

## **Godlevskite Ni<sub>9</sub>S<sub>8</sub> from Dobromirtsi, Central Rhodopes, Bulgaria: First report for the country and genetic implications**

*T. Kerestedjian, F. Gervilla, J.-M. Gonzalez-Jimenez, J. Proenza*

**Abstract.** Godlevskite Ni<sub>9</sub>S<sub>8</sub> is recorded for the first time in Bulgaria. The find comes from chromitites in serpentinitized ultramafics (dunites, peridotites), near the village of Dobromirtsi, Central Rhodopes. The postmagmatic assemblage of the chromitites comprises pentlandite, godlevskite, heazlewoodite, maucherite, orcelite, chalcopyrite and gersdorffite (in the order of decreasing abundance). The magmatic assemblage (in unaltered chromites) also includes pentlandite and less heazlewoodite and millerite as well as PGM – laurite, scarce OsIr alloys and Ir-sulpharsenides. The generalized formula of the recorded mineral, derived from microprobe analyses is: Ni<sub>8.82</sub> Fe<sub>0.14</sub> S<sub>8.04</sub>. Observed textural and structural specifics of the mineral are interpreted as evidences for a solid state re-equilibration from high-temperature MSS (Monosulfide Solid Solution), stable in the 577 – 436°C temperature range, followed by slow annealing below 379°C, well corresponding to the temperature conditions of the regional metamorphic events in the area.

**Томас Керестеджиян, Фернандо Хервия, Хосе-Мария Гонзалес-Хименес, Хоакин Проенца. Годлевският Ni<sub>9</sub>S<sub>8</sub> от Добромирци, Централни Родопи, България: първо съобщение за страната и генетични индикации**

**Резюме.** Годлевският Ni<sub>9</sub>S<sub>8</sub> се описва за първи път в България. Находката произхожда от хромитити в серпентинизирани ултрамафити (дунити, перидотити), в близост до с. Добромирци, Централни Родопи. Постмагматичната минерална асоциация в хромититите включва пентландит, годлевският, хейзълвудит, маухерит, орселит, халкопирит и герсдорфит (в реда на намаляващо обилие). Магматичната асоциация (в непроменени хромити) включва също пентландит и по-рядко хейзълвудит и милерит, както и минерали от групата на платината – лаурит, редки OsIr сплави и Ir-сулфоарсениди. Обобщената формула на описания минерал, по данни от микросондови анализи е: Ni<sub>8.82</sub> Fe<sub>0.14</sub> S<sub>8.04</sub>. Наблюдаваните текстурни и структурни взаимоотношения на минерала са интерпретирани като аргументи в полза на едно твърдофазно преуравновесяване на високотемпературен моносулфиден твърд разтвор, устойчив в температурния диапазон 577 – 436°C, последвано от продължително отвяряне под 379°C, добре съгласуващо се с температурните условия на регионално-метаморфните събития в областта.

*Key words:* godlevskite, Rhodopes, Bulgaria, postmagmatic, metamorphic, serpentinitized ultramafics

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## Introduction

Nickel sulphides are a common constituent of ultrabasic rocks. They can be represented by different stable or meta-stable phases with different Ni:S ratios. The specific compositions, associations and mineralogical characteristics of the phases presented indicate the conditions of formation of the respective assemblages and can serve as mineralogical evidences during reconstructing the geological history of the area. The presence of godlevskite in the dunite hosted chromites of Dobromirtsi is: 1. the first report of godlevskite for Bulgaria; 2. an evidence of sulphide equilibration during serpentinization and/or metamorphic events in the area.

## Previous studies

Phase relations in the Ni-S and Fe-Ni-S systems have been investigated by dry synthesis even before all natural examples have been established as mineral species. The sulphur-rich part of the Ni-S system appears to be rather simple with  $\text{Ni}_3\text{S}_4$  - polydymite and  $\text{NiS}_2$  - vaesite as the only phases (Lundqvist, 1947; Kullerud, Yund, 1962). Four phases are well established at both ends of the more Ni-rich part of the system – NiS - millerite and  $\text{Ni}_3\text{S}_2$  - heazlewoodite with their respective meta-stable high-temperature ( $\alpha$ ) modifications (Kullerud, Yund, 1962; Lin et al, 1978).

