

## Hydrothermal manganoan chamosite from the vein and replacement Pb-Zn ore deposits, Madan district, Bulgaria

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**Abstract.** Chlorites are common minerals from the vein and replacement Pb-Zn deposits in the Madan ore district. They are formed as a product of alteration of the mafic rock-forming silicates of the embedding gneissic rocks and of pre-ore skarns. In many cases chlorites are directly deposited from the hydrothermal fluids in the open space of druse cavities in veins and in pores and vugs of the porous replacement marble-hosted skarn-ore bodies. In these cases they crystallized as pseudo-hexagonal crystals and spherulitic aggregates on the surfaces of sulphide and quartz crystals. Chemically, chlorites are determined as manganoan chamosites. The Fe/(Fe+Mg) ratio varies in the range 0.55–0.87, whereas the Mn content reaches 0.54 *apfu*. As the <sup>VI</sup>Al is less than <sup>IV</sup>Al in the most of the analyses, the octahedral occupancy is lower than 6 *apfu*, resulting in the presence of up to 0.19 *apfu* octahedral vacancies ( $\square$ ). Besides the Tschermak substitution of type  $\text{Si}^{4+}\text{Mg}^{2+} \leftrightarrow \text{IVAl}^{\text{VI}}\text{Al}$ , other cation substitutions are also presented:  $\text{Fe}^{2+} \leftrightarrow \text{Mg}^{2+}$ ,  $2\text{Al}^{3+} \leftrightarrow 3\text{Mg}^{2+} + \square$ , and  $\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+}$ . The following unit-cell parameters were obtained from XRD study: *a* 5.384(9) Å; *b* 9.332(5) Å; *c* 14.196(2) Å;  $\alpha$  90.932(2)°;  $\beta$  97.264(9)°;  $\gamma$  88.814(7)°; *V* 707.471(9) Å<sup>3</sup>. The chlorites are trioctahedral, as indicated by the decreased intensity of the odd 00*l* reflections: 001 (14.06 Å / 16.0), 003 (4.70 Å / 18.9) and 005 (2.82 Å / 9.6) and belong to  $\Pi^b$  polytype. The calculated temperatures of formation using the Cathelineau's (1988) equation range from 300 to 360°C and are in accordance with those measured from fluid inclusions in associated quartz (*Th* 308–330°C). The formation of manganoan chamosites is closely related to the main sulphide vein and metasomatic mineralization in the Madan deposits.

**Key words:** chlorite, manganoan chamosite, spherulites, skarns, Pb-Zn deposits, Madan

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**Резюме.** Хлоритите са разпространени минерали в жилните и скарново-рудни Pb-Zn находища от Маданския руден район. Те възникват като променителен продукт по фемичните минерали на вместващите силикатни гнайсови скали и на прерудните скарни. В много случаи са отложени чрез директна кристализация от хидротермалните флуиди в друзовите празнини на рудните жили, както и в отворените пори и празнини на порьозните метасоматичните рудни тела, вместени в мрамори. Там те кристализират като псевдохексагонални кристали и сферолитови агрегати върху кристалните повърхности на кварца и сулфидите. Според химизма си тези минерали се определят като манган-съдържащи шамозити. Отношението Fe/(Fe+Mg) варира от 0,55 до 0,87, докато мангановото съдържание достига до 0,54 ат. ед. В повечето анализи <sup>VI</sup>Al е по-малко от <sup>IV</sup>Al, което води до октаедрична заселеност, по-ниска от 6 атомни единици, резултираща в наличието на октаедрични ваканции до 0,19 ат. ед. ( $\square$ ). Освен чермаковото заместване  $\text{Si}^{4+}\text{Mg}^{2+} \leftrightarrow \text{IVAl}^{\text{VI}}\text{Al}$ , в структурата на тези хлорити се наблюдават и следните катионни субституции:  $\text{Fe}^{2+} \leftrightarrow \text{Mg}^{2+}$ ,  $2\text{Al}^{3+} \leftrightarrow 3\text{Mg}^{2+} + \square$ , и  $\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+}$ . Параметрите на елементарната клетка, получени при рентгенографското изследване, са както следва: *a* 5,384(9) Å; *b* 9,332(5) Å; *c* 14,196(2) Å;  $\alpha$  90,932(2)°;  $\beta$  97,264(9)°;  $\gamma$  88,814(7)°; *V* 707,471(9) Å<sup>3</sup>. Изследваните хлорити са триоктаедрични, с намалени интензитети на нечетните 00*l* отражения:

001 (14,06 Å / 16,0), 003 (4,70 Å / 18,9) и 005 (2,82 Å / 9,6), и се отнасят към  $\Pi^b$  политип. Температурите на образуване, изчислени по метода на Cathelineau (1988), са в интервала от 300 до 360°C. Тези данни кореспондират с измерените температури на хомогенизация на флуидни включения в асоцииращ кварц, които варират от 308 до 330°C. Образуването на Mn-съдържащите шамозити в Маданските находища съвпада по време с отлагането на основната сулфидна минерализация, вместена в променените скарни.

## Introduction

Chlorite minerals are formed in diverse geological settings. Such minerals have been found in pegmatites and are a common constituent of altered basic rocks (Lopez-Minguira et al., 2002). They are also common accessory minerals in low-to-medium grade metamorphic rocks (Nieto, 1997; Sassi, Zane, 1997; Zane et al., 1998), where may be the most important minerals in the chlorite zone. Occasionally they occur also in igneous rocks or high-grade metamorphic rocks (Cathelineau, Nieva, 1985; Walshe, 1986; Cathelineau, 1988), and as alteration products after primary ferromagnesian minerals, such as mica, pyroxene, amphibole, garnet, and olivine. Chlorites usually present also in sedimentary rocks but in minor quantities (Whittle, 1986; Jahren, Aagaard, 1989; Humphreys et al., 1989; Wiewiora et al., 1998). Chlorites are a major component of the wall-rock alteration zones of hydrothermal ore bodies of different type.

