

MEIONITE ( $Me > 60$ ) FROM MISHEVSKO, CENTRAL  
RHODOPES – FIRST FIND OF YELLOW LW UV  
FLUORESCENT SCAPOLITE FOR BULGARIA

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**Abstract**

This article presents the results of preliminary mineralogical characterization of scapolite from a new for Bulgaria locality – Mishevsko, Central Rhodopes. The examined samples exhibit a characteristic yellow luminescence under long-wave ultraviolet light. There are compositional variations, primarily affecting the extra-framework cation and anion species in the structure of the studied mineral and thus also the meionite component ( $62 < Me < 74$ ). At the end, considerations on the factors controlling the scapolitization process, as well as speculations on possible causes of scapolite fluorescence are presented.

**Key words:** scapolite, yellow LW UV luminescence

**Introduction.** Minerals of the scapolite group are common rock-forming aluminosilicates that occur in a wide variety of metamorphic and altered igneous rocks. Scapolite forms solid solutions between the extreme end-members marialite,  $\text{Na}_4[\text{Al}_3\text{Si}_9\text{O}_{24}]\text{Cl} = Me0$  and meionite,  $\text{Ca}_4[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{CO}_3 = Me100$ , however a near end-member silvialite,  $\text{Ca}_4[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{SO}_4$ , has lately been also reported [1]. One of the earliest divisions concerning the marialite–meionite series is based on the introduction of the index of chemical composition, presenting the meionite ( $Me$ ) content in at. %. It has been defined as  $100(\text{Ca} + \text{Sr} + \text{Fe} + \text{Mn} + \text{Mg})/(\text{Na} + \text{K} + \text{Ca} + \text{Sr} + \text{Fe} + \text{Mn} + \text{Mg})$  or as its short form— $Me\%$  =

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$100 \times \text{Ca}/(\text{Na} + \text{Ca})$ . It was first introduced by SHAW in 1960 [2] but is still in active use by researchers of the group. The wide distribution of scapolite members in metamorphic terrains, as well as their high stability over a wide range of pressures and temperatures, turn scapolites into potential geothermometers and geobarometers. Thus, in 1996 TEERTSTRA and SHERRIFF [3] postulated that the meionite component increases with metamorphic grade, and typical samples of high-pressure scapolite are Ca-rich. Scapolites store volatiles in the lower crust and upper mantle and are indicators of the activities of the volatile components [1]. The volatile components in scapolite indicate that they may play a natural role in the capture and storage of greenhouse gases.

It is also of general interest to note that some scapolite representatives exhibit gem-quality features. In recent times, the efforts of researchers have been aimed at clarifying the nature and action of the colour and luminescence centres in the structures of scapolites that are directly related to the manifestation of certain of their practically important properties [4].

The general formula of this group of minerals is  $\text{M}_4[\text{T}_{12}\text{O}_{24}]\text{A}$ . The **M** position (extra-framework cations – EFC) is represented predominantly by  $\text{Ca}^{2+}$  and  $\text{Na}^+$  but may also contain  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Fe}^{2+}$ . The **T** position is occupied by  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ ;  $\text{Fe}^{3+}$  may also be present there; and the **A** position (extra-framework anion – EFA) stands for  $\text{Cl}^-$ ,  $(\text{CO}_3)^{2-}$ ,  $(\text{SO}_4)^{2-}$ ,  $\text{S}_2^-$ , and rarely  $\text{F}^-$ . As established by spectroscopic studies, hydrogen can be present in the structure in various forms –  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{OH}^-$ , etc. [5].

In Bulgaria, scapolites occur mainly as rock-forming minerals, less often in pegmatite or sulphide veins mainly in the Sredna Gora and Rhodopes regions [6]. There are very few specialized studies devoted to predominantly mineralogical characteristics. Recently, results of crystal–chemical studies of scapolites from two Bulgarian localities – Samurski dol, Central Rhodopes and Urdini lakes, North-western Rila, were published [7, 8]. Their goal was to use modern analytical methods to make a more precise determination of the meionite content (*Me*) than those previously made for samples from these localities.

Objective of the present study is to provide preliminary mineralogical characterization of scapolite group representatives, established in a new for Bulgaria locality – the vicinity of the village of Mishevsko, Central Rhodopes. Results from powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS) studies are reported. All studied samples exhibit yellow (long wave, 365 nm), ultraviolet (LW UV) fluorescence. Possible reasons for the occurrence of photoluminescence are discussed. Additionally, issues related to the metasomatic manifestations (scapolitization and albitization) at the type locality concerning some of the controlling it factors are addressed.

