

Melilite from skarns, Zvezdel-Pcheloyad ore deposit, Eastern Rhodopes, Bulgaria

Мелилит от скарни, Звездел-Пчелоядско рудно поле, Източни Родопи, България

*Yana Tzvetanova¹, Rositsa Titorenkova¹, Iskra Piroeva²
Яна Цветанова¹, Росица Титоренкова¹, Искра Пироева²*

¹ Acad. Ivan Kostov Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 1113 Sofia;
E-mail: yana.tzvet@gmail.com

² Acad. Rostislav Kaishev Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia

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Introduction

Skarn xenoliths (nodules) were found in mine gallery No 68 from Zvezdel-Pcheloyad Pb-Zn ore deposit. They are hosted by monzonitic rocks of the second intrusive phase (Nedialkov, Mavroudchiev, 1995) of the Zvezdel pluton without relation with the carbonate-bearing protolith. No surface exposures of the skarns are found so far and most probably they represent an upper part of more deeply situated body. The skarns consist of coarse grained clinopyroxene-garnet and garnet lenses (exoskarns) up to 30 cm in diameter, surrounded by the wollastonite-bearing zones (endoskarns). Melilite is observed as relicts in garnets from clinopyroxene-garnet zone in association with garnets of the grossular-andradite series ($Adr_{94,23-6,20}$), melanites with TiO_2 content of 8–11 wt.%, fassaïtic clinopyroxene (Al_2O_3 – up to 17.75 wt.%), calcite, quartz, and prehnite. Titanite, apatite and magnetite are present as accessory minerals.

The present study reports for the first time data on crystal chemistry and Raman spectra of melilite found in Bulgaria. The occurrence of melilite in the skarns is important in terms of interpretation of their genesis.

Methods

Melilite was detected and characterized using scanning electron microscopy (SEM), electron probe microanalyses (EPMA) and Raman spectroscopy. Polished specimens were studied using ZEISS SEM EVO 25LS equipped with an EDAX Trident system. Raman spectra were collected using a LabRam HR (Horiba) spectrometer equipped with an Olympus BH41 microscope, CCD detector, and gratings with 600 grooves per mm. The measurements were conducted using the 633-nm line of a He-Ne laser in backscattering geometry with an objective 100 \times . The diameter of the laser spot on the sample surface was approximately 2 μ m,

while the laser power on the sample surface was 3.8 mW. The spectra were collected with an acquisition time of 60 s, by averaging over 10 loops to improve the signal-to-noise ratio. The spectral evaluation was performed with the software package Origin 9.

Results and discussion

Melilite-group minerals have the general formula $X_2T_1(T_2)_2O_7$. The T2-site is mainly occupied by Si and (Si+Al) in the case of gehlenite member. The T1-site is occupied by Al, Fe, and Mg, while the X-site by Ca and Na.

Melilite from Zvezdel-Pcheloyad ore deposit occurs mainly as short prismatic crystals up to ~80 μ m in length (Fig. 1) enclosed in garnet crystals. Representative electron microprobe analyses of the studied melilite grains are given in Table 1. Melilite is composed mostly of a binary solid solution between gehlenite (Geh – $Ca_2Al(Al,Si)_2O_7$) and åkermanite (Ak – $Ca_2MgSi_2O_7$) with up to 15.74 mole% of the sodamelilite component (Na-mel – $NaCaAlSi_2O_7$) and up to 14.61 mole% Fe-åkermanite (Fe-Ak – $Ca_2FeSi_2O_7$).

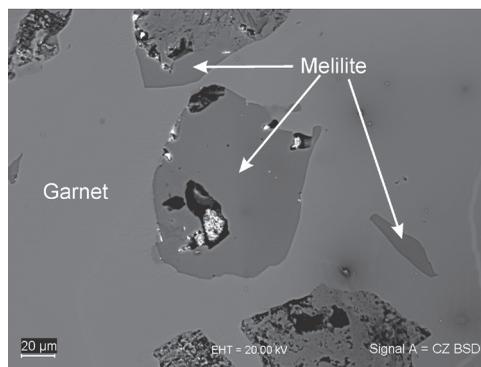


Fig. 1. Back-scattered electron image of the analysed grains of melilite (polished section)

Table 1. Representative compositions (wt.%) of skarn melilite from Zvezdel-Pcheloyad ore deposit (on the basis of 14 oxygen atoms per formula unit)

