>
600	51.9	600	55.5
620	52.4	620	56.2
640	53.0	640	56.8
<b>650</b>	<b>53.2</b>	<b>650</b>	<b>57.1</b>
680	53.8	680	58.0
700	54.2	700	58.6

## 5. Chemical Composition and X-Ray Crystallography

Chemical composition and X-ray data reveal that the empirical formula of grammatikopouosite, based on  $\Sigma(V + Ni + Co + Mo + Fe + Si) = 2$  apfu and taking into account the structural results (see below), is  $(Ni_{0.57}Co_{0.32}Fe_{0.11})_{\Sigma 1.00}(V_{0.63}Mo_{0.26}Co_{0.11})_{\Sigma 1.00}(P_{0.98}S_{0.02})_{\Sigma 1.00}$ . The simplified formula is  $(Ni,Co)(V,Mo)P$  and the ideal formula is NiVP, which corresponds to the composition of Ni = 41.74%, V = 36.23%, and P 22.03% (total 100 wt %).

A small grammatikopouosite grain (about 80  $\mu m$  in size) was handpicked from the polished section under a reflected light microscope and mounted on a 5  $\mu m$  diameter carbon fiber, which was, in turn, attached to a glass rod in preparation for the single-crystal X-ray diffraction study. The fragment consists of crystalline grammatikopouosite associated with minor, fine-grained polycrystalline awaruite. A total of 493 unique reflections were collected up to  $2\theta = 80.33^\circ$ . The mineral is orthorhombic, space group *Pnma*, with  $a = 5.8893(8)$ ,  $b = 3.5723(4)$ ,  $c = 6.8146(9)$  Å, and  $Z = 4$ . Given the similarity in unit-cell values and space groups, the structure was refined starting from the atomic coordinates reported for allabogdanite [21] using the software Shelxl-97 [22]. The site occupancy factor (s.o.f.) at the two cation sites was allowed to vary (Ni vs. Mo) using scattering curves for neutral atoms taken from the International Tables for Crystallography [23], leading to 27.5 and 28.4  $e^-$  for *M1* and *M2* sites, respectively. The P site was found to be fully occupied (P vs. structural vacancy) by phosphorous (site scattering = 15.0  $e^-$ ) and fixed accordingly. Taking into account the site distribution observed in florenskyite [24], allabogdanite [21], and andreyivanovite [25], and in most  $Co_2Si$ -structure-type synthetic compounds [26], we assigned Ni, Fe, and Co to fill the *M1* site (i.e.,  $Ni_{0.57}Co_{0.32}Fe_{0.11}$ ) and all the other elements (i.e.,  $V_{0.63}Mo_{0.26}Co_{0.11}$ ) to the *M2* site. The mean electron numbers calculated with such a site distribution were identical (27.36 and 28.38  $e^-$ ) to those obtained in the refinement. For this reason, the subsequent cycles of refinement were run with the above constrained site populations, yielding an  $R_1 = 0.0276$  for 465 reflections with  $F_o > 4\sigma(F_o)$  and  $R_1 = 0.0291$  for all the 493 independent reflections and 19 parameters. Refined atomic coordinates and isotropic displacement parameters are given in Table 3, whereas selected bond distances are reported in Table 4.

X-ray powder diffraction data for grammatikopouosite (Table 5) were obtained with a Bruker D8 Venture equipped with a Photon II CCD detector, with graphite-monochromatized  $CuK\alpha$  radiation ( $\lambda = 1.54138$  Å). The least squares refinement gave the following values:  $a = 5.8088(2)$ ,  $b = 3.5993(2)$ ,  $c = 6.8221(3)$  Å, and  $V = 142.634(8)$  Å<sup>3</sup>. The calculated powder diffraction pattern obtained using the site occupancies and atomic coordinates is reported in Table 3.

**Table 3.** Atoms, site occupancies, atom coordinates, and isotropic displacement parameters ( $\text{\AA}^2$ ) for grammatikopoulosite.