A narrow field of Ni:S ratios from 1.08 to 1.22, however, remains questionable for a long time. At least three phases are mentioned in the literature for this interval:  $\text{Ni}_6\text{S}_5$  (Schenck, Frost, 1939; Rosenqvist, 1954),  $\text{Ni}_7\text{S}_6$  (Peyronel, Pacilli, 1942) and  $\text{Ni}_9\text{S}_8$  (Sokolova, 1956). Kullerud and Yund (1962) discredit the existence of  $\text{Ni}_6\text{S}_5$  and  $\text{Ni}_9\text{S}_8$ , suggesting the existence of only two stable phases in this interval - both with composition  $\text{Ni}_7\text{S}_6$ , but having different stability ranges: the low temperature  $\beta$ - $\text{Ni}_7\text{S}_6$  was found to transform into high-temperature –  $\alpha$ - $\text{Ni}_7\text{S}_6$  at 397°C in the presence of excess  $\text{Ni}_3\text{S}_2$  or at 400°C in the presence of excess  $\alpha$ -NiS. The high-temperature

phase has orthorhombic symmetry, confirmed later by Fleet (1972), who determines its structure in Bmmb space group. The low-temperature phase, however, remains unindexed.

In 1969 Kulagov et al. discover a new nickel-excess nickel sulphide from bornite-chalcopyrite veins in Norilsk and Talnakh deposits in Siberia. Along with Ni it contains some 3% Fe and 0.6% Co and its Me:S ratio is 1.02. Its diffraction pattern, however, closely resembles the one for the low-temperature  $\beta$ - $\text{Ni}_7\text{S}_6$  of Kullerud and Yund (1962) and authors accept this composition as the ideal composition of the new species. It is given the name godlevskite, after the name of the Russian economic geologist M. N. Godlevskii. The mineral is affirmed by the IMA Commission of New Minerals and Mineral Names in 1970 (Fleischer, 1970).

Soon after the establishment of godlevskite, Naldrett et al. (1972) report a new occurrence of the mineral from serpentinized dunites in Texmont, Ontario. They confirm the X-ray identity of godlevskite and the synthetic  $\beta$ - $\text{Ni}_7\text{S}_6$  of Kullerud and Yund (1962).

The structure of godlevskite was determined 17 years later in the orthorhombic space group C222 by Fleet (1987), who solved it on ideal composition  $\text{Ni}_9\text{S}_8$ . New microprobe data for the classical godlevskite material from Norilsk (Fleet, 1988) show  $\text{Ni}_{8.7}\text{Fe}_{0.3}\text{S}_8$  confirming the ideal  $\text{Ni}_9\text{S}_8$  composition of the mineral. The structure of synthetic  $\beta$ - $\text{Ni}_7\text{S}_6$ , re-examined in the same study could also be indexed in C222 and solved on  $\text{Ni}_9\text{S}_8$  basis, thus confirming the identity of godlevskite and the synthetic phase. The high-temperature synthetic phase  $\alpha$ - $\text{Ni}_7\text{S}_6$  was found to disproportionate to  $\text{Ni}_9\text{S}_8$  and  $\text{Ni}_3\text{S}_2$  on annealing at 297°C.

Finally, in 1989 the commission of new minerals and mineral names of IMA corrects the godlevskite data, accepting the formula  $\text{Ni}_9\text{S}_8$  (Jambor, Burke, 1989). With this act, the only possible phases in the considered compositional range (Ni:S 1.08-1.22) remain godlevskite  $\text{Ni}_9\text{S}_8$  and the  $\alpha$ - $\text{Ni}_{7\pm x}\text{S}_6$ . The latter is not stable at ambient temperatures, not stoichiometric and highly disordered. This is

the reason why no mineral species with this composition is established. Theoretically, it may probably be formed in nature by very fast cooling geological event, producing natural quenching conditions. However, such case is not reported so far.

The most recent study of the phase relations between the above two phases (Stølen et al., 1994), which slightly corrects the previous data of Kullerud and Yund (1962) is very important from the geological point of view. Its results are summarized in Fig. 1, modified after (Stølen et al., 1994).

The recent studies of the 400 and 500°C sections of the Fe-Ni-S system (Ueno et al., 2000), that may also be important for geo-

logical interpretations can be summarized as follows: at 400°C godlevskite may contain up to 1%wt. Fe and coexist with pentlandite, pentlandite+heazlewoodite, or pentlandite+mss (monosulphide solid solution, corresponding in Ni-rich end to millerite high –  $\alpha\text{Ni}_{1-x}\text{S}$ ). At 500°C  $\alpha\text{-Ni}_{7\pm x}\text{S}_6$  exists instead of godlevskite. It may contain maximum of 3.3%wt. Fe. The tie line with pentlandite and the univariant assemblages around it are the same as those at 400°C.