The variations in the chemical composition of the chlorites have been an object of numerous studies (e.g. Curtis et al., 1985; Walshe, 1986; Whittle, 1986; Jahren, Aagaard, 1989; Wiewiora, Weiss, 1990; Nieto, 1997; Sassi, Zane, 1997; Zane et al., 1998; Martinez-Serrano, Dubois, 1998). A summarized procedure for classifying rock-forming chlorites based on microprobe data was proposed by Zane and Weiss (1998). Determination of the chlorite composition is also possible applying a refined XRD method (Shata, Hesse, 1998). Lopez-Minguira et al. (2002) applied HRTEM/AEM-EPMA-XRD comparative study in order to establish chlorite composition and geothermometry. Chlorite geothermometer based on amount of  $^{IV}Al$  was developed by Cathelineau and Nieva (1985), and lately modified by

Cathelineau (1988). De Caritat et al. (1993) call in question the usage of chlorite composition for geothermometric purposes. Nevertheless, such type of empirical geothermometer is widely used in a semiquantitative sense from direct chlorite electron microprobe analyses with relatively good results (e.g. Zang, Fyfe, 1995; Zimak, 1999; Paniagua et al., 2001).

In the Central Rhodope Pb-Zn deposits various layered silicates including chlorite minerals are important constituents, formed as a result of hydrothermal activity connected with ore mineralization. Chlorites are a part of the silicate mineral assemblages typical for the wall-rock alteration zones of the embedding gneissic rocks around ore veins but are also present in the metasomatic Pb-Zn bodies. In many cases they are formed by direct crystallization from the hydrothermal fluids.

Chlorites were identified in almost all ore deposits in the Madan district. Especially, these minerals are well developed in the veins and skarn-ore metasomatic bodies of the Gradishte, Borieva, Krushev Dol, Laykov Choukar, Petrovitsa, Murzyan, Mogilata, Ossikovo, and other deposits. Stefanov et al. (1988) described the main layered silicate minerals from the Madan ore district, identifying smectites, micas, hydromicas, chlorites, kaolinite and halloysite. The chlorite composition was estimated on the basis of X-ray data only, without chemical determinations by means of EPMA. More precise morphological, paragenetical and chemical characterization of the chlorites is one of the main aims of the present study. The knowledge of physical and crystal-chemical features of chlorites could bring more information about the wallrock and skarn alterations and ore-forming processes in the region.

## Geological setting

The Madan district includes the largest and economically most important ore deposits in the Central Rhodopes. The Tertiary (~30 Ma) Pb-Zn ores are deposited as both, veins and replacement skarn-ore bodies (Kolkovski et al., 1996). The steep to subvertical ore veins cut rocks of the Rhodopian metamorphic complex, which mainly consists of various gneisses, granite-gneisses and minor amphi-bolites and marbles. The veins are closely related to a system of large, steep to sub-vertical ore-controlling and ore-bearing faults with NNW orientation. The gently slopping metasomatic skarn-ore bodies of variable morphology (bed-like, mushroom shaped and irregular) are hosted in the marble horizons around the ore veins. The infiltration-type skarns usually occupy the uppermost parts of the marble layers just below the impermeable screens of the overlying gneissic rocks. They host economically important high-grade metasomatic galena-sphalerite-quartz ores overimposed on skarns. Except for Madan, similar Pb-Zn deposits are presented also in the other Central Rhodopian ore districts: Laki (vein and replacement), Davidkovo (ore veins) and Ardino (only replacement).

The ore mineralization in the veins and the metasomatic bodies is uniform and represented mainly by galena, sphalerite, chalcopyrite, pyrite, carbonates and quartz. The main constituents of the primary reduced skarns are manganoan clinopyroxenes, varying in composition from pure johannsenite to manganoan hedenbergite. They have undergone intensive hydrothermal alteration and replacement by a retrograde mineral association presented by manganoan amphiboles, pyroxenoids, bustamite, manganilvaite, manganoan chlorites and carbonate minerals, mostly manganoan calcite and rhodochrosite (Vassileva, 2002). The sulphide deposition is closely related to the processes of retrograde skarn alteration and especially to the widely distributed carbonatization.

## Materials and methods

Representative samples from the Mogilata, Ossikovo, Petrovitsa and Borieva deposits were studied. The mineral relationships were examined by light microscopy in transmitted light. The morphology of chlorite crystals and aggregates was studied by scanning electron microscopy (SEM) on carbon- and Au-coated samples. Chemical analyses were performed by a JEOL Superprobe 733 electronprobe microanalyser equipped with an ORTEC energy-dispersive system, at 15kV. The following standards were used: albite for Na, diopside for Mg and Ca,  $\text{Fe}_2\text{O}_3$  for Fe,  $\text{Al}_2\text{O}_3$  for Al,  $\text{SiO}_2$  for Si, K-feldspar for K, apatite for Ca,  $\text{TiO}_2$  for Ti,  $\text{MnO}_2$  for Mn.  $\text{H}_2\text{O}$  was not directly determined. The total FeO was divided to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  according to the method proposed by Droop (1987) on a basis of 14 O-atoms. X-ray diffraction studies (XRD) were carried out by using a Siemens-500 powder diffractometer with  $\text{Cu-K}\alpha$  radiation, operating at 40 kV. Diffraction patterns were taken with  $1^\circ/\text{min}$  in the  $2\theta$  range of 2-68 degrees. Thin double-polished sections of associated quartz crystals were prepared and examined for the presence of fluid inclusions. The temperatures of homogenisation of the fluid 2-phase (liquid-vapour) inclusions found were measured by a Chaixmeca microthermometric camera. Representative sample of the studied material is deposited at the collections of the Geological Institute under № M.1.2002.9.1.

