

Refinement of the crystal structure of wollastonite-2M (parawollastonite)

K.-F. Hesse

Mineralogisches Institut, Universität Kiel, D-2300 Kiel, Federal Republic of Germany

Received: February 29, 1984

Crystal structure / Wollastonite-2M / $\text{Ca}_3[\text{Si}_3\text{O}_9]$

Abstract. The structure of wollastonite-2M from Death Valley, California, USA, $\text{Ca}_3[\text{Si}_3\text{O}_9]$, is monoclinic with space group $P2_1/a$, $a = 15.409(3)$, $b = 7.322(1)$, $c = 7.063(1)\text{Å}$, $\beta = 95.30(2)^\circ$, $Z = 4$ and $D_x = 2.92\text{g cm}^{-3}$, and was refined to $R(\text{unweighted}) = 0.038$ and $R(\text{weighted}) = 0.031$ using 3886 non-equivalent reflections. Wollastonite-2M contains dreier single chains. Si–O distances vary between 1.580(2) and 1.664(2) Å (mean 1.627 Å), Ca–O distances between 2.224(2) and 2.640(6) Å (mean 2.395 Å).

Introduction

CaSiO_3 exists in two structurally quite different forms. The phase stable above ca. 1150 °C is a cyclosilicate called pseudowollastonite or α -wollastonite, which contains rings of three corner-shared $[\text{SiO}_4]$ tetrahedra. Depending on the stacking arrangement of the $[\text{Si}_3\text{O}_9]$ rings and cations a number of polytypes of pseudowollastonite have been described (Yamanaka and Mori, 1981).

Below ca. 1150 °C CaSiO_3 contains dreier single chains, i.e. chains with three $[\text{SiO}_4]$ tetrahedra in the repeat unit. A series of polytypes have been reported with different packing arrangements of the single chains (Wenk, 1969; Henmi et al., 1983). These polytypes are called β -wollastonite or wollastonites and are distinguished by the symbols nT and nM , where T and M stands for triclinic and monoclinic symmetry of the polytype and n indicates the number of subcells with $d_{\text{subcell}}(100) \simeq 7.7\text{ Å}$ in the unit cell of the polytype. The polytype 2M is often called parawollastonite. In both series of polytypes α - as well as β -wollastonite exist disordered phases. First X-ray studies of pseudowollastonite have been carried out by Jeffery and Heller (1953) and the structure has been determined by Yamanaka and Mori (1981).

Table 1. Positional and thermal parameters with standard deviations. The anisotropic temperature factors have the form $\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$. The standard deviations in parentheses refer to the last digit

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca(1)	0.2483(0)	0.3754(2)	0.9726(0)	0.0068(1)	0.0069(1)	0.0071(1)	-0.0002(4)	0.0010(1)	-0.0001(2)
Ca(2)	0.4006(0)	0.6236(6)	0.7389(1)	0.0078(2)	0.0075(2)	0.0076(1)	-0.0012(4)	0.0013(1)	-0.0010(4)
Ca(3)	0.3986(0)	0.1179(6)	0.7360(1)	0.0086(2)	0.0054(5)	0.0073(1)	0.0007(3)	0.0012(1)	0.0009(3)
Si(1)	0.4076(0)	0.0920(1)	0.2311(1)	0.0058(3)	0.0055(4)	0.0058(2)	-0.0006(2)	0.0003(2)	0.0002(2)
Si(2)	0.4075(0)	0.6585(1)	0.2310(1)	0.0057(3)	0.0065(4)	0.0058(2)	0.0005(2)	-0.0001(2)	0.0000(2)
Si(3)	0.3015(0)	0.3760(1)	0.4436(1)	0.0061(2)	0.0066(2)	0.0046(2)	0.0001(3)	0.0001(1)	0.0003(3)
O(1)	0.2991(1)	0.3722(8)	0.6706(2)	0.0091(5)	0.0101(6)	0.0045(5)	-0.0019(9)	0.0009(4)	0.0021(10)
O(2)	0.2141(1)	0.3737(8)	0.3010(2)	0.0074(5)	0.0114(6)	0.0075(5)	-0.0031(11)	-0.0012(4)	0.0031(10)
O(3)	0.3493(1)	0.1346(16)	0.0354(2)	0.0082(6)	0.0149(21)	0.0065(5)	0.0009(10)	-0.0006(4)	0.0020(11)
O(4)	0.3479(1)	0.6121(15)	0.0361(2)	0.0083(6)	0.0078(23)	0.0065(5)	0.0002(9)	-0.0009(4)	-0.0010(10)
O(5)	0.5096(1)	0.1187(15)	0.2369(2)	0.0059(6)	0.0077(15)	0.0176(7)	0.0019(9)	0.0004(5)	-0.0013(8)
O(6)	0.5088(1)	0.6134(13)	0.2332(3)	0.0063(6)	0.0044(21)	0.0176(7)	0.0016(9)	0.0001(5)	-0.0010(7)
O(7)	0.3641(1)	0.1969(3)	0.4060(3)	0.0107(9)	0.0095(8)	0.0076(7)	-0.0018(6)	0.0015(6)	0.0029(6)
O(8)	0.3640(1)	0.5553(3)	0.4075(3)	0.0124(9)	0.0097(8)	0.0074(7)	0.0021(6)	0.0003(6)	-0.0036(6)
O(9)	0.3908(1)	0.8753(3)	0.2753(2)	0.0158(6)	0.0063(5)	0.0143(6)	-0.0006(8)	0.0031(5)	0.0002(8)

