7T wollastonite from Fuka, Okayama Prefecture

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ABSTRACT

A 7T wollastonite was found at Fuka, Okayama Prefecture. Based on film intensity data, its stacking sequence has been found as (TTGTGTG). Here, T represents a (100) slab of wollastonite which is in continuous position with respect to the preceding one, and G a slab displaced by $b/2$. The structure may be regarded as a mixed-layer structure composed of three 2M and one 1T. The structure gave $R=0.13$ for 65 $hk0$ reflexions observed. The lattice constants are $a=54.3\pm0.3$ Å, $b=7.30\pm0.03$ Å, $c=7.08\pm0.03$ Å, $\alpha=90.0\pm0.2^\circ$, $\beta=95.5\pm0.2^\circ$, and $\gamma=92.1\pm0.2^\circ$.

Introduction

Ito (1950) studied the unusual diffraction symmetry characteristic of wollastonite and showed that it was originated in the existence of local mirror planes (Ito *et al.*, 1969) in the structure perpendicular to the b -axis. The result lead to a view that the structural relation-

ship between wollastonite and parawollastonite may be expressed in terms of a gliding by $b/4$ of the hypothetical protowollastonite cells, or (100) slabs of the structure, each having a space group $P2_1/m$. Structural studies of wollastonite (Buerger and Prewitt, 1961) and parawollastonite (Trojer, 1968) have confirmed his view. These two forms of CaSiO_3 are the two basic polytypes for this compound which have so far been established by X-rays; triclinic wollastonite and monoclinic parawollastonite are respectively denoted as 1T and 2M. Though Wenk (1969) suggested the existence of 4T, his result is ambiguous. This is because a composite crystal consisting of 2M, 1T and a twinned equivalent of the latter exhibits diffraction patterns which simulate those of 4T.

Beside the regular stackings of slabs, stacking disorder in wollastonite occurs frequently, giving diffuse streaks along k odd reciprocal rows. Jeffery (1953) explained the disorder qualitatively, and Jefferson and Bown (1973) on a quantitative basis. The disorder in stacking were further discussed by Ueda (1966), Wenk (1969), Akai (1975) and Müller and Wenk (1975). The types of stacking which involve disorder are denoted 1Td or 2Md depending upon whether the basic structures are of 1T or 2M type. When k odd rows are completely diffused out, the crystal is denoted as d-wollastonite.

On the other hand, Takéuchi (1971) discussed in terms of a symbolism a systematic derivation of possible polytypes of wollastonite. Though in view of the occurrence of the limited polytypes of wollastonite, this kind of work was thought to be of purely theoretical interest, our extensive studies in gehlenite-spurrite skarns at Fuka and Kushiro districts have now brought out the existence of various new polytypes. Among these, we report in the present paper the results of our study on the stacking sequence of a 7T polytype.

Material

Only one specimen of 7T wollastonite has been found to date; it is in fact an aggregate of 7T and 2M. The two polytypes have the directions of the *b*-axes and (100) planes in common. The specimen is 0.4 millimeters long along *b* and 0.2×0.2 millimeters in cross section. It was found at Fuka, the Town of Bitchu, Okayama Prefecture, Japan.

The main prograde skarn minerals from Fuka are spurrite and gehlenite, the former being partly altered by retrograde actions to tilleyite, wollastonite, xonotlite, foshagite and others. Wollastonite with calcite is found as vein-like aggregates (several millimeters to several centimeters in widths) in spurrite. Wollastonite occurs also with grossular as a retrograde mineral of gehlenite.

The wollastonite from Fuka is mainly of 2M polytype (Fig. 1-2), frequently of 2Md, rarely of 1T (Fig. 1-1), and very rarely of other

Fig. 1. The *h*10 reciprocal rows of various types of wollastonite crystals from Fuka (1, 2, 3, 6 and 7) and from Kushiro (1, 2, 3, 4 and 5), showing relative positions and intensities of the reciprocal points. ● Very strong, ● Strong, ● Medium, • Weak.

types. As rare polytypes, we have found, in addition to 7T (Fig. 1-7), some unidentified polytypes (Fig. 1-6). The specimen containing 7T was found among wollastonite crystals in a spurrite mass.

At Kushiro, the Town of Tojo, Hiroshima Prefecture, wollastonite is found in similar skarns as at Fuka. It is merely a minor component of skarns, but it is a little more abundant than at Fuka, and sometimes crystals with dimensions up to several ten centimeters are found. The wollastonite from Kushiro also is mainly of 2M polytype. It rarely coexists with 1T and its twinned equivalent (Fig. 1-4). Specimens of 3T mixed with 2M (Fig. 1-5) or with 1T are rarely found. 7T wollastonite has not been found at Kushiro.