**Geological setting.** The type locality is placed not far from the village of Mishevsko, Kardzhali district. It falls into an area built up by rocks of the Central Rhodopes Metamorphic Terrain and more specifically the Startsevo Lithotectonic

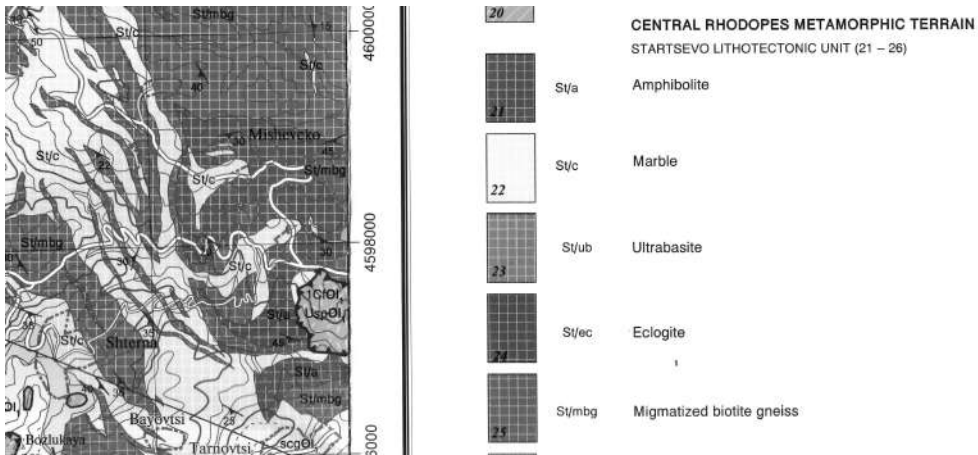


Fig. 1. Schematic presentation of the Mishevsko locality geological setting [9]

Unit. The latter is generally characterized by a varied lithological composition and variously migmatized rocks with abundant aplite-pegmatite injection. Various thick packages of fine- to medium-grained, massive, white and grey-white marbles are observed within the migmatized orthogneisses (Fig. 1). The metamorphism in the range of the unit was high-temperature (high amphibolite facies) with migmatization of the metatexite type. Where the marbles are incorporated as shortly thinning-out strips between the biotite gneisses and amphibolites or as xenoliths within the metagranites they are converted into skarns or altered metasomatically [10].

**Materials and methods.** Crystalline samples from the type locality were collected during a field expedition in the summer of 2024. Both in the field and in the collected macro-samples and the polished sections prepared from them, the layered nature of the mineral depositions is clearly visible (Fig. 2a-f). The scapolites from the altered areas are light- to dark-gray and even black in colour. When illuminated with an ultraviolet flashlight (365 nm) they luminesce in yellow.

**PXRD studies.** Powder X-ray diffraction experiments were performed on Empyrean, (Panalytical) powder diffractometer, PIXcel3D-Medipix3  $1 \times 1$  detector, using HDD Cu  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at 40 kV and 30 mA in the range  $5\text{--}100^\circ 2\theta$ . Phase identification was carried out using the HighScore Plus (HS+) program [11]. Semi-quantitative phase analysis was performed with the PowderCell (PC) program [12].

**SEM and EDS studies.** Scanning electron microscopy and energy dispersive spectral analyses were performed on JEOL JSM 6390 (Tokyo, Japan) electron microscope at 20 kV accelerating voltage and vacuum medium in the range of 10–4 Pa. The EDS has a  $15 \text{ mm}^2$  detector with 140 eV resolution and a produced by Oxford (AZtecOne).

