

Parawollastonite (wollastonite-2M polytype) from the skarns in Zvezdel pluton, Eastern Rhodopes – a single crystal study

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The wollastonite polytype in three samples from different zones of skarns in Zvezdel pluton was determined by single-crystal XRD structure refinement. The studied wollastonite crystals are nearly pure CaSiO_3 but containing a few tenths of FeO wt.% (determined using microprobe analysis). The structure refinement confirmed the monoclinic symmetry of the studied samples (space group $P2_1/a$ and unit cell parameters $a = 15.413(17)$ Å, $b = 7.336(5)$ Å, $c = 7.070(3)$ Å, $\beta = 95.24(5)^\circ$ for the crystal from the plagioclase-pyroxene-wollastonite+garnet zone; $a = 15.409(7)$ Å, $b = 7.320(3)$ Å, $c = 7.063(2)$ Å, $\beta = 95.36(3)^\circ$ – wollastonite from the plagioclase-pyroxene-wollastonite zone, and $a = 15.3770(11)$ Å, $b = 7.2990(4)$ Å, $c = 7.0491(5)$ Å, $\beta = 95.340(6)^\circ$ – wollastonite from the plagioclase-pyroxene-wollastonite+epidote zone). The latter structure was refined to $R_1 = 0.0521$ and $R_{(all)} = 0.0754$ using 1970 unique reflections. The Si–O bond lengths vary between 1.580(3) and 1.667(3) Å (mean 1.624 Å), Ca–O bond lengths between 2.251(3) and 2.662(3) Å (mean 2.390 Å), and the Si–O–Si angles are 140.03(17), 139.39(18), and 150.81(18)° (mean 143.31°).

The proved monoclinic wollastonite (wollastonite-2M) is regarded as a higher temperature polytype with respect to the triclinic one. The presence only of the wollastonite-2M polytype in the studied skarns indicates longer duration of the thermal influence at the contact of carbonate xenoliths with monzonite magma or could be a result of an external stress, which is probably the stretching of the crystals due to differences in the thermal expansion coefficient of wollastonite with respect to the surrounding matrix.

Key words: skarn, wollastonite-2M, single crystal X-ray diffraction.

INTRODUCTION

Wollastonite (CaSiO_3) occurs in two structurally different forms: high-temperature α -wollastonite stable above ca. 1150 °C and low-temperature β -wollastonite that is the common CaSiO_3 -polymorph found in crustal rocks. The low-temperature wollastonite contains dreier single chains, i.e. chains with three $[\text{SiO}_4]$ -tetrahedra in the repeat unit (pyroxenoid type). The chains are linked to three columns of Ca-centred octahedra. Because of the size mismatch of the tetrahedral repeat units and the octahedral bands, the tetrahedra are tilted to accommodate their apices to the octahedral apices [1–4]. Both chains and bands run parallel to the b -axis.

A series of natural polytypes have been reported [3–11] with different packing arrangements of the single chains: triclinic polytypes (1T, 3T, 4T, 5T, 7T) and monoclinic parawollastonite (wollastonite-2M). The structure of wollastonite-1T was determined by Mamedov and Belov [5] and refined by Buerger and Prewitt [6], and Ohashi and Finger [3]; that one of wollastonite-2M was solved by Tolliday [7], Trojer [8], Ohashi [4], and Hesse [9]. The structures of the higher polytypes 3T, 4T, 5T and 7T were described by Henmi et al. [10] and Henmi et al. [11]. The structural difference between triclinic wollastonite and monoclinic parawollastonite has been interpreted to be due to different modes of stacking along the direction of the a -axis. These forms are not easily distinguishable except by single-crystal XRD refinement, since they differ only in the reflexions with k odd, which are always weak [7]. The structural state of wollastonite is a useful petrogenetic indicator for the deformation and cooling history of a rock. The aim of this study is to identify the polytypic modification of wollastonite

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from different skarn zones and to interpret its occurrence at Zvezdel-Pcheloyad ore deposit (Eastern Rhodopes, Bulgaria).