Some of the minerals from the two localities were described in the following papers: Henmi *et al.*, 1971; Kusachi *et al.*, 1971; Kusachi, 1975; Henmi *et al.*, 1976; Henmi *et al.*, 1977 and others.

Experimental

Zero- and first-level Weissenberg photographs about b , and those of precession photographs about c were recorded using copper radiation. These photographs show that the crystal is not of a single structure type but a composite of 2M and a new polytype. A closer examination into the zero-level precession photograph about c , revealed that the reflexions of the new polytype occur in k odd rows with a regular interval which corresponds to $1/7$ of the a^* periodicity of 1T. It was then readily decided that the polytype was triclinic and fell into the category of 7T polytypes (Fig. 2). The cell dimensions obtained from the photographs are given in Table 1; they agree well with theoretical values which were later calculated from the stacking sequences determined (*vide infra*).

The intensities of reflexions with k =odd were visually estimated in the precession photographs showing the $hk0$ reciprocal plane. To do this, a standard scale was prepared based on four sets of photo-

Fig. 2. (a) Precession photograph, taken about c , of the composite crystal consisting of the 7T and 2M structures. (b) The corresponding reciprocal diagram; reflexions from 7T and 2M are respectively indicated by dots and crosses.

Table 1. Cell dimensions of 7T polytypes.

	6T 1G	5T 2G	4T 3G	
			observed	calculated
a	54.85 Å	54.36 Å	54.3 ± 0.3 Å	54.11 Å
b	7.32 Å	7.32 Å	7.30 ± 0.03 Å	7.32 Å
c	7.07 Å	7.07 Å	7.08 ± 0.03 Å	7.07 Å
α	90.03°	90.03°	90.0 ± 0.2°	90.03°
β	95.44°	95.49°	95.5 ± 0.2°	95.52°
γ	99.68°	95.84°	92.1 ± 0.2°	91.95°

graphs of different exposure times. After correcting Lorentz and polarization factors, the intensities were reduced to structure factors.

The volume ratio of the domains of 7T and 2M was calculated as follows; the ratio was found to be 3:2 in a very close approximation.

Domain of 7T : Domain of 2M

$$= \sum_{h=0}^{28} |F_o(h10)_{7T}| : \sum_{h=0}^8 |F_o(h10)_{2M}|$$

$$= 61 : 39$$

$$= 3 : 2$$

Determination of the stacking sequence

As mentioned already, the polytypism of wollastonite can be discussed in terms of stacking of the (100) slabs, each one unit cell thick, of the wollastonite structure. Let a cell of wollastonite be denoted T when it is in continuous position with respect to the preceding one, and G when it is displaced by $b/2$. Then the stacking sequence of wollastonite (the 1T polytype) may be expressed by T, T,

Fig. 3. Stacking sequences of some polytypes of wollastonite. Thick lines show the unit cells. See the text about the symbols T and G.

T, or (T), and that of parawollastonite (the 2M polytype) by T, G, T, G, or (TG) (Fig. 3). Similarly, the possible stacking sequences for 3T are given by (TTG) and (TGG) which may be rewritten as (2T 1G) and (1T 2G). As TTG and TGG are enantiomorphic with each other, we can consider that the stacking sequence of TTG is identical with that of TGG. For the study of possible stacking sequences of the general form ($nT\ mG$), therefore, it is adequate to consider only one of the cases in which $n \geq m$ and $n \leq m$.

Based on the above consideration, we can readily show that there

Fig. 4. Eight kinds of possible stacking sequences for the 7T polytypes. The unit cells are shown by thick lines.

are eight and only eight possible stacking sequences for 7T polytypes (Fig. 4). As shown in Table 2, these stacking sequences can be classified into three categories, (6T 1G), (5T 2G), and (4T 3G). The stacking sequences which belong to the same category have a common cell type regardless the difference in order of T and G in the repeat unit. Thus these pairs of symbols in parentheses may each be regarded as a representation of a specific cell type. The metrical differences and relations of these cell types are compared in Table 1 and Fig. 5. For these coordinate systems, the plane indices are related to each

Table 2. Kinds of the 7T wollastonite and their notations.