Sample	33_3	34_3	43_3	44_3	45_3	46_3	47_3
SiO ₂	34.89	32.99	33.55	33.2	32.55	32.82	33.20
Al ₂ O ₃	16.80	18.2	18.13	17.99	18.91	19.13	19.15
FeO	2.57	2.63	2.63	2.47	3.68	2.51	2.99
MnO	0.05	—	—	—	—	—	—
MgO	5.60	5.11	5.05	5.11	3.99	4.65	4.53
CaO	38.63	38.29	38.55	38.79	37.93	38.67	38.16
Na ₂ O	1.74	1.57	1.59	1.6	1.53	1.45	1.62
Total	100.28	98.79	99.5	99.16	98.59	99.23	99.65
				<i>apfu</i>			
Si T2 sites	3.190	3.068	3.096	3.078	3.044	3.036	3.058
Al	0.810	0.932	0.904	0.922	0.956	0.964	0.942
Al T1 sites	0.999	1.061	1.066	1.042	1.127	1.12	1.136
Mg	0.763	0.709	0.695	0.706	0.556	0.641	0.622
Fe	0.197	0.205	0.203	0.192	0.288	0.194	0.230
Mn	0.004	—	—	—	—	—	—
Ca X sites	3.785	3.816	3.811	3.853	3.801	3.833	3.766
Na	0.309	0.283	0.284	0.288	0.277	0.26	0.289
<i>End-members (mol.%)</i>							
Na-mel	15.74	14.33	14.46	14.85	14.05	13.30	14.54
Geh	35.15	39.39	39.82	38.87	43.13	43.99	42.61
Ak	38.87	35.90	35.39	36.39	28.21	32.79	31.29
Fe-Ak	10.24	10.38	10.34	9.90	14.61	9.92	11.57

*Total iron as FeO

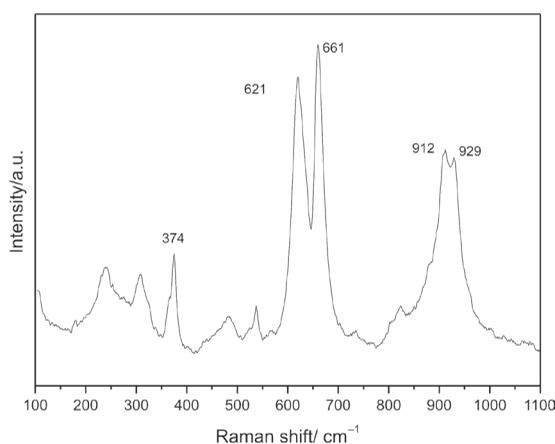


Fig. 2. Raman spectra of the studied skarn melilite

Aluminium at the T1-site (after Louisnathan, 1971) was found to prevail over Mg, which implies that the studied samples may be referred to as gehlenite.

Minerals from the melilite group have a tetragonal structure, space group $P4_2m$. The most intense peaks in the Raman spectra of all studied samples are observed at 661 and 621 cm^{-1} . Peak at 661 cm^{-1} is characteristic for the symmetric stretching vibrations of bridging Si-O-Si in the Si_2O_7 dimer in åkermanite end-member. It was shown that the position of this peak is linearly related to the T-O-T bridging angle of pyrosilicate group (where T=Al, Si) (Sharma et al., 1988). The Al^{3+} for Si^{4+} substitution results in an increase in the bond lengths and decrease in the bond angle in T-O-T linkages. The peak near 621 cm^{-1} is due to the bridging T-O-T in gehlenite (Sharma et al., 1983). The appearance of two intensive peaks in the Raman spectra of studied samples (Fig. 2) reveals the presence of both $\text{Si}_2\text{O}_7^{6-}$ and substituted $(\text{Al,Si})_2\text{O}_7$ dimers, which is characteristic for the natu-

ral melilites and is in accordance with the chemical composition (Table 1). Less intense peaks are observed at 912 and 929 cm^{-1} . They are assigned to the symmetric stretching of nonbridging oxygen and antisymmetric stretching of pyrosilicate group, respectively. The intensity of the peak at 912 cm^{-1} is reduced as compared to the other pyrosilicates which was explained by the effect of Al^{3+} substitution in tetrahedral T1 site (Sharma et al., 1988).

The conditions of formation of skarn rocks containing melilite and associated with calcium silicates such as fassaitic clinopyroxene are estimated to be at least 800 °C (e.g., Reverdatto et al. 1979). Such a high temperature strongly suggests that the melilite-bearing skarn have been formed by high temperature interaction between magma and calcareous wall rock at the time of magma emplacement. The products of this synmagmatic stage were overprinted by minerals formed during later postmagmatic process, which is marked by assemblages of garnets with clinopyroxene and wollastonite.

References

- Louisnathan, S. J. 1971. Refinement of the crystal structure of a natural gehlenite, $\text{Ca}_2\text{Al}(\text{Al,Si})_2\text{O}_7$. – *Can. Mineral.*, 10, 822–837.
- Nedialkov, R., B. Mavroudchiev. 1995. Geochemical and mineralogical peculiarities of the Zvezdel pluton (East Rhodopes, Bulgaria). – In: *Proceedings of the XV Congress of the Carpatho-Balkan Geological Association. Geol. Soc. Greece, Sp. Publ.*, No 4/2. September 17–20, Athens, Greece, 561–565.
- Reverdatto, V. V., N. N. Pertsev, V. N. Korolyuk. 1979. PCO_2 -T evolution of zoning in melilite during the regressive stage of contact metamorphism in carbonate-bearing rocks. – *Contr. Mineral. Petrol.*, 70, 203–208.
- Sharma, S., B. Simons, H. Yoder. 1983. Raman study of anorthite, calcium Tschermak's pyroxene, and gehlenite in crystalline and glassy states. – *Amer. Mineral.*, 68, 1113–1125.
- Sharma, S., H. Yoder, D. Matson. 1988. Raman study of some melilites in crystalline and glassy states. – *Geochim. Cosmochim. Acta*, 52, 1961–1967.