### Geological setting

The samples were collected in an old chromite mine, close to Dobromiritsi village, (SE Bulgaria). The Dobromiritsi ultramafic massif is

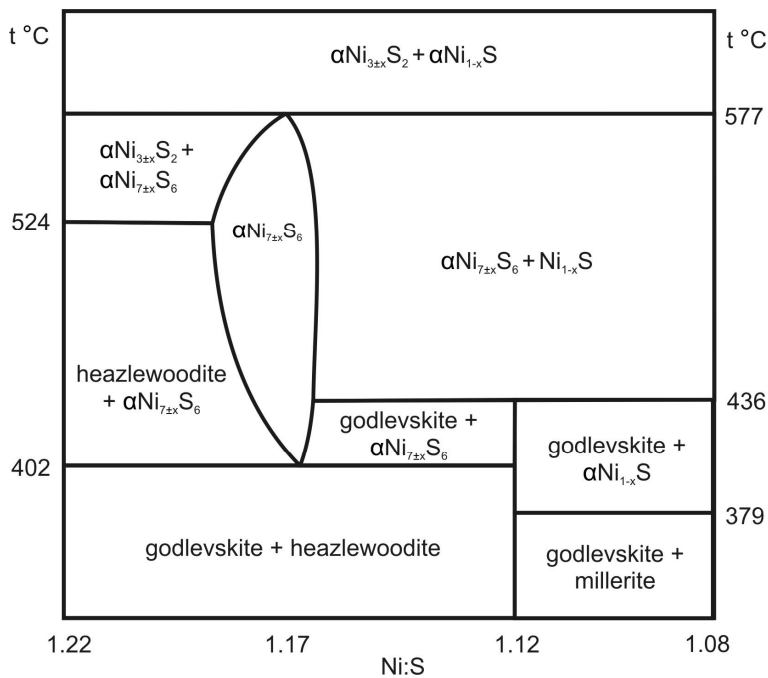


Fig. 1. Phase relations in a portion of the Ni-S system, modified after Stølen et al. (1994). Modifications concern minor changes for compatibility with the geological context: x-axis transformed to Ni:S ratio; y-axis transformed to centigrade; stable phases given with respective mineral names;  $\alpha$  notation added where necessary for compatibility with other citations

located in the easternmost part of the Central Rhodope Mountains and belongs to the Borovitsa lithotectonic unit - the upper most unit of the Variegated Complex, comprising marbles, biotite gneisses and gneissoschists, porphyric and equigranular granites, massive metabasic and the studied serpentinitised rocks (Ovtcharova et al., 2001). The unit is separated from the underlying Startsevo unit by the Borovitsa fault zone, where small granite bodies are emplaced during the Upper Oligocene. The grade of metamorphism is amphibolitic, without any signs of migmatisation. The unit is limited above by the Kurdjali shear zone.

The considered ultramafic body crops out over 11 km<sup>2</sup> and has a SW-NE oriented, elongated shape (Fig. 2). The western part of the body thrusts over Paleozoic metamorphic rocks - biotitic gneisses hosting amphibolite bodies, while the eastern part is tectonically covered by the continental sediments of the Kurdjali lithotectonic unit, bearing Oligocene volcanic rocks. The ultramafic rocks consist of peridotites, harzburgites and dunites with tectonite fabric, as well as minor, cross-cutting pyroxenites. All these rocks are affected by regional, greenschist-amphibolite facies metamorphism. It is possible to identify two differ-