MATERIALS

The studied wollastonite crystals were collected from zoned skarn nodules included in monzonites of the Zvezdel pluton. The following zones are determined from the proximal parts of the nodules towards the contact with the monzonites: garnet, pyroxene-garnet, plagioclase-pyroxene-wollastonite+garnet (Pl-Px-W-Gt), plagioclase-pyroxene-wollastonite (Pl-Px-W), plagioclase-pyroxene-wollastonite+epidote (Pl-Px-W-Ep), and plagioclase-pyroxene. Wollastonite, clinopyroxene, plagioclase, calcite, and grossular-andradite garnet are the major constituents of the wollastonite-bearing zones. Quartz is a subordinate phase and the associated minor minerals include epidote, prehnite, and chlorite. Titanite, apatite and magnetite are present as accessories.

The wollastonite-bearing zones exhibit massive or banded fabrics (Fig. 1a, b, c) with no visible preferred orientation of the crystals. The content of wollastonite averages 25–30%, but locally attains 70%. Wollastonite occurs mainly as nodular aggregates or forms prismatic grains up to about 3 mm in length along *b* (Fig. 1d, e, f). Wollastonite

displays an overlapping composition among the three zones. It is nearly pure CaSiO_3 , typically containing a few tenths of FeO wt.% (determined with microprobe analysis).

EXPERIMENTAL

Three wollastonite crystals from the zones Pl-Px-W-Gt, Pl-Px-W, and Pl-Px-W-Ep were selected for single-crystal XRD study. The specimens used in this study have prismatic habit, 0.2–0.3 mm long (along *b*), and cross sections of 0.1–0.2 mm. The crystals were mounted on glass fibres and measured on an Oxford diffraction Supernova diffractometer equipped with an Atlas CCD detector. X-ray data collection was carried out at room temperature with monochromatized $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection strategy was chosen for 100% completeness and redundancy of 4. Data reduction and analysis were carried out with the CrysAlisPro program [12]. Lorentz and polarization corrections were applied to intensity data using WinGX [13]. Reliable model with satisfactory R-values was obtained using the $P2_1/a$ space group and it was chosen for the refinement. Starting atomic coordinates were taken from [9]. Structure refinements were performed using the program SHELXTL [13], employing neutral atom scattering factors. At the final stage of refinement, anisotropic temperature factors were introduced.