## Mineral associations

Macroscopic, microscopic and SEM observations of samples from the Madan district revealed that chlorites are associated mainly with hydrothermal quartz and calcite, and also with the main ore sulphides, galena, sphalerite, pyrite, and chalcopyrite. Two main forms of occurrence of chlorites are observed: (1) as alteration products metasomatically replacing the mafic rock-forming minerals (biotite, pyroxenes, amphiboles, etc.) of the



Fig. 1. Chlorite spherulites closely associated with quartz crystals in druse cavities of the Mogilata deposit. Natural size

Фиг. 1. Хлоритови сферолити, асоцииращи с кварцови кристали от находище Могилата. Естествена големина

embedding silicate wall-rocks, mainly various gneisses and amphibolites, and (2) as fine-crystal clay aggregates directly deposited from the hydrothermal fluids. Often chlorites form fine spherulites and thin layers of tabular

crystals on the crystal faces of quartz (Fig. 1) and sulphides, especially on large galena crystals (typical for the ore bodies in Petrovitsa and Laykov Choukar deposits). Inclusions and aggregates of fine-platy chlorite crystals can also be found included in quartz. Although chlorites are important products of the hydrothermal alteration processes, direct metasomatic relationships with skarn clinopyroxenes were not observed. However, clayey chlorite masses are abundant in the highly porous and cavernous replacement skarn-ore bodies.

### Morphology and physical properties

The metasomatically formed chlorite is characterized by poorly shaped flaky crystals with irregular outlines, as shown by Stefanov et al. (1988, Plate II, Fig. 3). The chlorite clays filling smaller or larger druse cavities in the ore veins and also in many of the replacement ore bodies are formed by direct growth in open space. As seen microscopically and under

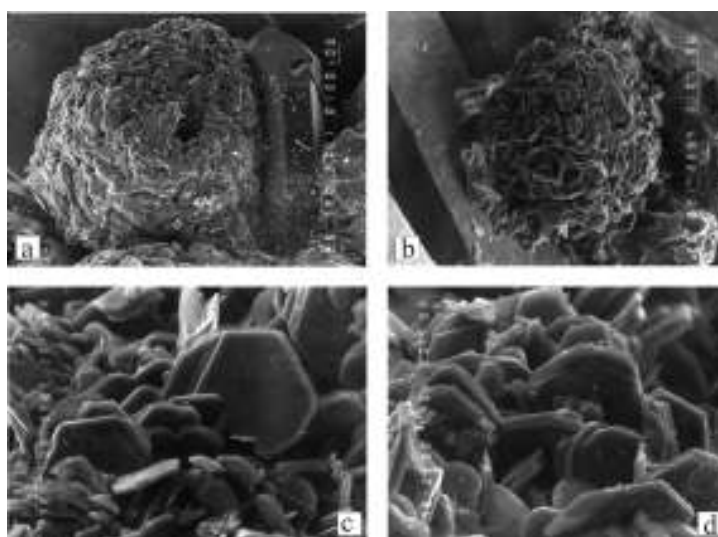


Fig. 2. Chlorite spherulites, composed of radial flake-like crystals with random mutual orientation and small angular (often triangular) open pores inbetween (a, b). The single pseudohexagonal flake-like (001) crystals have narrow pyramidal side faces (c, d). The Petrovitsa deposit. SEM, scale - in  $\mu\text{m}$

Фиг. 2. Хлоритови сферолити, съставени от радиални финоплохести кристали без определена взаимна ориентация и с малки ъглести празнини между тях (a, b). Единичните псевдохексагонални плохести по (001) кристали имат тесни пирамидални странични стени (c, d). Находище Петровица. СЕМ, мащаб – в  $\mu\text{m}$

SEM, they consist of fine spherulitic aggregates (Figs. 1, 2, 3). Sulphide mineralization in the metasomatic bodies is developed by hydrothermal alteration and replacement of primary skarns and relics of them, which are often preserved in the overimposed ores. Unchanged by the retrograde alteration skarns may be observed only in the distal, peripheral parts of the skarn-ore bodies. Pyroxenoids and manganoan amphiboles topotactically replacing the primary skarn pyroxenes also occur. The coarse- to medium-grained metasomatic ores are typical with their high porosity and permeability, with abundant opened pores and large cavities, formed as a result of hydrothermal leaching of the alteration products, most intensive in the proximal areas around the ore veins.

Formation of aggregations with spherulitic morphology appears by subparallel intergrowth of small crystals or by geometrical selection as pointed out by Sunagawa (1987) at increased supersaturation and high growth rate. Like other layered silicates, the symmetry of chlorites is triclinic, nearly monoclinic, although they usually have pseudo-hexagonal

platy (001) morphology reflecting the structure.

Several varieties of chlorite crystals and aggregates were observed during detailed SEM observations:

1) Spherulites, composed of radial flake-like crystals with random mutual orientation and small angular (often triangular) open pores in-between (found in the Petrovitsa deposit, Fig. 2a, b). The thin usually euhedral to subhedral single flakes have pseudo-hexagonal outlines and in addition to the pinacoidal faces are bounded by steep pyramidal side faces (Fig. 2c, d). The diameter of spherulites is up to 0.5-1 mm, whereas the single flakes are 10-50  $\mu\text{m}$  wide and up to 1-2  $\mu\text{m}$  thick.

