

CRYSTAL STRUCTURE OF SCAPOLITE FROM URDINI
LAKES, NORTHWESTERN RILA, BULGARIA

Vladislav Kostov-Kytin[#], Rositsa Nikolova, Milen Kadiyski*,
Iliya Dimitrov**

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Abstract

The paper provides new insight on the choice of correct space group for description of scapolite crystal structures, with a view of the preferred positions by Si and Al ions and their framework ordering. Samples of scapolite from a skarn zone around Urdini lakes, Northwestern Rila have been analysed with SEM-EDS and single crystal X-ray diffraction. The obtained value for the meionite component (*Me*) is around 70. The crystal structure of the studied sample has been refined in the tetragonal $I4/m$ and $P4_2/n$ space groups, traditionally assigned to scapolite members. In addition, structural determination has been conducted in $C2/m$.

Key words: scapolite, single-crystal X-ray analysis, space group

Introduction. Scapolites are rock-forming minerals with well-pronounced crystal chemical complexity. It is widely accepted that natural scapolites form a solid-solution series between two theoretical end-members: $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}$ (marialite *Me0*) and $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$ (meionite *Me100*). Traditionally, the meionite (*Me*) content in atomic % is defined as follows: $Me=100(\text{Ca}+\text{Sr}+\text{Fe}+\text{Mn}+\text{Mg})/$

[#]Corresponding author.

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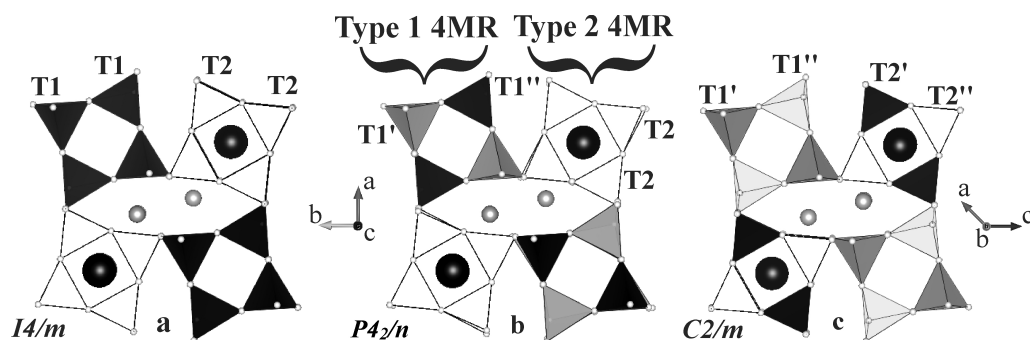


Fig. 1. Crystal structure of scapolite presented in a) $I4/m$, b) $P4_2/n$, and c) $C2/m$ space groups. The symmetry-equivalent tetrahedral sites are depicted with the same colour and correspondingly designated with T-letters followed by numbers with or without apostrophes

(Na+K+Ca+Sr+Fe+Mn+Mg) [1]. The interest in such compounds originates mainly from their application as geothermometers, and their potential for greenhouse gas storage [2,3]. Scapolite crystal structure is composed of a $[(\text{Si},\text{Al})_n\text{O}_{2n}]$ framework containing eight- and four-membered rings. Calcium and sodium (and sometimes Mg, K, Fe) cations are located in the channels, formed by the eight-membered rings (depicted as medium-sized grey circles in Fig. 1) and carbonate, sulphate and chlorine anions (but sometimes also H_2O , HCO_3^- , HCl , OH^- , S, etc. [4]) occupy channels formed by the four-membered rings (large black circles in Fig. 1).

There are three types of heterovalent isomorphism for group members, generally represented as follows: $\text{Si} \leftrightarrow \text{Al}$ (framework cations), $\text{Ca} \leftrightarrow \text{Na}$, and $\text{CO}_3 \leftrightarrow \text{SO}_4 \leftrightarrow \text{Cl}$ (extra-framework species). Relations between the three schemes are not always explicit and unambiguous, but essentially, their joint manifestation leads to electroneutrality.