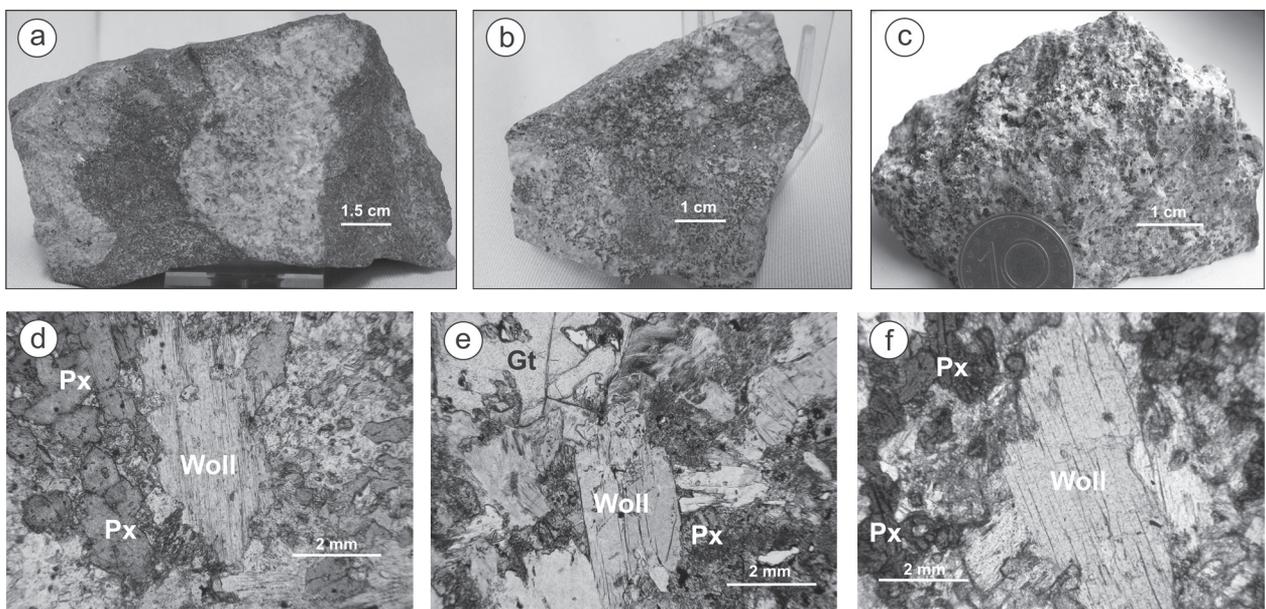


Fig. 1. Hand specimens of wollastonite-bearing skarn zones showing banded and massive texture (a–c); Photomicrographs (plane polarised light) showing wollastonite crystals of: (d) plagioclase-pyroxene-wollastonite-epidote skarn zones, (e) plagioclase-pyroxene-wollastonite-garnet zone; and (f) plagioclase-pyroxene-wollastonite zone. Woll – wollastonite, Px – clinopyroxene, Gt – garnet.

RESULTS AND DISCUSSION

The results after the refinement confirmed the monoclinic symmetry of the studied samples with space group $P2_1/a$ (Fig. 2). The final refinement unit cell dimensions are presented in Table 1.

The structure of a crystal selected from the Pl-Px-W-Ep zone was refined to $R_1 = 0.0521$ and $R_{(all)} = 0.0754$ using 1970 unique reflections. The experimental details are given in Table 2. Final atomic coordinates and thermal displacement parameters are listed in Tables 3 and 4. The Si–O bond lengths vary between 1.580(3) and 1.667(3) Å (mean 1.624 Å), Ca–O bond lengths are between 2.251(3) and 2.662(3) Å (mean 2.390 Å), and Si–O–Si angles are 140.03(17), 139.39(18) and 150.81(18)° (mean 143.31°) (Table 5). The re-

sults are in good agreement with those obtained by Hesse [9] and Ohashi [4].

Wollastonite-2M polytype was established for all wollastonite-bearing zones in the skarns at Zvezdel. This polytype is regarded as a higher temperature polytype with respect to the triclinic one [e.g. 10, 14]. Interesting results were reported by Henmi et al. [10]. The authors studied wollastonites from zoned skarns, which were formed around andesite dike at Kushiro, Hiroshima Prefecture, Japan and determined 1T, 2M, 3T, 4T, and 5T polytypes. The ratios of 2M to 1T in the skarns decrease gradually with increasing distances from the dike, and that 3T, 4T and 5T polytypes were found only at localities where both 1T and 2M exist. Mazzucato and Gualtieri [14] studied experimentally the wollastonite polytypes in the system CaO–SiO₂ in the temperature range

Table 1. Unit cell parameters of the studied samples

Parameter	Sample	wollastonite from Pl-Px-W-Gt zone	wollastonite from Pl-Px-W zone	wollastonite from Pl-Px-W-Ep zone
a [Å]		15.413(17)	15.409(7)	15.3770(11)
b [Å]		7.336(5)	7.320(3)	7.2990(4)
c [Å]		7.070(3)	7.063(2)	7.0491(5)
β [°]		95.24(5)	95.36(3)	95.340(6)
V [Å ³]		796.0(7)	793.2(7)	787.68(9)