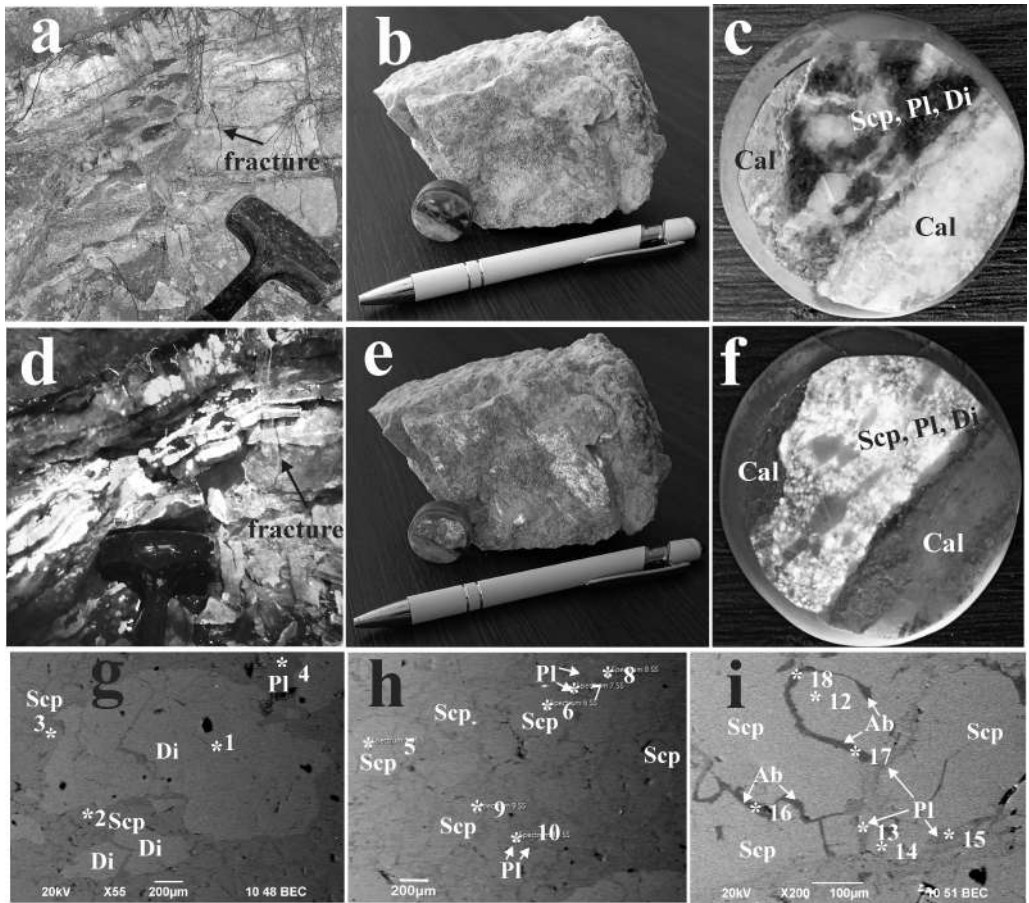


Fig. 2. Photo collage of scapolitization related objects from field to laboratory; a, d – geological field photos (d under UV light); b, e – mineral rock images of scapolitized specimens with or without UV light; c, f – polished section of scapolite-containing sample (f under UV light); g-i – backscattered electron composition (BEC) mode images of the studied mineral assemblages with designated sites of the EDS analyses

**Results and discussion.** All efforts to separate a monomineral scapolite sample proved unsuccessful. The PXRD patterns collected from the selected material invariably register a typical skarn type mineralization presented mainly by scapolite, calcite, as well as representatives of the plagioclase and pyroxene groups (Fig. 3). Intimate mineral intergrowths as well as intense grain fragmentation and cracks can be detected even macroscopically (Fig. 2a-f). The SEM and EDS analyzes provide additional information on the mineral association (Fig. 2g-i, Table 1). The scapolite compositions exhibit variations mostly in terms of extra-framework cation and anion species. It should be noted that the position of the extra-framework cations (*M*-position in the general formula) is not always occupied to its full capacity – 4 *apfu*, although at low contents,  $K^+$ ,  $Fe^{2+}$ , and  $Sr^{2+}$

T a b l e 1

Selected chemical analyses, formulae, and compositional characteristics for the main silicate minerals detected

Analyses sites in the BEC images	Chemical analyses, wt%											Chemical formula	Mineral name and compositional characteristics	
	Si	Al	Ca	Mg	Mn	Fe	Na	Sr	K	S	Cl			
	1	2	3	4	5	6	7	8	9	10	11	12	13	
1	33.18	0.35	24.68	13.12	0.03	0.33	0.11	0	0.05	0	0	$Ca_{1.00}(Mg_{0.91}^{2+}Al_{0.02}^{3+}Fe_{0.01}^{2+}Mn_{0.001}^{2+}Na_{0.008}^{+}K_{0.002}^{+})Si_2O_6$	diopside Wo=52.8; En=46.2; Fs=0.6; Ac=0.4 *	
2	35.36	22.03	14.88	0	0	0	3.17	0.51	0.06	0.11	0.00	$(Ca_{2.51}Na_{0.89}K_{0.04}Sr_{0.03}Fe_{0.03})_{3.5}$	scapolite	
3	32.10	19.30	18.08	0	0	0.47	3.45	0.31	0.39	0.65	0.650	$(Al_{4.67}Si_{7.33})O_{24}(0.83CO_3, 0.11SO_4, 0.06Cl)$	Me=62.75 **	
5	31.53	19.28	17.96	0.04	0	0	3.40	0.26	0.46	0.82	0.31			
6	31.75	19.40	18.09	0	0	0.06	3.40	0.31	0.31	0.87	0.35	$(Ca_{2.96}Na_{0.96}K_{0.07}Sr_{0.02}Fe_{0.01}Mg_{0.01})_{4.0}$	scapolite	
8	31.45	19.34	18.25	0	0	0	3.38	0.10	0.37	0.89	0.39	$(Al_{4.67}Si_{7.33})O_{24}(0.77CO_3, 0.17SO_4, 0.06Cl)$	Me=74.00 **	
9	31.46	19.23	18.37	0.03	0.03	0.03	3.33	0.38	0.46	0.80	0.27			
12	31.19	19.24	8.74	0.01	0.04	0.08	3.42	0.43	0.34	0.75	0.48	$Ca_{2.94}Na_{0.98}K_{0.06}Sr_{0.03}Fe_{0.03}Mn_{0.01})_{4.0}$ $(Al_{4.69}Si_{7.31})O_{24}(0.76CO_3, 0.15SO_4, 0.09Cl)$	scapolite Me=73.50 **	
4	38.68	17.82	7.92	-	-	-	6.19	-	0.14	-	-	$Na_{0.53}Ca_{0.39}Al_{1.29}Si_{12.69}O_8$	plagioclase An <sub>42.35</sub> Ab <sub>57.65</sub> *	