Atom	Site Occupancy	$x/a$	$y/b$	$z/c$	$U_{\text{iso}}$
M1	Ni <sub>0.57</sub> Co <sub>0.32</sub> Fe <sub>0.11</sub>	0.35709(6)	$\frac{1}{4}$	0.93703(5)	0.00578(10)
M2	V <sub>0.63</sub> Mo <sub>0.26</sub> Co <sub>0.11</sub>	0.47087(6)	$\frac{1}{4}$	0.33109(5)	0.00595(9)
P	P <sub>1.00</sub>	0.23639(12)	$\frac{1}{4}$	0.62449(10)	0.00547(13)

**Table 4.** Selected bond distances ( $\text{\AA}$ ) for grammatikopoulosite.

Atoms	Bond Distance
M1–P	2.2453(8)
M1–P (×2)	2.2639(5)
M1–P	2.2728(8)
M1–M1 (×2)	2.6000(6)
M1–M2 (×2)	2.7280(5)
M1–M2 (×2)	2.7487(5)
M1–M2	2.7677(5)
M1–M2	2.7696(5)
M2–P	2.4299(8)
M2–P (×2)	2.5008(6)
M2–P (×2)	2.5811(6)
M2–M1 (×2)	2.7280(5)
M2–M1 (×2)	2.7487(5)
M2–M1	2.7677(5)
M2–M1	2.7696(5)
M2–M2 (×2)	2.9339(6)

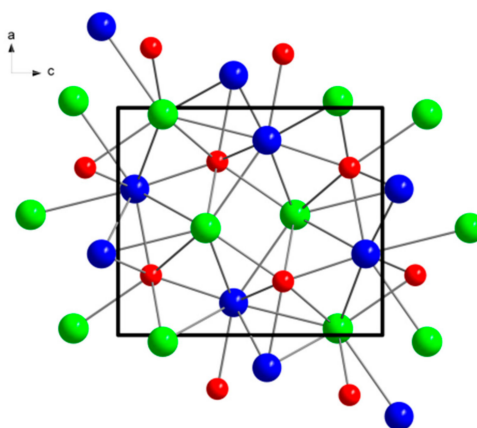
**Table 5.** Observed and calculated X-ray powder diffraction data ( $d$  in  $\text{\AA}$ ) for grammatikopoulosite. The strongest observed reflections are given in bold.

Indices	1		2		
	$hkl$	$d_{\text{obs}}$	$I_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{calc}}$
	101	4.43	10	4.4559	14
	002	-	-	3.4073	5
	<b>102</b>	<b>2.950</b>	<b>20</b>	<b>2.9493</b>	<b>19</b>
	<b>111</b>	<b>2.785</b>	<b>25</b>	<b>2.7872</b>	<b>24</b>
	201	2.699	5	2.7031	5
	<b>112</b>	<b>2.273</b>	<b>60</b>	<b>2.2743</b>	<b>65</b>
	210	2.269	10	2.2722	8
	201	2.230	10	2.2279	9
	<b>211</b>	<b>2.157</b>	<b>100</b>	<b>2.1555</b>	<b>100</b>
	<b>103</b>	<b>2.118</b>	<b>25</b>	<b>2.1194</b>	<b>27</b>
	013	1.915	15	1.9168	14
	301	1.888	10	1.8864	12
	113	1.824	15	1.8227	20
	<b>020</b>	<b>1.784</b>	<b>20</b>	<b>1.7861</b>	<b>21</b>
	004	1.702	10	1.7036	10
	302	1.700	15	1.7010	22
	213	1.608	10	1.6065	7
	114	1.489	5	1.4878	6
	303	1.482	5	1.4853	6
	400	1.470	5	1.4723	6
	123	1.367	10	1.3658	7
	322	1.233	10	1.2318	9
	314	1.211	5	1.2106	6
	215	1.170	10	1.1688	9
	511	1.102	5	1.1038	6
	513	1.005	5	1.0035	5