2) Spherulites, composed of rosette-like groups of subparallel radial-divergent crystal flakes (found in Borieva deposit, Fig. 3a-d). A few such groups are usually seen in a single spherulite (Fig. 3a) and every one group seems to arise by divergent splitting of one initial platy crystal. The spherulites, like in the former case, are up to 1 mm wide. Sometimes they have polyspherical shape (Fig. 3b). The width

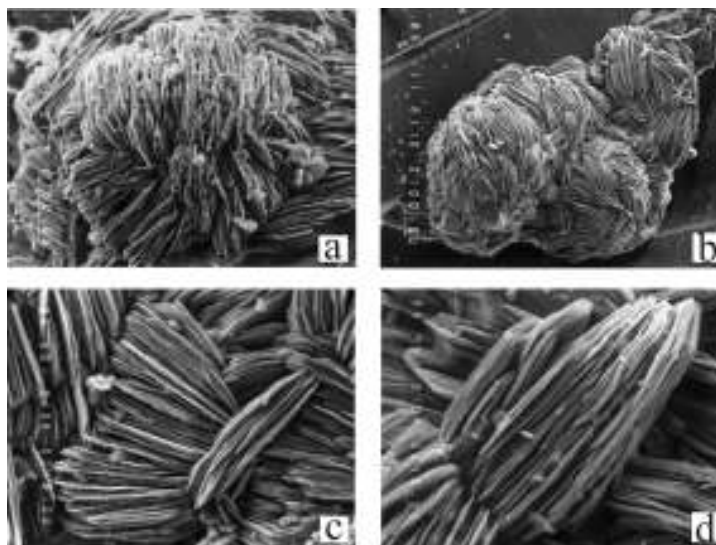


Fig. 3. Radial spherulites (simple - a, and polyspherical - b), composed of rosette-like groups of subparallel radial-divergent crystal (001) flakes (c and d). The Borieva deposit. SEM, scale - in  $\mu\text{m}$

Фиг. 3. Радиални хлоритови сферолити (единичен - а, и сложен - б), съставени от розетковидни групи от субпаралелни радиално-разходящи се плочки по (001) кристали (с и d). Находище Бориева. СЕМ, мащаб - в  $\mu\text{m}$

of the single flakes (Fig. 3c, d) varies in the range 10-70  $\mu\text{m}$  and their thickness is not larger than 2  $\mu\text{m}$ . The side faces of flakes again are narrow oblique pyramidal faces.

3) In other cases, as found in the Laykov Choukar deposit, chlorite masses consist of slightly curved columnar-vermicular crystals of subparallel aggregated flakes (Fig. 4a). Such elongated in  $c$  direction formations have a length below 0.2 mm. Their single flakes are up to 20-30  $\mu\text{m}$  wide and below 1  $\mu\text{m}$  thick, and again have narrow oblique pyramidal side faces. This peculiar development of chlorite can be assumed as transition from an initial thin fibrous growth along  $c$  axis crystal, to a subsequent fine-plate growth in the transverse (001) plane. Following Kostov and Kostov (1999), such habit change can be denoted as  $P_1^c \rightarrow P_{(001)}^c$  and is indicative for a decrease in supersaturation. Columnar chlorite crystals resembling the "kaolinite booklets" also occur (Fig. 4b). They also consist of subparallel slightly divergent thin (001) flakes but with prismatic side faces.

Chlorites show perfect basal (001) cleavage. Their flakes are flexible. Lustre is pearly in the massive aggregates, but dull and earthy in the spherulites. The hardness on the cleavage is 2.5. They have the typical for chlorite-group minerals green color varying from pale green, for some massive aggregates

to dark green, for the spherulites.

Chlorites have negative (-) optical sign and positive (+) elongation. As usually (Bailey, 1988), the sign of elongation is opposite to the optical one, the optical plane is almost parallel to (010), and the acute bisectrix is nearly normal to (001). Under microscope these minerals are characterized by pleochroism in green colours but sometimes show blue abnormal interference colour, which is in accordance with the octahedral occupancy of heavy atoms (Bailey, 1988). The optical absorption spectra of chlorites from several deposits in the Madan district were studied by Stefanov et al. (1988).

## Nomenclature

Because of the variety of chemical substitutions in the chlorite structure, numerous mineral names and classifications schemes have been proposed. An excellent review of the early classifications made by Tschermak, Clarke, Dalmer, Gossner, Orcel, Winchell, Hey, Hallimond, Lapham, Foster, and Phillips, was compound by Bailey (1975). According to the recommendations of the Nomenclature Committee of AIPEA (Association Internationale Pour l'Etude des Argiles), a simplified classification scheme for clay minerals is

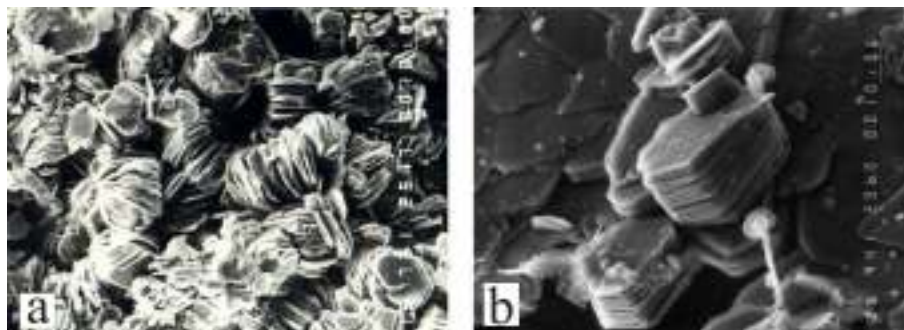


Fig. 4. a) A crust of vermicular chlorite aggregates composed of sub-parallel platy (001) crystals. The Laykov Choukar deposit. b) Columnar chlorite crystals with prismatic side faces. The Petrovitsa deposit. SEM, scale - in  $\mu\text{m}$