Table 1  
Continued

Analyses sites in the BEC images	Chemical analyses, wt%											Chemical formula	Mineral name and compositional characteristics
	Si	Al	Ca	Mg	Mn	Fe	Na	Sr	K	S	Cl		
	1	2	3	4	5	6	7	8	9	10	11	12	13
10	26.97	12.18	0.81	–	–	–	9.38	0.81	–	–	–	$\text{Na}_{1.13}\text{Ca}_{0.06}\text{Al}_{1.30}\text{Si}_{2.70}\text{O}_8$	plagioclase $\text{An}_{4.73}\text{Ab}_{95.27}$ *
13	25.73	13.23	3.68	–	–	–	6.27	3.68	–	0.05	–		
14	25.43	13.45	3.76	–	–	–	6.00	3.76	–	0.03	–	$\text{Na}_{1.22}\text{Ca}_{0.02}\text{Al}_{1.22}\text{Si}_{2.55}\text{O}_8$	plagioclase $\text{An}_{1.77}\text{Ab}_{98.23}$ *
15	25.74	15.76	2.84	–	–	–	6.01	2.84	–	–	0.03		
16	24.21	11.89	0.09	–	–	–	9.74	0.09	–	0.02	–	$\text{Na}_{0.73}\text{Ca}_{0.24}\text{Al}_{1.45}\text{Si}_{2.53}\text{O}_8$	plagioclase $\text{An}_{24.40}\text{Ab}_{75.60}$ *
17	23.79	11.79	0.41	–	–	–	9.75	0.41	–	–	–		
18	23.68	11.63	0.45	–	–	–	10.74	0.45	–	–	–		

\* Chemical formulae and compositional characteristics are based on calculations from the GabbroSoft website: <https://www.gabbrosoft.org/spreadsheets/>. Trace amounts of Mn, Fe, K, S, and Cl detected in some of the samples have been ignored.

\*\* Chemical formulae of the studied scapolites have been calculated under the following assumptions: (i)  $\text{Al}+\text{Si} = 12$  *apfu* ( $Z=2$ ); (ii)  $\text{CO}_3 = 1-\text{Cl}-\text{SO}_4$ ; conversion factors  $\text{S}\rightarrow\text{SO}_4(3)$ ,  $\text{Cl}\rightarrow\text{Cl}(1)$ ; (iii) % *Me* =  $\text{Ca}^*100/4$ .

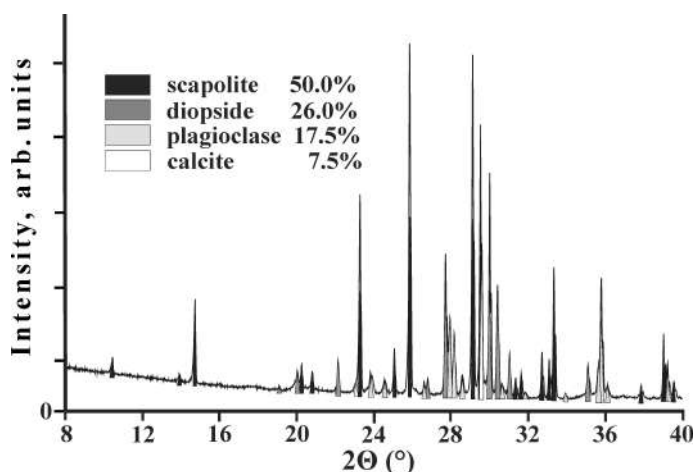


Fig. 3. PXR D pattern of a scapolitized rock sample from Mi-shevsko, Central Rhodopes