The highest symmetry space group used in crystal structures refinement in the marialite-meyonite series is the tetragonal $I4/m$. Typically it is applicable to the representatives falling within the compositional ranges in the vicinities of the two end-members. In the middle region, however, additional reflections are observed in the diffraction patterns, which require the use of the primitive $P4_2/n$ of the tetragonal syngony. These are $(h+k+l)$ odd reflections forbidden for $I4/m$. Drawing boundaries between the representatives of the two space groups, especially those with high calcium content, is still controversial. The range of the $P4_2/n$ scapolite, as defined by various authors, may comprise group members as follows: from (Me18) to (Me90); from (Me21) to (Me77); from (Me6) to (Me93), and even from (Me0) to (Me100) [5–7].

The scapolite framework indeed contains two types of four-membered rings (4MRs), each of which is made up of AlO_4 and SiO_4 tetrahedra together designated also as T-tetrahedra [8]. The type 1 ring (Type 1 4MR) consists of T1 (in $I4/m$;

equipoint rank 16; Fig. 1a) or T1' and T1'' tetrahedra (in $P4_2/n$; each with an equipoint rank of 8; Fig. 1b). The tetrahedra from this type rings point alternately up and down. The type 2 ring (Type 2 4MR) consists only of T2 tetrahedra that point in the same direction. Their equipoint rank is 8 when the structure is described in tetragonal symmetry. If lowering of symmetry continues to the monoclinic and structurally related $C2/m$ space group, the T2 tetrahedra will “split” into two symmetry non-equivalent tetrahedral sites designated as T2' and T2'', as shown in Fig. 1c. In addition, the two types of rings are connected in a way to form five-membered rings each one composed of one T2 and four T1 (in SG $I4/m$) or composed of one T2, two T1', and two T2'' (in SG $P4_2/n$) tetrahedra, stacked along the c axis [6].

The aluminium-silicon ordering in the structure of the scapolite group members may find manifestation in the preferential occupation of certain cation framework tetrahedral positions by Al (Si) according to the LOEWENSTEIN rule [9] or at least in an attempt of its maximal obeying. The experimental data received so far clearly give evidence that with increase of its content in the structure, Al first enters the tetrahedra from the Type 1 4MRs [6,7]. With further increase to 1–4 *apfu*, preferential cationic occupancy of selected tetrahedral positions in the Type 1 4MRs begins. Since the radii of the $^{IV}\text{Al}^{3+}$ and $^{IV}\text{Si}^{4+}$ -ions are 0.39 Å and 0.26 Å, respectively, [10] the polyhedral size differences result in “splitting” of T1 tetrahedra (Fig. 1a) into T1' and T1'' and thus predetermining symmetry lowering from $I4/m$ to $P4_2/n$ (Fig 1b). Upon reaching levels of Al:Si = 1:2, aluminium atoms already start to enter Type 2 4MRs sites, because this decreases the probability of the formation of unstable Al-O-Al linkages in the Type 1-rings [8].

The present study provides new crystal chemical data for the scapolite from Urdini lakes locality, Northwestern Rila. Based on energy-dispersive spectroscopy (EDS) and single crystal structure determinations (SXDA), a more precise determination of the meionite content than those previously made for this locality has been carried out. The crystal structure of the studied sample has been solved in both $I4/m$, $P4_2/n$ space groups, traditionally assigned to scapolite members, and additionally in $C2/m$. The aim is to shed more light on the still controversial question for the correct choice of space group in the description of this group's representatives [6,7].