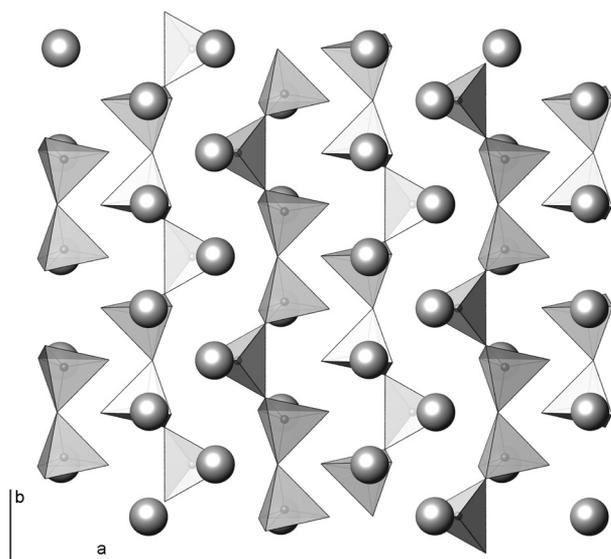


Fig. 2. Polyhedral model of the crystal structure of wollastonite-2M showing the stacking sequence of the a [(100) module] slabs (crystal from the Pl-Px-W-Ep zone)

Table 2. Experimental details for wollastonite-2M from the Pl-Px-W-Ep zone

№ of reflections	6826
R_{int}	0.0541
R_{sigma}	0.0446
h min	–20
h max	19
k min	–9
k max	10
l min	–9
l max	8
theta min [°]	3.75
theta max [°]	29.68
unique reflections	1970
Ref. $F_o > 4\sigma F_o$	1290
№ of parameters	131
R_1	0.0521
$R_{(all)}$	0.0754
Goof	1.081

Table 3. Atomic coordinates, $U_{iso}(U_{eq})$ parameters and occupancies for wollastonite-2M from the Pl-Px-W-Ep zone

Label	x	y	z	U_{iso} or U_{eq}	Occ.
Si1	-0.69845(7)	0.12375(16)	-0.44502(14)	0.0107(3)	1
Si2	-0.59235(7)	-0.15867(15)	-0.23179(15)	0.0101(3)	1
Si3	-0.59227(7)	0.40752(15)	-0.23147(15)	0.0105(3)	1
Ca1	-0.59925(6)	-0.12739(15)	-0.74079(11)	0.0117(2)	1
Ca2	-0.60095(5)	0.37808(15)	-0.73757(11)	0.0119(2)	1
Ca3	-0.74879(5)	-0.37530(17)	-0.02460(11)	0.0109(2)	1
O1	-0.6527(2)	-0.1142(5)	-0.0375(4)	0.0143(6)	1
O2	-0.6510(2)	0.3645(5)	-0.0365(4)	0.0146(6)	1
O3	-0.4912(2)	-0.1210(5)	-0.2326(4)	0.0150(6)	1
O4	-0.7856(2)	0.1246(5)	-0.3011(4)	0.0143(6)	1
O5	-0.7008(2)	0.1259(5)	-0.6727(4)	0.0123(6)	1
O6	-0.4903(2)	0.3720(5)	-0.2350(4)	0.0162(6)	1
O7	-0.6355(2)	0.3033(4)	-0.4073(4)	0.0147(6)	1
O8	-0.63592(19)	-0.0552(4)	-0.4087(4)	0.0143(6)	1
O9	-0.6082(2)	-0.3755(4)	-0.2759(4)	0.0202(7)	1

Table 4. Anisotropic displacement parameters for wollastonite-2M (sample from the Pl-Px-W-Ep zone)