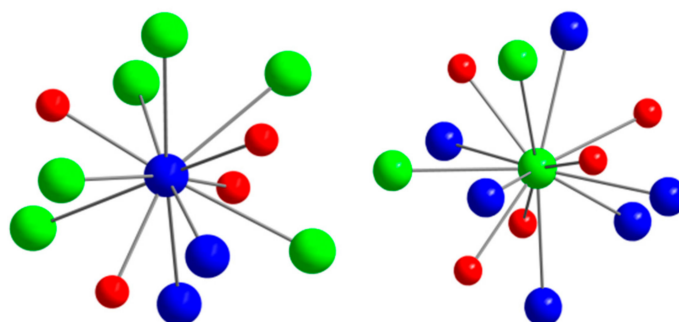
1 = observed diffraction pattern; 2 = calculated diffraction pattern obtained with the atomic coordinates reported in Table 3 (only reflections with  $I_{\text{rel}} \geq 4$  are listed).

## 6. Description of the Structure and Relations to Other Species

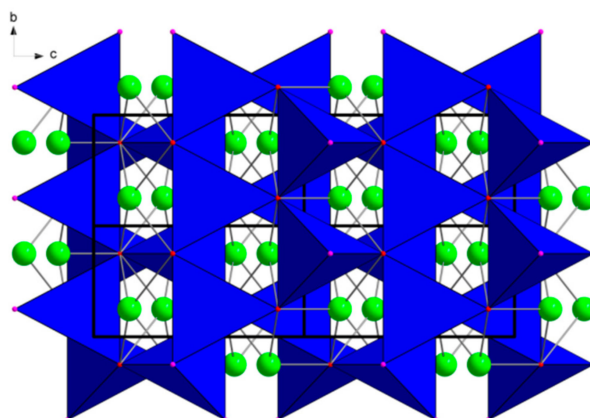
In the structure of grammatikopouosite (Figure 4),  $M1$  links four  $P$  atoms and eight  $M2$  (Figure 5—left), whereas  $M2$  links five  $P$ , six  $M1$ , and two  $M2$  (Figure 5—right). The metal–phosphorous distances are much shorter in the  $M1$  coordination sphere than in that of  $M2$  (Table 4). Interestingly, if only the  $M$ – $P$  distances are considered in the coordination polyhedra of the  $M$  atoms,  $M1P_4$  tetrahedra (Figure 6) forming corner-sharing chains along the  $b$ -axis or  $M2P_5$  square pyramids forming zig-zag chains along the  $a$ -axis (Figure 7) can be observed.



**Figure 4.** The crystal structure of grammatikopouosite projected down  $[10]$ . Blue, green, and red circles refer to  $M1$ ,  $M2$ , and  $P$ , respectively.

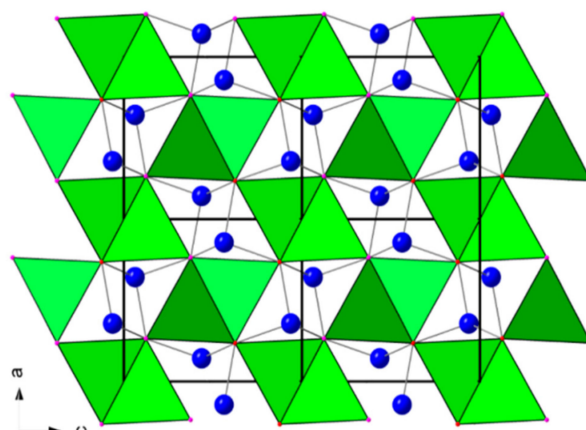


**Figure 5.** Coordination environment of  $M1$  (left) and  $M2$  (right) sites in the crystal structure of grammatikopouosite. Colors and symbols as in Figure 4.



**Figure 6.** Polyhedral representation of the  $M1P_4$  tetrahedra in the crystal structure of grammatikopouosite. Colors and symbols as in Figure 4.





**Figure 7.** Polyhedral representation of the  $M_2P_5$  distorted pyramids in the crystal structure of grammatikopoulosite. Colors and symbols as in Figure 4.