Фиг. 4. а) Слой от хармоникоподобни хлоритови агрегати, съставени от субпаралелни плочести по (001) кристали. Находище Лайков чукар. б) Хлоритови кристали с призматични околни стени. Находище Петровица. СЕМ, мащаб – в  $\mu\text{m}$

applied (see Bailey, 1980). The chlorite group is subdivided into four sub-groups: trioctahedral, dioctahedral di-trioctahedral and tri-dioctahedral. The trioctahedral chlorite species are named on the basis of the suggestions, made by Bayliss (1975), according to the dominant divalent octahedral cation. Taking into consideration not only the chlorite chemistry, but also certain structural aspects such as the octahedral occupancy, Wiewiora and Weiss (1990) used a similar concept. Recommended species names for chlorites are: clinochlore (for Mg-dominant), chamosite (for Fe<sup>2+</sup>-dominant), pennantite (for Mn-dominant), nimite (for Ni-dominant), and baileychlore (for Zn-dominant). All other names of species and varieties are discarded. Adjectival modifiers, such as manganoan, can be used in order to indicate important octahedral cations other than the dominant ones.

### X-ray data

In accordance with the nomenclature recommendations of the AIPEA (Bailey, 1980), the chlorites from the Madan district belong to the trioctahedral chlorite group with compositions varying within the clinochlore-chamosite solid solution series. As known from the mineralogical literature (Bailey, 1980), such chlorites usually have (001) reflections at 14.0-14.4 Å, their peak positions remaining unchanged by ion saturation, solvation with ethylene glycol, or heating. The major characteristics of the studied chlorites determining them as trioctahedral chlorites are: (1) the measured  $d_{(060)}$  values is very near to 1.55 Å (1.557 – 1.558 Å); (2) the odd 00 $l$  reflections show decreased intensities, *e.g.* for 001 (14.06 – 14.35 Å), 003 (4.70 – 4.73 Å) and 005 (2.82 – 2.83 Å), the intensity values are 16.0 – 14.6, 18.9 – 17.9 and 9.6 – 8.3, respectively (Fig. 5); (3) the even 00 $l$  (*e.g.* 002, 004) reflections have increased intensities (100.0 and 69.5 – 72.8, respectively), typical for chlorites with Fe-dominant octahedral cations (Bailey, 1988).

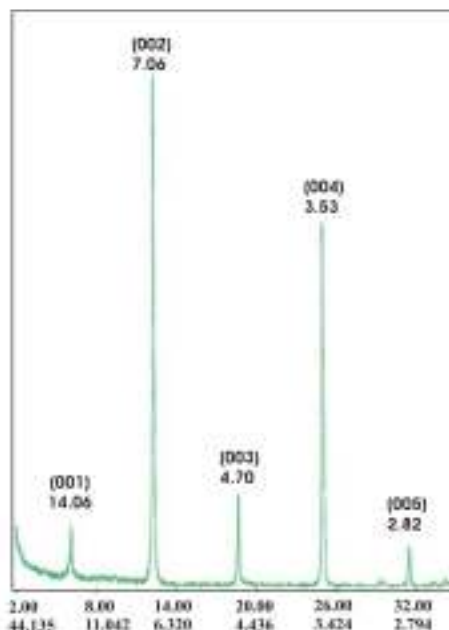


Fig. 5. The intensities of the even 00 $l$  of chamosites from the Madan deposits are systematically increased, whereas the odd 00 $l$  reflections have decreased intensities

Фиг. 5. Интензитетите на четните 00 $l$  отражения на шамозити от Маданските находища са систематично високи, докато нечетните 00 $l$  отражения са слабо интензивни

All chlorites studied belong to the II<sup>b</sup> polytypes, as it was also established earlier (Stefanov et al., 1988). The important diagnostic reflexes for this polytype (2.66, 2.59, 2.55, 2.45, 2.39, 2.26, 2.01 Å - Bailey, 1980) match with the diffraction lines of the Madan manganoan chamosite (2.682, 2.615, 2.569, 2.462, 2.404, 2.278, and 2.018 Å), although the lines registered on their powder diffractograms are slightly increased compared to the pure Fe-member, due to the manganoan content.

The following unit-cell parameters were obtained from the XRD study:  $a$  5.384(9) Å;  $b$  9.332(5) Å;  $c$  14.196(2) Å;  $\alpha$  90.932(2)°;  $\beta$  97.264(9)°;  $\gamma$  88.814(7)°. The calculated cell-volume is  $V$  707.471(9) Å<sup>3</sup>.



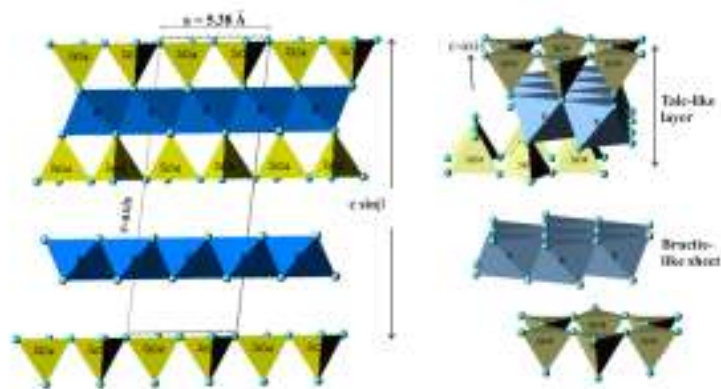


Fig. 6. Crystal structure of chlorite. Projection in the  $ac$  plane and a model of chlorite structure. Modified after Shata and Hesse (1998)