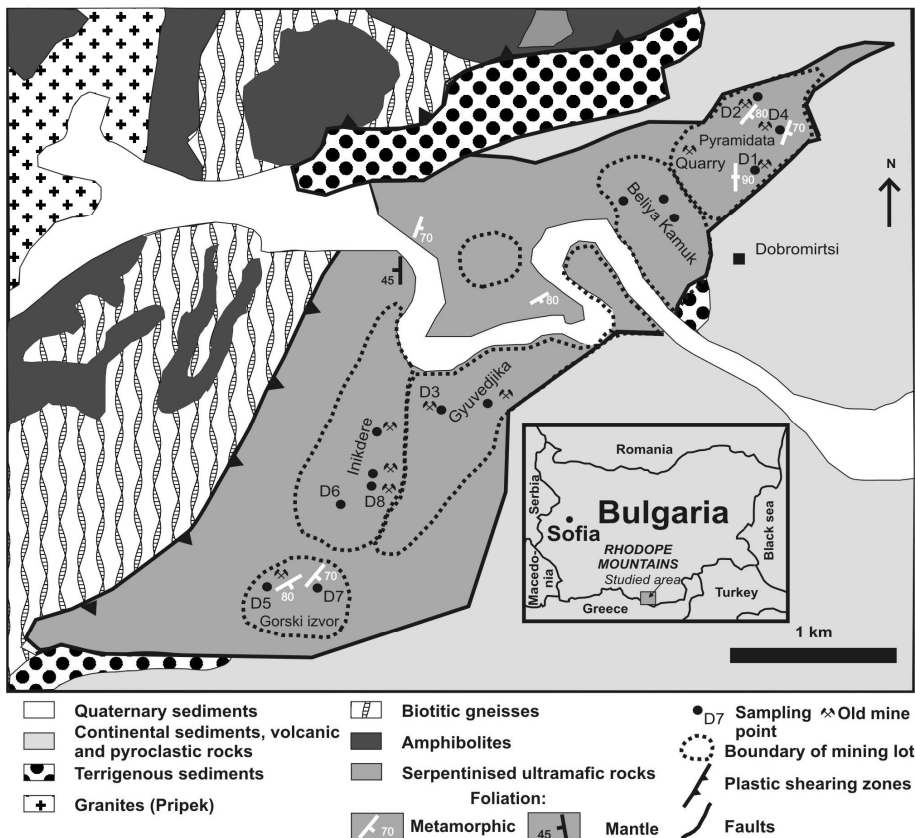


Fig. 2. Dobromiritsi ultramafic massif: Simplified geological map, modified after Ovtcharova et al., (2001)

rent foliations in the ultramafic body: an earlier one, probably related to plastic flow in mantle conditions (black on Fig. 2) and a late mylonitic one (white on Fig. 2) which over-prints the mantle foliation and can be attributed to the crustal emplacement of the body or to the greenschist-amphibolite facies metamorphism.

## Mineralogy of chromitites

### *Chromitites*

Chromitite bodies, recognized in the Dobromirski massif are all concordant to the mylonitic foliation of the host peridotites and locate along a single, dunite-rich horizon. This means that they probably formed at similar deepness in the ophiolitic mantle. Accordingly, mineral chemistry of unaltered chromite in the different bodies investigated is relatively homogeneous, having Cr# between 0.57 and 0.77 (Kerestedjian et al., 2006). Chromitites are predominantly massive, grading to disseminated towards the borders of the body. Most of them are variably fractured and altered along grain boundaries and cracks. During alteration, chromites lose  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , and become rich in  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , giving rise to a phase known as ferritechromite.

### *Platinum-group minerals (PGM)*

According to previous study (González-Jiménez et al., 2006) the platinum-group element (PGE) contents also vary within a restricted range (from 60 to 234 ppb total PGE). Like in most ophiolitic complexes, the studied chromitites are rich in Os, Ir and especially Ru (varies from 37 to 135 ppb) and strongly depleted in Pt and Pd (mostly below 2 ppb). Platinum-group minerals occur as single or composite, minute ( $<50\mu\text{m}$ ) inclusions in chromite. The most abundant PGM recognized is laurite ( $\text{RuS}_2$ ) which constitutes more than 70% of the total PGM and has a similar

chemical composition in the different chromitites (contains between 0.1 and 8 at.% Os and less than 2.5 at.% Ir). Other mineral phases identified are OsIr alloys and Ir-sulpharsenides. The dominant mineral phase in aggregates is laurite, mostly as single grains, euhedral or subhedral in fresh chromites, tending to subhedral in altered chromites and mostly anhedral in the silicate matrix. Less often laurite is accompanied by minor OsIr alloys of irarsite, Ir or base-metal sulphides.