are almost constantly present there. The meionite component ( $Me$ ) varies between 62 and 74. According to the calculation methodology used, the **A**-position is occupied mainly by  $CO_3^{2-}$  anions;  $SO_4^{2-}$  is in a subordinate amount, and the chlorine content is extremely low. It is interesting to note that in some of the EDS analyses performed on scapolite grains the content of uranium has reached up to 0.6 wt%. Traces of light rare earth elements (Ce, Dy, etc.) have also been detected.

The pyroxene analysis determines it to be almost pure diopside (line 1, Table 1). Plagioclase compositions range from  $An_{1.8}Ab_{98.2}$  to  $An_{42.4}Ab_{57.6}$  (lines 4–18, Table 1). This fact implies the occurrence of at least two generations for these aluminium silicates. The latest one is represented by nearly pure albite appearing as veinlets or filling cracks that cut across the early mineralizations in the sample studied (Fig. 2g-i).

#### Considerations about the factors controlling the scapolitization.

The composition of the involved host rocks and metamorphic fluid phase are the main controlling factors for scapolite growth. In most circumstances, scapolite forms by replacement of plagioclase. Such replacement is thought to be driven by interaction of plagioclase with fluids containing  $Cl^-$ ,  $CO_2$ ,  $SO_3$  and  $Na^+$ , rather than by isochemical transformation [13, 14]. Development of subsequent albitization, consuming the excess of  $Na^+$  liberated from alteration of plagioclase cannot be ruled out [15]. In our opinion, such a scenario has developed in the studied locality. The facts about the geological setting of the area, as well as the observed relationships between the minerals and the chemical analyses made, speak in favour of this. The following scheme of mineral formation for the studied segment is proposed:

- (i) initial skarnization at the boundary between marbles and metamorphites with increased content of plagioclase leading to formation of scapolite and diopside;
- (ii) tectonic deformation that resulted in intense cracking and fragmentation of the skarn matrix and host rocks;
- (iii) albitization carried out by fluid phase transported along the fractures and the subgrain boundaries of the scapolite-diopside matrix.

The data presented in Table 1 bring additional information about the process-controlling factors as follows:

- (i) enrichment of the altered zone with calcium, which is an indication of the source of transport – the host marbles;
- (ii) low chlorine contents in the scapolites composition, indicating a generally low activity of this element in the fluid phase. Additional confirmation of this is the absence of amphiboles representatives and micas in the studied area, which are known to be hosts for this element;
- (iii) the large compositional variations of the studied scapolite and plagioclase representatives may be indicative for the large local variations in the composition and volatile activities of the evolved fluids [13].

**Speculations on possible causes of scapolite fluorescence.** The colouration and luminescent properties of scapolites have long attracted the attention of both jewelers and researchers who are looking for the mechanisms that cause them. In one of the early reports on this subject, Shaw suggested that the strong fluorescence of the yellow scapolite from Grenville, Quebec was due to the presence of small amounts of uranium, which is the activating agent [2]. Over the years, it has been established that, even with low contents, other extra-framework cations ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ce}^{3+}$ ) can also cause luminescence of various colours [4, 16]. Recently, more researchers have come together around the opinion that the characteristic yellow (according to some orange) luminescence of scapolites is associated with  $\text{S}_2^-$  centres located in the **A**-position ([4] and references, therein). Although clarifications are pending on the issue of the size and orientation of the single charged sulphur dimers relative to the structure of the mineral, their presence is accepted as indisputable when experimentally proven spectroscopically by obtaining a characteristic photoluminescence spectrum with a pronounced vibronic structure. However, there is still no supporting evidence for the presence of  $\text{S}_2^-$  centres obtained by other methods such as X-ray structural analysis. For now, only the fact that the yellow luminescence is due to an activating agent belonging to the groups of EFC and/or EFA species remains evident.

**Conclusions.** For the first time, data on scapolites from a new locality in Bulgaria – Mishevsko, Central Rhodopes, are being reported. These are the first finds of yellow luminescent representatives of this mineral group in our country. Initial studies indicate that the scapolite formed as a result of skarn metasomatism. Further in time follow tectonic deformations that resulted in intense cracking and



fragmentation of the skarn matrix and development of albitization. Geological processes primarily affect the speciation and occupancies of the extra-framework cation and anion sites and lead to noticeable scapolite compositional variations ( $62 < Me < 74$ ).

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