Фиг. 6. Кристална структура на хлорит. Проекция в равнината  $ac$  и модел на хлоритова структура по Shata & Hesse (1998)

### Chemical composition

The trioctahedral chlorite structure consists of 2:1 layers ideally of composition:

$(R^{2+}, R^{3+})_3(Si_{4-x}Al_x)O_{10}(OH)_2$  ("talc-like layers") that alternate with octahedral interlayer sheets ideally of composition  $(R^{2+}, R^{3+})_3(OH)_6$  ("brucite-like layers") (Fig. 6). The tetrahedral portion of each 2:1 layer has a negative charge  $x$  owing to substitution of  $x$  ions generally by  $Al^{3+}$ . The interlayer sheet has positive charge due to substitution of  $R^{3+}$  ions for  $R^{2+}$  and serves to neutralize the negative charge on the 2:1 silicate layer (Bailey, 1988). Thus, the general formulae of chlorites can be assigned:  $(R^{2+}, R^{3+})_6(Si_{4-x}Al_x)O_{10}(OH)_8$ . In our case  $Fe^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$  present  $R^{2+}$ , whereas  $R^{3+}$  may be  $Fe^{3+}$  and  $Al^{3+}$ . Any medium-sized cation will fit in the octahedral sites but it is unlikely that the larger Na, Ca and K cations can occupy either octahedral sites or sites located between the 2:1 layer and interlayer sheet in the structure of the common chlorites. The (Na + K + Ca) values are generally low, showing no correlation patterns with octahedral vacancies in chlorite, indicating that compositional variations are not due to the intergrowth of smectite or illite.

Representative microprobe analyses of chlorites from the Madan ore district are given in Table 1. The chemical data show that they belong to the clinocllore-chamosite solid solution series, generally with high-iron chamosite compositions. Total Fe measured as FeO varies in the range 25.87–44.13 wt. %, whereas the MgO values are in the range from 3.74 to 12 wt. %. The  $Al_2O_3$  content is more than 14.97 wt. %, reaching up to 24.30 wt. %. Additionally, as typical for the most hydrothermal silicates in the region, the chlorite is characterized with high Mn content, varying generally in the range 2.38–5.61 wt. %.

$Si^{4+}$  and  $Al^{3+}$  occupy tetrahedral positions in the chlorite structure. The amount of Si varies from 2.33 to 2.83 *apfu*.  $Al^{3+}$  fulfills the amount of atoms with tetrahedral coordination to 4. Mostly, the chlorites have  $^{VI}Al < ^{IV}Al$ . In the Madan chlorites generally  $^{VI}Al > ^{IV}Al$ . Foster (1962) showed that in such cases the total octahedral occupancy is less than 6.00 atoms by an amount equal to one-half the excess of octahedral trivalent cations over  $^{IV}Al$ . This relation indicates that the excess of trivalent octahedral cations replaces divalent



Table 1. *Representative electron microprobe analyses of manganoan chamosites*  
Таблица 1. *Представителни микросондови анализи на мангансъдържащи шамозити*

Deposit	Borieva			Petrovitsa		
Anal. №	1	2	3	4	5	6
SiO <sub>2</sub>	27.01	28.01	26.16	26.41	24.00	24.80
Al <sub>2</sub> O <sub>3</sub>	22.11	22.31	23.04	23.24	18.52	21.72
MgO	10.33	11.99	10.18	9.73	5.77	5.96
FeO	24.75	26.16	26.29	25.87	34.97	33.77
MnO	3.05	4.11	5.00	5.27	5.61	2.78
TiO <sub>2</sub>	0.07	0.00	0.28	0.00	0.02	0.00
Na <sub>2</sub> O	0.21	0.06	0.12	0.04	0.06	0.24
K <sub>2</sub> O	0.30	0.03	0.00	0.08	0.04	0.10
CaO	0.18	0.00	0.12	0.00	0.00	0.09
Σ	88.01	92.67	91.19	90.64	88.99	89.46
O = 14						
Si	2.85	2.83	2.71	2.75	2.71	2.71
<sup>IV</sup> Al	1.15	1.17	1.29	1.25	1.29	1.29
<sup>VI</sup> Al	1.61	1.48	1.52	1.60	1.17	1.52
Mg	1.63	1.80	1.57	1.51	0.97	0.97
Fe <sup>2+</sup>	2.18	2.20	2.27	2.24	2.30	3.01
Fe <sup>3+</sup>	0.00	0.00	0.00	0.00	1.00	0.06
Mn	0.27	0.35	0.44	0.46	0.54	0.26
Ti	0.01	0.00	0.02	0.00	0.00	0.00
Σ octahedra	5.69	5.83	5.83	5.81	5.97	5.82
Na	0.04	0.01	0.02	0.01	0.01	0.05
K	0.04	0.00	0.00	0.01	0.01	0.01
Ca	0.02	0.00	0.01	0.00	0.00	0.01
Fe/(Fe+Mg)	0.57	0.55	0.59	0.60	0.77	0.76
T°C	307.04	316.20	353.31	341.59	354.12	351.83

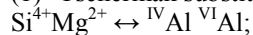
Temperatures calculated according to the equation proposed by Cathelineau (1988)

cations in the 2:3 ratio. Thus, the following generalized composition can be written:

$(R^{2+}_{6-x-3y}R^{3+}_{x+2y}\overset{\uparrow}{})_3(Si_{4-x}R^{3+}_x)O_{10}(OH)_8$ ,  
where  $\overset{\uparrow}{}$  denotes vacancy. The analysed chlorites from the present study show amounts of octahedral vacancies up to 0.19 *apfu*. In some earlier classifications such chlorites with vacancies in the octahedral sites are called lepto-chlorites (Bailey, 1988).