Label	U11	U22	U33	U23	U13	U12
Si1	0.0093(6)	0.0122(5)	0.0114(6)	0.0000(4)	-0.0044(4)	0.0004(5)
Si2	0.0062(6)	0.0139(7)	0.0105(6)	0.0002(4)	-0.0021(4)	0.0002(4)
Si3	0.0061(6)	0.0140(7)	0.0117(6)	-0.0002(4)	-0.0024(4)	-0.0004(4)
Ca1	0.0147(4)	0.0133(4)	0.0074(4)	-0.0015(5)	0.0045(3)	-0.0020(5)
Ca2	0.0104(5)	0.0131(4)	0.0125(4)	0.0025(3)	-0.0032(3)	-0.0028(3)
Ca3	0.0070(5)	0.0115(4)	0.0148(4)	0.0006(3)	-0.0048(3)	-0.0002(3)
O1	0.0099(16)	0.0200(15)	0.0127(14)	0.0023(15)	0.0001(11)	0.0044(15)
O2	0.0119(16)	0.0190(14)	0.0126(14)	0.0009(15)	0.0003(11)	-0.0031(16)
O3	0.0072(15)	0.0165(13)	0.0221(16)	0.0016(17)	-0.0048(12)	-0.0003(17)
O4	0.0113(16)	0.0176(13)	0.0140(15)	-0.0004(13)	-0.0013(12)	0.0004(14)
O5	0.0097(15)	0.0139(12)	0.0138(14)	0.0004(13)	-0.0038(11)	-0.0035(14)
O6	0.0061(15)	0.0179(14)	0.0246(16)	0.0007(17)	-0.0015(12)	0.0008(18)
O7	0.0137(17)	0.0135(13)	0.0174(16)	-0.0012(11)	-0.0032(12)	-0.0032(12)
O8	0.0131(16)	0.0152(13)	0.0151(15)	0.0033(11)	-0.0053(12)	0.0043(12)
O9	0.0216(17)	0.0116(13)	0.0294(17)	-0.0009(13)	-0.0134(13)	0.0002(13)

700–1000 °C using *in situ* synchrotron X-ray powder diffraction data for determination of the kinetics of phase transformation. The authors observed the following reaction sequence of crystallisation of the CaO–SiO₂ parent glass: 1T-wollastonite forms first and progressively transforms in an intermediate 1Td-wollastonite metastable disordered form. Both phases in turn transform into 2M-wollastonite polytype at 950–1000 °C.

The presence only of a higher temperature polytype (wollastonite-2M) in the studied skarn samples could be interpreted as a result of a longer duration of thermal influence at the contact of carbonate xenoliths with monzonite magma by infiltration of hot fluids that were derived during the crystallisation of the pluton. The crystallisation temperature of the second monzonite phase of the Zvezdel pluton according to the two-feldspar geothermometer

Table 5. Si–O bond lengths [Å], Ca–O bond lengths [Å], and Si–O–Si angles [°] for polyhedra of wollastonite-2M (sample from the Pl-Px-W-Ep zone)

Si–O bond	Distance [Å]	Ca – O bond	Distance [Å]
Si1 – O4	1.604(3)	Ca1 – O6	2.251(3)
Si1 – O5	1.608(3)	Ca1 – O3	2.283(3)
Si1 – O8	1.656(3)	Ca1 – O1	2.319(3)
Si1 – O7	1.667(3)	Ca1 – O8	2.414(3)
mean	1.634(3)	Ca1 – O5	2.436(3)
Si2 – O3	1.580(3)	Ca1 – O4	2.530(3)
Si2 – O1	1.613(3)	Ca2 – O6	2.301(3)
Si2 – O9	1.634(3)	Ca2 – O2	2.311(3)
Si2 – O8	1.653(3)	Ca2 – O3	2.347(3)
mean	1.620(3)	Ca2 – O7	2.404(3)
Si3 – O6	1.586(3)	Ca2 – O5	2.415(3)
Si3 – O2	1.605(3)	Ca2 – O4	2.501(3)
Si3 – O9	1.637(3)	Ca3 – O1	2.325(3)
Si3 – O7	1.644(3)	Ca3 – O5	2.339(2)
mean	1.618(3)	Ca3 – O2	2.345(3)
Si–O–Si angle	Angle [°]	Ca3 – O4	2.406(3)
Si3–O7–Si1	140.03(17)	Ca3 – O1	2.408(3)
Si2–O8–Si1	139.39(18)	Ca3 – O2	2.418(3)
Si2–O9–Si3	150.81(18)	Ca3 – O9	2.662(3)

is estimated at about 675 °C [15]. The occurrence of wollastonite+plagioclase assemblages in the skarn zones indicates that the temperature was in excess of 600 °C [16] during the formation of early anhydrous minerals in the skarns. This temperature supplies the energy needed for the shift of the tetrahedral chains by 1T→2M polytype transition in wollastonite. This is possible through breaking Ca–O bonds bridging the chains with the 2M-polytype remaining stable during cooling of the system in the late stages of the skarn processes. Swami and Dubrovinsky [17] observed indications of Ca–O bonds breaking by 1T→2M polytype transition in Raman spectra. The estimated lower temperature of formation of wollastonite-2M polytype compared to the experimentally obtained results [14] could be interpreted as due to other factors like inhomogeneity of the rock, the chemical composition of the protolith and the fluid.