Geological setting on scapolites from Northwestern Rila. The Malyovitsa area of the Northwestern Rila Mountains is composed of biotite gneisses, among which marble lenses, amphibolites, serpentinites, and granites are located. Pegmatite dykes are intruded along or oblique with respect to the metamorphic foliation. At the pegmatite/marble contact, skarn zones are often formed, the thickness of which varies from 0.1 to 8–10 m [11]. The scapolites form almost monomineral accumulations in the skarn zones between the pegmatite veins and the marbles [11]. PETRUSSENKO [11] described scapolites from several localities in this part of Northwestern Rila Mountain. Based on classical chemical analysis,

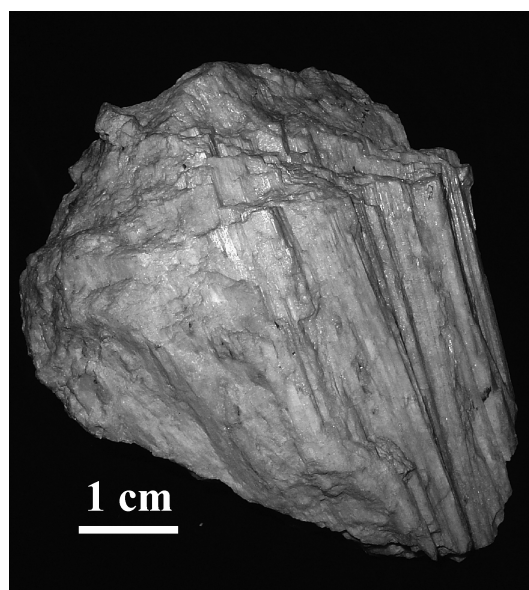


Fig. 2. Macro photograph of a monomineral scapolite sample from Urdini lakes locality

he defined the findings as carbonate-sulphate type *mizzonite* ($Me_{50} - -80$) with meionite content of 62.6 (Petlite summit), 69.6 (Urdina river) to 71.7 % (Urdini lakes).

Materials and methods. A crystalline sample with glassy to pearly lustre from the Urdini lakes locality currently preserved in the National Museum of Natural History at the Bulgarian Academy of Sciences, Sofia under number 1608 was used in the present study (Fig. 2).

Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS). SEM and EDS analyses were done on a polished, carbon-coated section of a scapolite-containing sample from Urdini lakes using X-MaxN 50 mm² EDS detector by Oxford Instruments (20 kV accelerating voltage), mounted on a Tescan Vega 3 XMU electron microscope at the Research and Development Department of Aurubis Bulgaria AD, Pirdop. Aztec Energy software was used for data collection, integration and corrections, using integrated factory standards. The chemical formula of the studied scapolite has been calculated based on 13 analyses under the following assumptions: (i) $Al+Si = 12 \text{ apfu}$ ($Z=2$); (ii) $CO_3 = 1-Cl-SO_4$; conversion factors $S \rightarrow SO_4(3)$, $Cl \rightarrow Cl(1)$; (iii) negligible amounts of detected di- and monovalent extra-framework cations (EFC) together with possible vacancies have been treated as a monovalent fictive cation M^+ ; (iv) $\% Me = Ca \cdot 100/4$.

Single crystal X-ray diffraction analysis (SXDA). A single crystal with a size of $0.15 \times 0.1 \times 0.1$ mm from the studied compound was mounted on glass

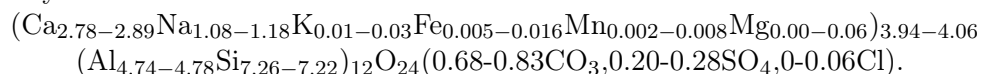
capillary and analysed by a single crystal diffraction method. Data collection and data reduction were performed by CrysAlisPro, Rigaku Oxford Diffraction, 2017, version 1.1.171.37.35 [12]. The crystal structure was solved by direct methods using ShelxS and refined with ShelxL programs [13] using full-matrix least-squares method of F^2 . All atom positions were assigned successfully from the produced Fourier electron density map. The tetrahedral positions are assumed to be mixed Si/Al with occupancy parameters of Al and Si fixed accordingly to the deviations from the standard Si/Al – O distances and then compared to those obtained by EDS analyses. The Ca and Na cations share common crystallographic position and the same is valid for C, S and Cl anions. The overall occupancy of the Ca and Na position(s) was fixed to 98% for all used structural models to better match the chemical analysis data. The occupancy parameters of the anion groups in the structure were refined with a constraint to maintain 100% occupancy of the common anion position (except chlorine due to its very low content). The differences between the theoretical and analytical structural factors were first done with isotropic temperature displacement parameters and then for the anisotropic refinement including all atoms. The obtained structural models are optimal with respect to the reliability factors and the chemical analysis data. Other common for all used models' experimental conditions include temperature 290(2) K; MoK α radiation $\lambda = 0.71073$ Å.