Symbol	cell type	present notation	Takéuchi's notation (1971)
7T ₁	6T 1G	TTTTTTG	[0 S 2S 3S 4S 5S 4S] (mod 5S)
7T ₂	5T 2G	TTTTTG	[0 S 2S 3S 4S 3S 2S] (mod 3S)
7T ₃	"	TTTTGTG	[0 S 2S 3S 2S 3S 2S] "
7T ₄	"	TTTGTTG	[0 S 2S S 2S 3S 2S] "
7T ₅	4T 3G	TTTTGGG	[0 S 2S 3S 2S S 0] (mod S)
7T ₆	"	TTTGTTG	[0 S 2S S 2S S 0] "
7T ₇	"	TTGTGTG	[0 S 0 S 2S S 0] "
7T ₈	"	TTGTGTG	[0 S 0 S 0 S 0]* "

* The difference from the set of symbols given in Fig. 7(c) is due to the difference in choice of origin.

Fig. 5. Relationships of the three cell types of 7T. The cells were shown by dot-dash lines for (6T 1G), solid lines for (4T 3G), and dashed lines for (5T 2G).

* Note that the cell of the (5T 2G) type indicated is in fact its enantiomorphic equivalent (2T 5G).

other in the following way.

$$\langle hkl \rangle_{(4T\ 3G)} = \langle h-k, k, l \rangle_{(6T\ 1G)} = \langle h-k, -k, l \rangle_{(6T\ 2G)}$$

In order to determine the kind of the polytype of the specimen, the observed structure factors (F_o) should be compared with the calculated structure factors (F_c) for each of the eight possible polytypes. The structure factors were calculated with the program UNICS (Sakurai, 1971) partly revised for the calculation of polytypes by Kawahara, using the atomic parameters of 1T wollastonite (Buerger and Prewitt, 1961). In order to ascertain the method of the calculation,

Fig. 6. Comparison of $|F_o|$ with $|F_c|$ for every kind of 7T wollastonite.

Table 3. Observed and calculated structure factors of the 7T₈ wollastonite.

<i>hkl</i>	<i>F</i> _o	<i>F</i> _c	<i>hkl</i>	<i>F</i> _o	<i>F</i> _c	<i>hkl</i>	<i>F</i> _o	<i>F</i> _c	<i>hkl</i>	<i>F</i> _o	<i>F</i> _c
0 $\bar{3}$ 0	0	0.0	3 $\bar{1}$ 0	0	-0.2	0 1 0	0	0.1	33 1 0	0	0.5
1 $\bar{3}$ 0	0	-0.0	4 $\bar{1}$ 0	0	-0.5	1 1 0	0	0.1			
2 $\bar{3}$ 0	0	-0.0	5 $\bar{1}$ 0	0	-0.0	2 1 0	0	0.1	0 3 0	0	0.0
3 $\bar{3}$ 0	0	-0.1	6 $\bar{1}$ 0	0	0.1	3 1 0	0	0.5	1 3 0	0	0.0
4 $\bar{3}$ 0	0	-0.2	7 $\bar{1}$ 0	2	1.2	4 1 0	0	0.1	2 3 0	0	0.1
5 $\bar{3}$ 0	0	-0.1	8 $\bar{1}$ 0	1	0.8	5 1 0	0	-0.0	3 3 0	0	0.2
6 $\bar{3}$ 0	0	0.0	9 $\bar{1}$ 0	1	0.7	6 1 0	0	-0.3	4 3 0	0	0.0
7 $\bar{3}$ 0	0	0.1	10 $\bar{1}$ 0	1	0.6	7 1 0	2	-1.6	5 3 0	0	-0.0
8 $\bar{3}$ 0	0	0.6	11 $\bar{1}$ 0	6	5.8	8 1 0	1	-0.7	6 3 0	0	-0.4
9 $\bar{3}$ 0	0	0.2	12 $\bar{1}$ 0	2	1.8	9 1 0	1	-0.9	7 3 0	0	-0.3
10 $\bar{3}$ 0	0	0.3	13 $\bar{1}$ 0	2	2.1	10 1 0	5	-5.1	8 3 0	0	-0.2
11 $\bar{3}$ 0	1	1.3	14 $\bar{1}$ 0	10	9.4	11 1 0	2	-2.3	9 3 0	0	-0.4
12 $\bar{3}$ 0	0	0.5	15 $\bar{1}$ 0	4	3.6	12 1 0	3	-1.7	10 3 0	1	-1.4
13 $\bar{3}$ 0	0	0.3	16 $\bar{1}$ 0	3	2.3	13 1 0	4	-3.2	11 3 0	0	-0.3
14 $\bar{3}$ 0	0	0.4	17 $\bar{1}$ 0	4	3.6	14 1 0	9	-9.8	12 3 0	0	-0.3
15 $\bar{3}$ 0	0	0.6	18 $\bar{1}$ 0	11	9.1	15 1 0	3	-2.6	13 3 0	0	-0.9
16 $\bar{3}$ 0	0	-0.0	19 $\bar{1}$ 0	2	1.9	16 1 0	3	-2.5	14 3 0	0	-0.1
17 $\bar{3}$ 0	0	-0.3	20 $\bar{1}$ 0	1	1.5	17 1 0	10	-9.6	15 3 0	0	0.1
18 $\bar{3}$ 0	2	-2.1	21 $\bar{1}$ 0	5	4.3	18 1 0	4	-3.0	16 3 0	0	0.6
19 $\bar{3}$ 0	1	-1.2	22 $\bar{1}$ 0	0	1.0	19 1 0	2	-1.5	17 3 0	3	2.6
20 $\bar{3}$ 0	1	-1.0	23 $\bar{1}$ 0	0	0.3	20 1 0	3	-1.8	18 3 0	1	1.0
21 $\bar{3}$ 0	2	-2.1	24 $\bar{1}$ 0	0	0.1	21 1 0	5	-3.5	19 3 0	1	1.3
22 $\bar{3}$ 0	8	-7.6	25 $\bar{1}$ 0	0	-0.7	22 1 0	0	-0.5	20 3 0	7	6.9
23 $\bar{3}$ 0	2	-2.2	26 $\bar{1}$ 0	0	-0.4	23 1 0	0	-0.2	21 3 0	3	2.9
24 $\bar{3}$ 0	2	-2.4	27 $\bar{1}$ 0	0	-0.7	24 1 0	0	0.2	22 3 0	3	2.1
25 $\bar{3}$ 0	11	-10.1	28 $\bar{1}$ 0	4	-3.7	25 1 0	0	0.4	23 3 0	4	3.6
26 $\bar{3}$ 0	4	-3.7	29 $\bar{1}$ 0	1	-1.6	26 1 0	0	0.5	24 3 0	11	10.3
27 $\bar{3}$ 0	2	-2.2	30 $\bar{1}$ 0	1	-1.1	27 1 0	1	1.2	25 3 0	3	2.5
28 $\bar{3}$ 0	2	-3.0	31 $\bar{1}$ 0	2	-1.6	28 1 0	4	4.1	26 3 0	3	2.2
			32 $\bar{1}$ 0	4	-3.9	29 1 0	1	1.2	27 3 0	6	7.7
0 $\bar{1}$ 0	0	0.1	33 $\bar{1}$ 0	0	-0.7	30 1 0	1	1.2			
1 $\bar{1}$ 0	0	-0.1	34 $\bar{1}$ 0	0	-0.4	31 1 0	4	4.3			
2 $\bar{1}$ 0	0	-0.1				32 1 0	1	1.2			