It was reported that the departure from the hexagonal, high-temperature  $P-62m$  structure (barringerite structure) was linked to some ordering between the metals at the  $M$  sites. This was not immediately evident in both allabogdanite [21] and andreyivanovite [25] because of the close site scattering of Fe, Ni, and Cr. On the contrary, the ordering is evident if we take into consideration florenskyite [24] and grammatikopoulosite with ideal formulae  $FeTiP$  and  $NiVP$ , respectively. Ti and V preferentially enter the larger  $M_2$  site in agreement with their larger metallic radius (1.47 and 1.35 Å, respectively [27]).

Grammatikopoulosite does not correspond to any valid or invalid unnamed mineral [28] and it belongs to the group of natural phosphides with the  $Co_2Si$  orthorhombic  $Pnma$  structure, i.e., florenskyite [24], allabogdanite [21], and andreyivanovite [25].

## 7. Discussion and Genetical Implications

Grammatikopoulosite, similar to tsikourasite, is natural in origin despite the fact that both phases were found in heavy mineral concentrates and not in situ [1]. This assumption is supported by the following observations: during the sampling, the only tool used to collect the chromitite was a steel hammer; the concentrates were obtained in a laboratory that uses a grinder manufactured by TM Engineering, with media Alloy 1 composed of Cr and Mo, and does not contain Ni, V, Co, Fe, or P; the used material is very hard and is recognized to be best for applications where abrasion and impact is the norm; and the chemical composition of grammatikopoulosite indicates crystallization under reducing conditions, similar to what has been previously proposed for other phosphides found in ophiolitic chromitites [1,3–6]. According to literature data, the crystallization temperature of most of the terrestrial phosphides is generally comprised between 700 °C and 1150 °C [4]. However, a conclusive model to explain the origin of grammatikopoulosite cannot be provided yet, since it may have a terrestrial origin or represent fragments of a meteorite. The following models, which imply the crystallization in a terrestrial environment from low to high temperatures, can be suggested for the origin of grammatikopoulosite: (i) alteration of chromitite during sub-oceanic or on-land serpentinization at temperatures between 400 °C and 150 °C, which is a typical reducing process [29]; (ii) reaction of the chromitite with high-temperature reducing fluids in the mantle; and (iii) interaction of the chromitite and their host serpentinized peridotites with a surface lightning strike. Phosphide minerals occurring in ophiolitic chromitites in Othrys and Gerakini–Ormylia (Greece), as well as in Alapaevsk (Russia), are closely associated with highly reducing phases such as awaruite, typically forming during serpentinization [1,3–6]. Likewise, grammatikopoulosite is also associated with awaruite and other reducing phases, likely suggesting a low-temperature origin during serpentinization. This hypothesis is strongly supported by the discovery of a Ni-phosphide in situ in

the serpentine-rich matrix of the Alapaevsk chromitite of Russia [3]. Recently, Etiope et al. [30,31] have shown that the Agios Stefanos chromitite is the source rock of abiogenic CH<sub>4</sub> measured in the west Othrys springs. These authors argued that CH<sub>4</sub> formation took place at temperatures below 150 °C via Sabatier reaction during oceanic and on-land serpentinization. This observation provides further evidence that reducing conditions can be achieved at a low temperature during the alteration of mantle-derived rocks. Alternatively, Xiong et al. [32] suggested that reducing conditions can be achieved in mantle rocks, including chromitites, in the shallow lithosphere due to the interaction of mantle-derived fluids enriched in CH<sub>4</sub> and H<sub>2</sub> with basaltic melt. However, no phosphides are reported in the ultra-reduced, high-temperature mineralogical assemblage described by Xiong et al. [32]. Natural phosphides and other ultra-reduced minerals have been rarely described in few fulgurites [33,34] but they are very common accessory phases in meteorites [21,24,25,35–39] or. The rare and localized occurrence of the Othrys phosphides may provide some support to the two last models. However, the probability to have collected a fragment of a meteorite or a fulgurite in the Othrys ophiolite during the sampling of the studied chromitite seems improbable, and for the discrimination of the meteoritic materials, a more detailed isotopic study may be needed. To conclude, an indisputable genetic model to explain how grammatikopouosite is crystallized still needs further investigation.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2075-163X/10/2/131/s1>, CIF: grammatikopouosite.

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

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