The following types of ionic substitutions were observed in the studied chlorites:

(1) Tschermak substitution



(2) substitution  $Fe^{2+} \leftrightarrow Mg^{2+}$ ;

(3) substitution  $2Al^{3+} \leftrightarrow 3Mg^{2+} + \square$ , the so called "dioctahedral" substitution, producing one vacancy in the sheets of octahedra;

(4) substitution of  $Fe^{2+}$  by  $Mn^{2+}$ , typical for the studied silicate minerals from the Madan skarn-ore deposits.

Close relationship between some chemical components of chlorite is illustrated in Fig. 7. A positive correlation was found between Si - Al<sub>total</sub>; Si - Mg; Mg - Al; Fe/(Fe+Mg) - Al.  $Mg^{2+}$  is negatively correlated with Fe; such relationship is also valid for  ${}^{IV}Al$  -  ${}^{VI}Al$ .

Zane and Weiss (1998) proposed a simplified procedure for classifying the chlorites based on microprobe data. Considering the general formulae, the trioctahedral chlorites should have  $R(\text{Fe, Mg, Mn, Al}) = 5$  to  $6$  and vacancy  $\text{□} = 0$  to  $1$ , which is the case in the analyzed chlorites. The increase of Al is usually accompanied by an increase of the vacant positions. Zane and Weiss (1998) distinguished two chlorite types:

type I, with  $X_{\text{Mg}} + X_{\text{Fe}_{\text{tot}}} \geq X_{\text{Al}} + X_{\text{□}}$  ( $X$  in *apfu*);  
type II, with  $X_{\text{Mg}} + X_{\text{Fe}_{\text{tot}}} < X_{\text{Al}} + X_{\text{□}}$ .

The chlorites from the Madan ore deposits should be considered as members of type I. The compositional fields for I and II types of chlorites may be represented in the  $\text{Fe}_{\text{tot}} - \text{Mg} - (\text{Al} + \text{□})$  plot (Fig. 8).

For definition of a mineral name, the dominant octahedral cation and the adjectival modifiers should be considered. Thus, the conclusion can be made that the chlorites from

the Madan Pb-Zn deposits are high-iron members of the clinocllore–chamosite solid solution, entirely falling in the chamosite field, with  $\text{Fe}/(\text{Fe} + \text{Mg})$  ratio in the range  $0.55$ – $0.87$ . The presence of up to  $0.6$  *apfu* Mn in the chlorite structure determines this chlorite as *manganoan chamosite*.

In the rare, Mn dominated chlorite, pennantite, which occurs only in a few low-iron Mn deposits (Minerals, 1992), the Mn content, is very high, reaching  $39$ – $43$  wt. %. Though, it appears that chamosite with increased Mn content is even more uncommon, and is mentioned (Minerals, 1992) only for the Tari Ekan polymetallic deposit in Tadzhikistan, with  $2.84$  wt. % MnO, and for a Japanese deposit, with  $3.33$  wt. % MnO. However, Meinert (1987) reported chamosite from the Groundhog Mine, Central Mining District of New Mexico, USA, with a MnO content of  $7.22$  wt. %).

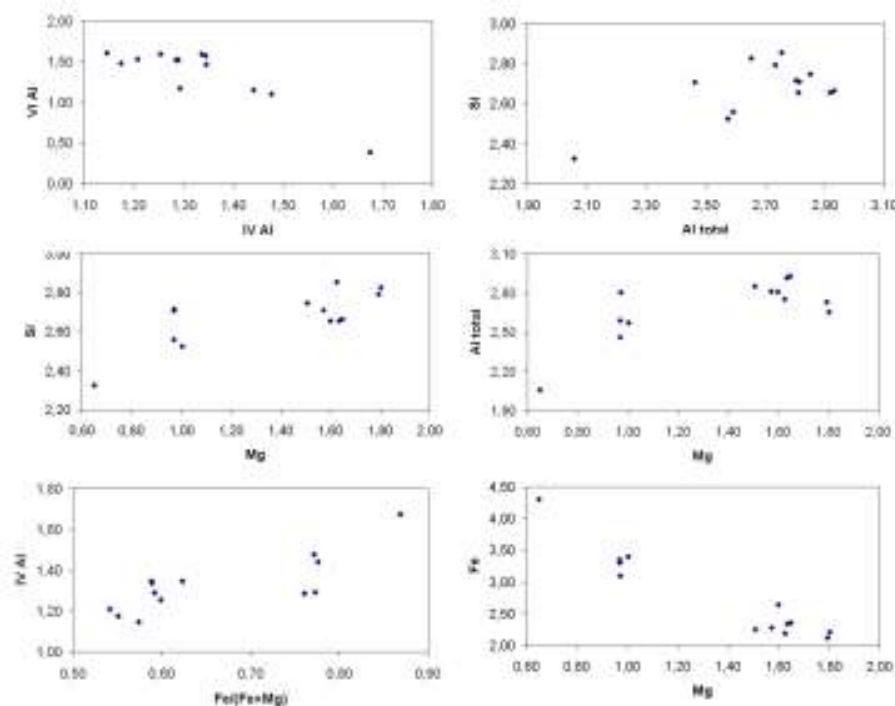


Fig. 7. Compositional diagrams of chlorites from the Madan deposits. Values in *apfu*

Фиг. 7. Композиционни диаграми на хлорити от Маданските находища. Стойностите са в *apfu*