Considerations on the proper choice of space group for scapolites.

Both tetrahedral symmetry space groups used so far for description of the scapolite crystal structures ($I4/m$ and $P4_2/n$) do not provide opportunity to differentiate by size the tetrahedra building up the Type 2 4MRs because all these sites are symmetrically equivalent. Such an opportunity may be provided by using the monoclinic $C2/m$ space group since it allows “splitting” of the T2 tetrahedra from the Type 2 rings into T2' and T2” (Fig. 1c). The necessary conditions to detect size differences depend on the precision of the used equipment and model as well as on the sufficiency of the aluminium atoms entering these positions and their propensity for ordering according to the Loewenstein rule. It is also worth noting that all three of these space groups are in group-subgroup relations [14].

Results and discussion. Figure 3 presents a SEM image of scapolite (Scp) from Urdini lakes with inclusions of apatite (Ap) and secondary minerals (possibly zeolites) filling the microfissures of the main matrix. Their presence explains the slightly enhanced meionite content and detection of P_2O_5 for this mineral obtained by data from the classical chemical analysis applied in previous investigations [11].

The chemical composition of unaltered scapolite as determined by EDS and its crystal chemical formula is



The variations in the extra framework cations contents imply the following suggestions: (i) part of the iron in the form of Fe^{3+} may enter the framework in

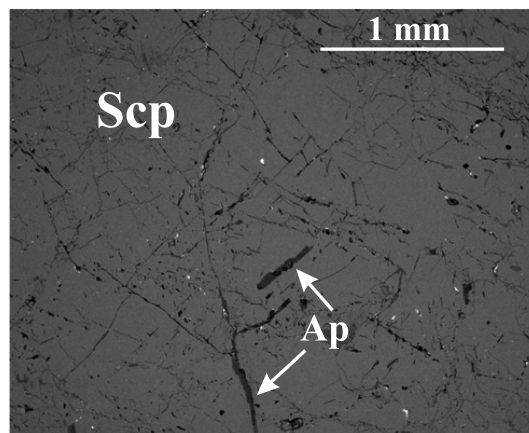


Fig. 3. SEM image of scapolite (Scp) from Ur-dini lakes with inclusions of apatite (Ap) and secondary minerals filling the microfissures of the matrix

the tetrahedrally coordinated cation positions where the sum of EFC exceeds 4 *apfu*; (ii) there are vacancies in this position in cases when the EFC sum falls below 4 *apfu*. The overall effect of the very low content and not always constant presence of the minor EFCs, as well as the possible presence of vacancies in these positions can be presented as a fictive monovalent cation M^+ whose occupancy does not exceed 0.05 *apfu*. Thus, the average (from 13 analyses) crystal chemical formula can be presented as: $(Ca_{2.82}Na_{1.13}M_{0.05})_4(Al_{4.76}Si_{7.24})_{12}O_{24}(0.76CO_3, 0.23SO_4, 0.01Cl)$, where $M^+ = K^+, Fe^{2+}, Mn^{2+}, Mg^{2+}, \square$; $Ca/Na=2.5$; % Me = 70.5. This is also the reason why only Ca^{2+} and Na^+ have been refined in the extra framework sites of all used structural models during the single crystal X-ray experiments and their overall occupancy has been fixed to 98%.