### *Base-metal minerals (BMM)*

Just a small part of the BMM are found as small (below  $20\mu\text{m}$ ) euhedral or subhedral grains in fresh chromites. They are represented mainly by pentlandite and less heazlewoodite and millerite. Main amounts of BMM are found in altered chromites. The main mineral here is again pentlandite, followed by godlevskite, heazlewoodite, maucherite, orcelite, chalcopyrite and gersdorffite. In most cases these minerals are euhedral or subhedral. Pentlandite is the most abundant mineral also in the altered silicate matrix of chromite, followed by heazlewoodite and only scarce grains of godlevskite, maucherite and gersdorffite. Detailed description of the above relations will be given in a forthcoming study (González-Jiménez et al., 2007), especially dedicated to the postmagmatic evolution of PGM and BMM here. Some of the less common mineral phases are shown on the photographs in Fig. 3.

### *Godlevskite*

A total of 55 grains of godlevskite are identified in the studied samples from the stock pile in front of an old mining (point D3 on Fig. 2). Almost all of them are found in altered chromites. In most cases godlevskite grains are euhedral or subhedral, with sizes hardly reaching  $5\mu\text{m}$ . In reflected light it is pale

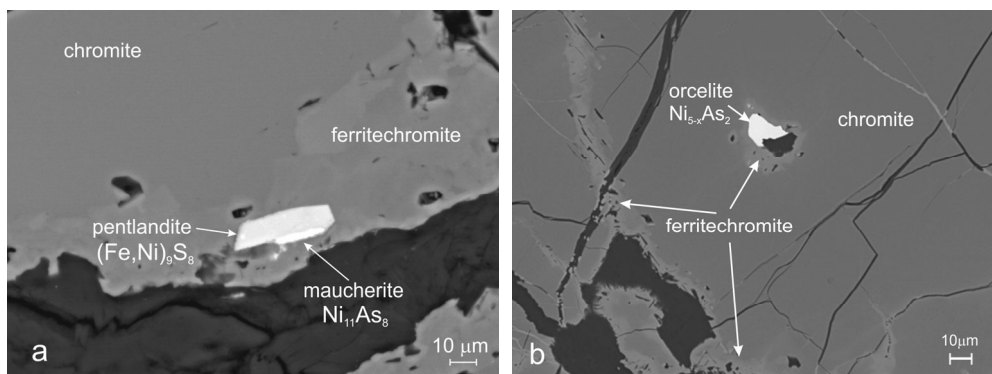


Fig. 3. Back-scattered electron (a) and reflected light (b) images of Fe-Ni sulphides and arsenides in altered portions (ferritechromites) of chromitites

yellow or creamy with weak birefringence in shades of yellow. Anisotropy is strong with colour effects from bluish to reddish. Its reflectivity is similar to that of millerite and lower than heazlewoodite. It shows slightly higher relief against millerite and heazlewoodite in accordance to its slightly higher hardness 4-5. Unfortunately only the biggest grains allow optical identification. In most cases the mineral is too small for any optical features to be employed.

Some godlevskite grains are single, but the majority are found intergrown with pentlandite, heazlewoodite or millerite. Lamellar intergrowths of godlevskite and millerite or godlevskite and heazlewoodite are common.

The composition of godlevskite was determined by a CAMECA SX50 microprobe using accelerating voltage of 20 kV, beam current of 20 nA, beam diameter of 2  $\mu\text{m}$ . Spectral lines measured were:  $K_{\alpha}$  for S, Fe, Co, Ni, Cu, and Se;  $L_{\alpha}$  for Te;  $L_{\beta}$  for As. The standards used were:  $\text{FeS}_2$  (for Fe and S), metallic Co (for Co), metallic Te (for Te), NiO (for Ni),  $\text{CuFeS}_2$  for Cu,  $\text{Bi}_2\text{Se}$  (for Se) and GaAs (for As). Four grains, big enough for obtaining reliable microprobe results were

chosen. They are shown in Table 1. Negligible amounts of Co and Cu on the metallic side as well as As, Se and Te on the non-metallic one were registered. Fe is the only impurity approaching 1 wt.% in the first three analyses and exceeding 2 wt.% in the fourth one. The numbers of atoms per formula unit (*apfu*) are calculated on 17 atom formula base. Conceptual formulae, supposing that all metals take Ni positions and all non-metals – S positions are calculated too. The values of both conceptual Ni and conceptual S firmly lay within a standard deviation of 0.05 for the first 3 analyses, which show a pretty high analytical reproducibility. Including the fourth analysis in the distribution almost doubles the standard deviation. This is just one of the reasons why this analysis is treated separately. Other arguments for the separation of this analysis will be given in the discussion.