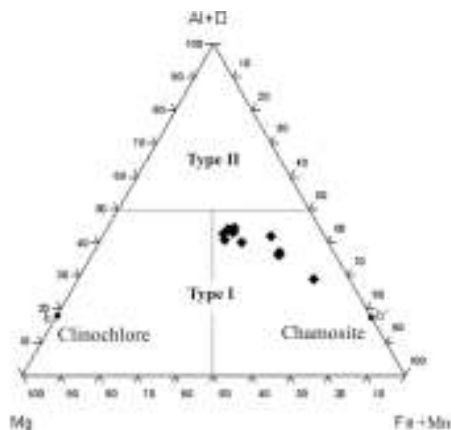


Fig. 8. Type I chamosites from the Madan deposits. Modified after Zane and Weiss (1998)

Фиг. 8. Шамозити от тип I от Маданските находища, съгласно диаграмата на Zane & Weiss (1998)

The manganoan chamosite in the Madan deposits, precipitated from the hydrothermal ore-forming fluids in a high Fe- and Mn-rich environment. That is why it is not so extremely Mn-rich as the earlier Mn skarn pyroxenes and the replacing them pyroxenoids, amphiboles, and manganilvaite (Vassileva, 2002), and is of a relatively high for chamosite Mn content, reaching the maximal known values of 5.61 wt. % (0.57 apfu Mn).

### Chlorite compositional geothermometry

Cathelineau and Nieva (1985) and Cathelineau (1988) found out a relationship between the composition ( $^{IV}Al$ ,  $\text{ф}$ ) and the crystallization temperature of chlorites. In order to determine the temperature of formation for the hydrothermal chlorites studied, an equation proposed by Cathelineau (1988) was applied:

$$(1) T^{\circ}\text{C} = -61.9229 + 321.9772 * (^{IV}Al).$$

The calculated temperatures vary in the 300–360°C range according to the  $^{IV}Al$  occupancy (Fig. 9). Taking into account the accuracy of the chemical analyses, it is obviously that the applied thermometer is in a good accordance with the temperatures of homogenisation ( $Th$ ) determined from fluid inclusions of ore-bearing quartz from the district (Bonev, 2002). In order

to verify these results thin sections of quartz crystals, associated with the analysed chlorites from Petrovitsa deposit were examined. The measured  $Th$  of fluid inclusions are in the range 308–330°C. (From other samples of the deposit the range of  $Th$  is 320–360°C).

The thermometers proposed by Cathelineau and Nieva (1985) on the basis of  $^{IV}Al$  content and the amount of the octahedral vacancies calculated by the equation:

$$(2) T = (0.0826 + ^{IV}Al)/0.00471,$$

determined some lower temperatures of formation, in the temperature range of 260 to 330°C. On the other hand, the fluid inclusions measured in quartz from metasomatic skarn-ore bodies of the Mogilata and Enyovche deposits also gave such results (260–320°C range by our unpublished data).

The temperatures calculated on the basis of the octahedral occupancy (octahedral vacancies) are in the interval of 245–281°C:

$$(3) T = -(2.41)/0.00857 \text{ (Cathelineau, Nieva, 1985)}.$$

Applying the chlorite geothermometers and taking into consideration the  $Th$  measured on fluid inclusions in quartz, the formation of chlorites in the Madan ore deposits can be attached to the main stage of sulphide mineral deposition.

### Conclusions

1. The hydrothermal chlorites from the Madan ore deposits are common minerals of the main mineralization stages, formed both by replacement of the Fe-Mg rock-forming minerals of the embedding silicate rocks, and by direct deposition from the ore-forming fluids during the main mineralization stage.
2. The chlorites can be defined as Fe-members of the clinocllore-chamosite solid solution series with Fe/(Fe+Mg) ratio in the range 0.55–0.87. The presence of up to 0.6 apfu Mn in the chlorite structure determines them as the very rare *manganoan chamosites*. The high Mn content reflects the Mn geochemical specialization of the Madan deposits.
3. XRD patterns of manganoan chamosite is characterized by decrease in the intensities

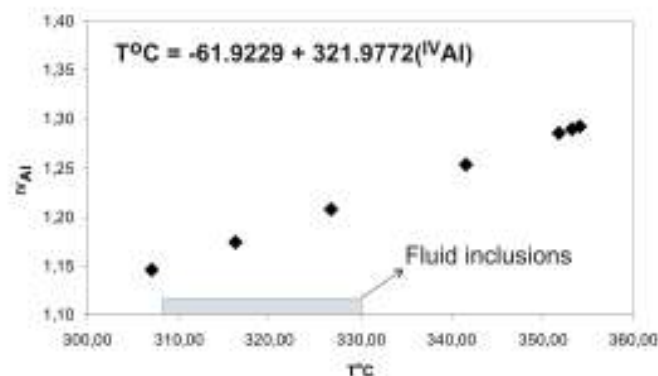


Fig. 9. Calculated temperatures of crystallization of the Madan chlorites on the basis of  $^{IV}Al$  occupancy, according to the equation proposed by Cathelineau (1988).  $Th$  of fluid inclusions in associated quartz are in the interval 308–330°C

Фиг. 9. Температури на кристализация на хлоритите, в зависимост от съдържанието на  $^{IV}Al$ , определени по метода на Cathelineau (1988). Температурите на хомогенизация  $Th$  на флуидни включения в кварц, асоцииращ с хлорита, са в интервала 308–330°C

of the odd 00l (001, 003, 005) reflections and increase of the even ones (002, 004), as typical for the Fe-chlorites. The manganoan chamosite is of  $II^b$  polytype.

4. The calculated temperatures of formation of the manganoan chamosites at the interval 300–360°C are in accordance with those measured at the homogenisation of fluid inclusions in associated quartz  $Th = 308$ –330°C.

5. The manganoan chamosites are generally deposited directly from hydrothermal fluids forming pseudohexagonal crystals and spherulites onto the sulphide and quartz crystals in open pores and druse cavities of the ore bodies.

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