The data in Table 1 show that the three space groups, used to solve the structure are plausible with respect to the obtained reliability factors values. However, best results in terms of the applied single crystal investigations methodology and the received Al/Si ratio in the scapolite framework from EDS analyses, are achieved for the $P4_2/n$ case. This is also the space group used and recommended by most researchers that have studied scapolites of similar chemical compositions and Me contents, correspondingly [6,7].

The single crystal determinations in $C2/m$ did not provide reliable evidence for tetrahedra “splitting” in Type 2 4MR (Fig. 1c). The measured averaged bond length distances are as follows: $|T2'-O|_{av}=1.636(3) \text{ \AA}$; $|T2''-O|_{av}=1.633(4) \text{ \AA}$. These values are statistically not significant with respect to their estimated standard deviations. Subsequently, the use of $C2/m$ is not justified in this case. The main reasons for these results are related to the precision of the used equipment and model as well as to the low content of aluminium entering these posi-

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Crystal data and structure refinement parameters for the scapolite from Urdini lakes locality

Compound UE	<i>C</i> 2/ <i>m</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>I</i> 4/ <i>m</i>
Chemical formula, Z=2	(Ca _{2.771} Na _{1.149}) _{3.92} (Al _{4.655} Si _{7.345}) ₁₂ O ₂₄ (0.862CO ₃ , 0.138SO ₄)	(Ca _{2.730} Na _{1.19}) _{3.92} (Al _{4.754} Si _{7.246}) ₁₂ O ₂₄ (0.84CO ₃ , 0.16SO ₄)	(Ca _{2.755} Na _{1.165}) _{3.92} (Al _{4.646} Si _{7.354}) ₁₂ O ₂₄ (0.84CO ₃ , 0.16SO ₄)
Formula weight	918.43	918.36	919.03
Crystal system	Monoclinic	Tetragonal	Tetragonal
<i>a</i> (Å)	17.1581(11)	12.1350(7)	12.1293(9)
<i>b</i> (Å)	7.5556(4)	12.1350(7)	12.1293(9)
<i>c</i> (Å)	12.1316(8)	7.5560(5)	7.5552(7)
α (°)	90	90	90
β (°)	135.009(2)	90	90
γ (°)	90	90	90
Volume (Å ³)	1111.92(12)	1112.68(15)	1111.52(19)
ρ_{calc} (g/cm ³)	2.743	2.741	2.746
μ (mm ⁻¹)	1.442	0.632	1.464
<i>F</i> (000)	912	912	913
Θ range for data collection ((°))	2.374 to 28.294	2.374 to 28.264	2.375 to 28.296
Limiting indices	-22<= <i>h</i> <=22, -10<= <i>k</i> <=10, -16<= <i>l</i> <=16	-16<= <i>h</i> <=16, -6<= <i>k</i> <=15, -10<= <i>l</i> <=10	-15<= <i>h</i> <=16, -16<= <i>k</i> <=15, -10<= <i>l</i> <=10
Reflections collected/unique	13464/1489 [<i>R</i> (int) = 0.0570]	13464/1372 [<i>R</i> (int) = 0.0670]	7245/745 [<i>R</i> (int) = 0.0602]
Data/restraints/parameters	1489/0/124	1141/0/108	745/0/66
Goodness-of-fit on <i>F</i> ²	1.080	1.044	1.073
Final <i>R</i> indexes [<i>I</i> >=2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0302 <i>wR</i> ₂ = 0.0673	<i>R</i> ₁ = 0.0461 <i>wR</i> ₂ = 0.0857	<i>R</i> ₁ = 0.0319 <i>wR</i> ₂ = 0.0736
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0412 <i>wR</i> ₂ = 0.0726	<i>R</i> ₁ = 0.1002 <i>wR</i> ₂ = 0.1052	<i>R</i> ₁ = 0.0431 <i>wR</i> ₂ = 0.0795
Largest diff. peak/hole (e Å ⁻³)	1.131/-0.587	0.689/-0.551	0.930/-0.463

tions, being insufficient for some Al/Si ordering to be manifested there. Research is underway on scapolite samples with higher aluminium content to test the hypothesis of Al-Si arrangement in Type 2 4MRs leading to a distinct size differentiation of the two types of tetrahedra that build them.