the values of F_c of 2M polytype calculated by the program were compared with the results of F_c determined by Trojer (1968). The resultant value of $\sum[|F_{c(\text{present})}| - |F_{c(\text{Trojer})}|] / \sum|F_{c(\text{present})}|$ was 0.023. This result will secure the reliability of the present method for the determination of the wollastonite polytypes. The calculations of structure factors of 62 reflexions of the $h10$ and $h30$ types yielded R values of 0.98, 0.72, 0.60, 0.90, 0.97, 0.60, 0.55 and 0.22 respectively for $7T_1$, $7T_2$, $7T_3$, $7T_4$, $7T_5$, $7T_6$, $7T_7$ and $7T_8$. A part of the results are shown in Fig. 6. Thus the polytype of $7T_8$ (TTGTGTG) was uniquely determined as a possible polytype, giving the value of R 0.21 for 126 $F(hk0)$'s, and 0.13 omitting 61 non-observed reflexions. The observed and the calculated structure factors are listed in Table 3. The $7T_8$ polytype (Fig. 7a) can be considered also as the composite structure of three 2M slabs and one 1T slab (Fig. 7b). The stacking scheme according to the Takéuchi's notation is also shown in Fig. 7c.

Based on the stacking sequence, the cell dimensions of the new

Fig. 7. Three kinds of notations for the determined polytype: (a) the present scheme, (b) the mixed-layer scheme and (c) the Takéuchi's scheme (1971).

polytype were calculated (Table 1). As mentioned earlier, they agree well with the observed values.

Conclusion

A specimen of wollastonite from Fuka was ascertained as a mixture of 2M and 7T polytypes. The stacking sequence has been determined to be $7T_8$ (TTGTGTG), according to the newly proposed notation. The structure is characterized by a regular alternation, along the a -axis, of triple 2M cell and one 1T cell.

More detailed descriptions and discussions on the polytypes of wollastonite, including 3T from Kushiro and some other polytype from Fuka, will be made in the near future.

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