The mean Ni:S ratio (conceptual) of 1.11 is very close to the theoretical 9/8 (1.125) for the first three analyses. The fourth analysis deviates also on this criteria, having ratio of 1.14. Generalized formula:  $\text{Ni}_{8.82}\text{Fe}_{0.14}\text{S}_{8.04}$  can be drawn out of the available data.

Table 1. Microprobe analytical data and calculation results for the 4 analyzed grains of godlevskite. Analysis 4 (in italics) is excluded in the calculation of means and standard deviations in the two bottom rows. Arguments in the text

An. Num.		Ni	Fe	Co	Cu	S	As	Se	Te	Total
1	wt. %	65.05	0.84	0.03	0.03	32.71	0.03	0.00	0.00	98.69
2		64.84	1.01	0.03	0.11	32.41	0.00	0.00	0.14	98.55
3		63.90	1.07	0.00	0.12	31.54	0.00	0.01	0.07	96.72
4		<i>64.36</i>	<i>2.14</i>	<i>0.15</i>	<i>0.07</i>	<i>31.61</i>	<i>0.65</i>	<i>0.00</i>	<i>0.09</i>	<i>99.07</i>
1	at. %	51.68	0.70	0.02	0.02	47.56	0.02	0.00	0.00	100.00
2		51.70	0.84	0.02	0.08	47.30	0.00	0.00	0.05	100.00
3		51.99	0.92	0.00	0.09	46.97	0.00	0.01	0.03	100.00
4		<i>51.40</i>	<i>1.79</i>	<i>0.12</i>	<i>0.05</i>	<i>46.20</i>	<i>0.40</i>	<i>0.00</i>	<i>0.03</i>	<i>100.00</i>
1	apfu	8.79	0.12	0.00	0.00	8.08	0.00	0.00	0.00	17.00
2		8.79	0.14	0.00	0.01	8.04	0.00	0.00	0.01	17.00
3		8.84	0.16	0.00	0.02	7.99	0.00	0.00	0.00	17.00
4		<i>8.74</i>	<i>0.30</i>	<i>0.02</i>	<i>0.01</i>	<i>7.85</i>	<i>0.07</i>	<i>0.00</i>	<i>0.01</i>	<i>17.00</i>
		Ni conceptual (Ni+Fe+Co+Cu)			S conceptual (S+As+Se+Te)			Ni:S		
1	conceptual	8.91			8.09			1.10		
2		8.95			8.05			1.11		
3		9.01			7.99			1.13		
4		<i>9.07</i>			<i>7.93</i>			<i>1.14</i>		
	mean	8.96			8.04			1.11		
	stadard dev.	0.05			0.05					

## Discussion

From the compositional point of view, the mineral phase from the first three analyses resembles very closely the ideal  $Ni_9S_8$  formula. Its small Fe content is characteristic feature of the mineral even from its type localities (Kulagov et al., 1969, Naldrett et al., 1972) and the determined values are entirely in the limits of the 400°C Fe miscibility range (Ueno et al., 2000). The rhombic or rhomboidal sections of

the observed grains comply with the orthorhombic symmetry of godlevskite. The environment of the finding – serpentized ultramafic rocks and the assemblage – chromite, pentlandite, heazlewoodite, millerite and maucherite resemble almost literally the one in the Texmont type locality (Naldrett et al., 1972). All together the above features of the finding leave no room for uncertainty about its mineral identification as godlevskite. Taking