Conclusions. Based on EDS and SXDA, a more precise determination of the meionite component of a representative of the scapolite group from Urdini lakes, Northwestern Rila was made. Solving the crystal structure in three possible space groups being in group-subgroup relations sheds new light on the proper choice of space group for description of scapolite crystal structures, as well as on the preferred by silicon and aluminium ions positions and hence for their ordering in the framework construction.

REFERENCES

- [1] SHAW D. M. (1960) The geochemistry of scapolite part I. Previous work and general mineralogy, *Journal of Petrology*, **1**(1), 218–260.
- [2] TEERTSTRA D. K., B. L. SHERRIFF (1996) Scapolite cell-parameter trends along the solid-solution series, *Am. Mineral.*, **81**(1–2), 169–180.
- [3] ANTAO S. M. (2013) Unit-cell parameters for scapolite solid solutions and a discontinuity at Me75, ideally NaCa₃[Al₅Si₇O₂₄](CO₃), *Powder Diffr.* **28**(4), 269–275.
- [4] SWAYZE G. A., R. N. CLARK (1990) Infrared spectra and crystal chemistry of scapolites: Implications for Martian mineralogy, *Journal of Geophysical Research: Solid Earth*, **95**(B9), 14481–14495.
- [5] SETO Y., N. SHIMOBAYASHI, A. MIYAKE, M. KITAMURA (2004) Composition and I4/m-P4₂/n phase transition in scapolite solid solutions, *Am. Mineral. (USA)*, **89**, 257–265.
- [6] SOKOLOVA E., F. C. HAWTHORNE (2008) The crystal chemistry of the scapolite-group minerals. I. Crystal structure and long-range order, *Can. Mineral.*, **46**, 1527–1554.
- [7] ANTAO S. M., I. HASSAN (2011) The structures of marialite (Me6) and meionite (Me93) in space groups P4₂/n and I4/m, and the absence of phase transitions in the scapolite series, *Powder Diffr. (USA)*, **26**, 119–125.
- [8] HASSAN I., P. R. BUSECK (1988) HRTEM characterization of scapolite solid solutions, *Am. Mineral.*, **73**, 119–134.
- [9] LOEWENSTEIN W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates, *American Mineralogist: Journal of Earth and Planetary Materials*, **39**(1–2), 92–96.
- [10] SHANNON R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, **32**(5), 751–767.
- [11] PETRUSSENKO S. (1969) Scapolite from Northwestern Rila – *Bulletin of the Geological Institute – Series Geochemistry, Mineralogy and Petrography*, **18**, 153–160 (in Bulgarian with English abstract).

- [¹²] Agilent (2010) CrysAlis PRO (version 1.171.35.15), Yarnton, England, Agilent Technologies, Ltd.
- [¹³] SHELDRICK G. M. (2008) A short history of SHELX, *Acta. Cryst.*, **A64**, 112–122.
- [¹⁴] HAHN T. (Ed.) (2002) *International Tables for Crystallography. Volume A, Space-Group Symmetry*. Dordrecht; London: Published for the International Union of Crystallography by Kluwer Academic Publishers.

Institute of Mineralogy and Crystallography
Bulgarian Academy of Sciences
Akad. G. Bonchev St, Bl. 107
1113 Sofia, Bulgaria
e-mail: vkytin@abv.bg
rosica.pn@clmc.bas.bg

** Aurubis Bulgaria AD*
Research and Development
Industrial zone Pirdop
2070 Pirdop, Bulgaria
e-mail: m.kadiyski@aurubis.com

*** National Museum of Natural History*
Bulgarian Academy of Sciences
1 Tsar Osvoboditel Blvd
1000 Sofia, Bulgaria
e-mail: lakichepelare@abv.bg