These polytype transformations have been explained as a result of deformation under conditions of shear stress or strain by some authors [18–21]. Guggenheim [19] stated that a combination of several processes may be necessary to produce the periodic faulting that yield polytypes with a repeat unit along [100] greater than one. During the field observation we could not find evidence for shear stress at

the time of formation of that polytype, but we cannot exclude the possibility that the shear displacement leading to the formation of wollastonite-2M could be a result of an external stress. The latter explains the stretching of the crystals due to difference in the thermal expansion coefficient of wollastonite with respect to the surrounding matrix.

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ПАРАВОЛАСТОНИТ (ПОЛИТИП ВОЛАСТОНИТ-2М) ОТ СКАРНИТЕ В ЗВЕЗДЕЛСКИЯ ПЛУТОН, ИЗТОЧНИ РОДОПИ – МОНОКРИСТАЛНО РЕНТГЕНОСТРУКТУРНО ИЗСЛЕДВАНЕ

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(Резюме)

Структурните разлики между политипите на триклинния воластонит и моноклинния параволастонит се състоят в различния начин на подредба на пироксеноидния тип вериги по посока на *a*-оста. Тези форми са трудно различими, освен с монокристална рентгенова дифрактометрия, тъй като се различават само по рефлексите с *k*-нечетно число, които обикновено са много слаби.

С монокристална рентгенова дифрактометрия е изследвана политипията на воластонит от три различни скарни зони от Звезделския плутон. Химичният състав на изследваните монокристали се доближава до идеалния – CaSiO₃, като данните от рентгеноспектралния микроанализ показват незначително присъствие на FeO (0,п тегл.%). Структурните уточнения показват моноклинна симетрия на анализирания воластонитови кристали (пространствена група *P2₁/a* и параметри на елементарната клетка *a* = 15.413(17) Å, *b* = 7.336(5) Å, *c* = 7.070(3) Å, β = 95.24(5)° за воластонита от зоната плагиоклаз-пироксен-воластонит+гранат; *a* = 15.409(7) Å, *b* = 7.320(3) Å, *c* = 7.063(2) Å, β = 95.36(3)° – от зоната плагиоклаз-пироксен-воластонит, и *a* = 15.3770(11) Å, *b* = 7.2990(4) Å, *c* = 7.0491(5) Å, β = 95.340(6)° – от зоната плагиоклаз-пироксен-воластонит+епидот). При рафинацията са достигнати удовлетворителни стойности на *R*₁ = 0.0521 и *R*_(all) = 0.0754. Връзките Si–O варират между 1.580(3) и 1.667(3) Å (средно 1.624 Å), дължината на връзките Ca–O – между 2.251(3) и 2.662(3) Å (средно 2.390 Å), а ъглите между Si–O–Si са 140.03(17), 139.39(18) и 150.81(18)° (средно 143.31°).

По експериментални данни моноклинната модификация воластонит-2М се определя като по-високотемпературния политип по отношение на триклинния. Присъствието само на моноклинния политип във всички скарни зони (независимо от тяхната отдалеченост от монзонита) би могло да се обясни с по-продължителното времетраене на термичното влияние на монзонитовата магма на контакта с карбонатните ксенолити. Възможно е образуването му да е резултат и от външни напрежения, възникващи при растежа на кристалите, поради разлики в термичния коефициент на разширение на воластонита по отношение на заобикалящата го матрица по време на прогресивния етап на метасоматичния процес.