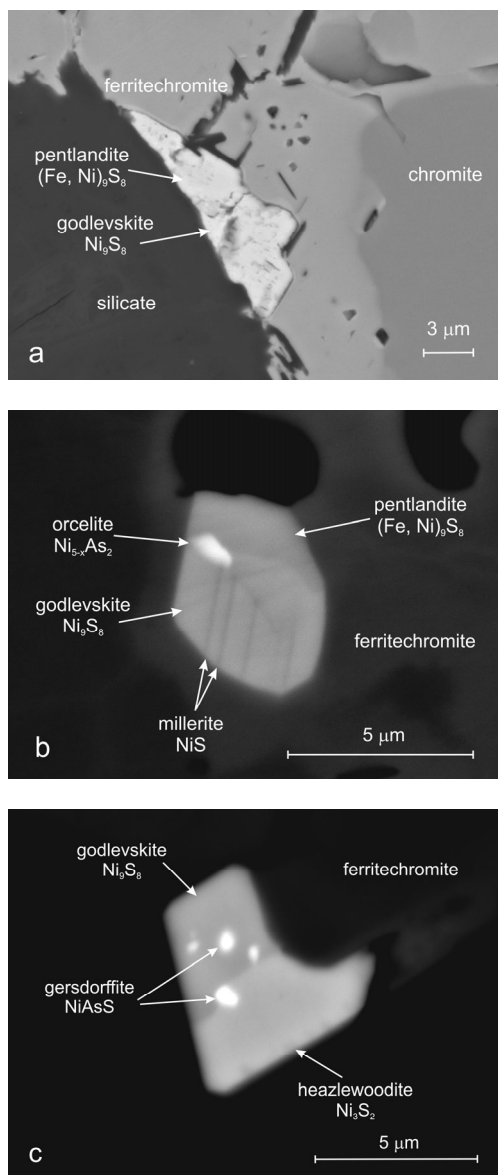


Fig. 4. Reflected light (a) and back-scattered electron images (b, c) of godlevskite intergrowths with other minerals of the assemblage: pentlandite (a, b), millerite (b), heazlewoodite (c), orcelite (b) and gersdorffite (c)

evidence from its absence in the registry of Bulgarian minerals (Mincheva-Stefanova, Kostov, 2000) we claim that this is the first record of godlevskite in Bulgaria.

Another feature of godlevskite in Dobromirtsi deserves some discussion: the intimate association of the mineral with As phases seems rather characteristic – orcelite on Fig. 4b and gersdorffite on Fig. 4c. In both cases As phases look like solid state exsolutions. A possible explanation of this fact can be the formation of godlevskite at the expense of the high temperature MSS -  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub>. Although the As miscibility in  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub> has never been investigated, it can be expected on common sense grounds. High temperature solid solutions are as a rule more tolerant to impurities and become less tolerant on cooling. If cooling is slow enough to provide the required time for structure transformation, while still providing enough kinetic energy for the atoms to cross the potential barriers (annealing conditions), the solid solutions re-equilibrate by admixing the alien atoms in separate mineral phases. This process, however, is not limited only to external elements. The high-temperature solid solution can disproportionate to two or more phases based on the same elemental composition but different stoichiometry. This mechanism can well explain the godlevskite-heazlewoodite and godlevskite-millerite associations observed in Figs. 4b and 4c. Combined disproportionation and admixing of Fe can also explain the godlevskite-pentlandite association (Fig. 4b) in agreement with the tie-lines  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub>-pentlandite on the 500°C and godlevskite-pentlandite on 400°C phase diagrams of Ueno et al. (2000). Additional support for this hypothesis gives the study of Putnis (1976), who observes that the transformation of  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub> into godlevskite passes through a series of reversible polymorphic transformations, forming polysynthetic twins parallel to the prismatic planes. These twin planes are a favorable



place for the nucleation of admixed or disproportionated phases that can explain the specific regular relations observed on Fig. 4b and 4c.

Finally, with the above hypothesis in mind, let us have another look on the analysis 4. It deviates from the expected values for godlevskite at least on 3 parameters: its Ni:S ratio is too high for godlevskite and approaches that of  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub>; its Fe content exceeds more than twice the Fe miscibility limit in godlevskite and approaches that of  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub>; its As content is not negligible. Each of the above statements can be a reason to disregard this analysis as low quality analysis. However, all together they form a picture which should be expected for a quenched remnant of  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub>. Of course, we can not insist on a hypothesis supported by a single analysis only, but we just propose a possible explanation of the fact.

## Conclusions

The first report of godlevskite from Dobromiritsi inscribes well in the overall picture of the postmagmatic evolution of the chromitites there. The adherence of godlevskite in almost all cases to the zone of altered chromites (ferri-chromites) proves its genesis in postmagmatic conditions. The existence of the mineral and some mineral features – intergrowths and assemblage - give some outlines for the temperature range of its formation: the mineral was initially formed as high temperature  $\alpha$ -Ni<sub>7±x</sub>S<sub>6</sub> MSS in the range 577 – 436°C. Further development in slow cooling conditions included long enough annealing at temperatures below 379°C, to allow disproportionation to godlevskite and the respective intimately associated heazlewoodite or millerite. Described development complies with the conditions of the regional metamorphism of the area, which is the most probable geological event, responsible for the formation of the considered assemblage.

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