Table 2. Bond lengths (Å) and angles (°) compared with corresponding values from Trojer (1968). The standard deviations in parentheses refer to the last digit

[SiO ₄]tetrahedra Si—O distances	(Trojer)	O—O-distances	O—Si—O angles	(Trojer)
Si(1)—O(3)	1.608(3)	O(3)—O(5)	2.736(2)	12500'
Si(1)—O(5)	1.580(2)	O(3)—O(7)	2.646(3)	10830'
Si(1)—O(7)	1.648(2)	O(3)—O(9)	2.586(9)	10531'
Si(1)—O(9)	1.643(2)	O(5)—O(7)	2.697(3)	10425'
Mean	1.620	O(5)—O(9)	2.587(8)	10606'
		O(7)—O(9)	2.576(3)	10559'
		Mean	2.638	Mean 109.2
Si(2)—O(4)	1.619(3)	O(4)—O(6)	2.730(2)	12407'
Si(2)—O(6)	1.595(3)	O(4)—O(8)	2.645(3)	10834'
Si(2)—O(8)	1.652(2)	O(4)—O(9)	2.608(8)	10408'
Si(2)—O(9)	1.643(2)	O(6)—O(8)	2.680(3)	10411'
Mean	1.627	O(6)—O(9)	2.678(7)	10900'
		O(8)—O(9)	2.570(3)	10535'
		Mean	2.652	Mean 109.3
Si(3)—O(1)	1.606(2)	O(1)—O(2)	2.811(2)	12930'
Si(3)—O(2)	1.606(2)	O(1)—O(7)	2.547(4)	9639'
Si(3)—O(7)	1.665(2)	O(1)—O(8)	2.568(4)	9610'
Si(3)—O(8)	1.662(2)	O(2)—O(7)	2.693(4)	11217'
Mean	1.635	O(2)—O(8)	2.711(4)	11213'
		O(7)—O(8)	2.625(3)	10711'
		Mean	2.659	Mean 109.2

Table 2. (Continued)

[CaO ₆]polyhedra Ca—O distances	(Trojer)	(Trojer)	(Trojer)	(Trojer)
Ca(1)—O(1)	2.339(2)	2.214(5)	Ca(2)—O(1)	2.434(6)
Ca(1)—O(2)	2.426(2)	2.356(5)	Ca(2)—O(2)	2.543(8)
Ca(1)—O(3)	2.367(9)	2.392(8)	Ca(2)—O(4)	2.321(2)
Ca(1)—O(3')	2.420(9)	2.445(9)	Ca(2)—O(5)	2.337(10)
Ca(1)—O(4)	2.330(8)	2.396(9)	Ca(2)—O(6)	2.224(9)
Ca(1)—O(4')	2.430(8)	2.407(9)	Ca(2)—O(8)	2.409(2)
Ca(1)—O(9)	2.640(6)	2.895	Mean	2.378
Mean [CaO ₆]	2.385	2.368	2.402	2.402
Mean [CaO ₇]	2.422	2.444	all other >	3.72
all other ≥	3.641		all other ≥	3.253
Si—O—Si angles		(Trojer)		
Si(1)—O(9)—Si(2)	150.2(1)	151.48'		
Si(1)—O(7)—Si(3)	140.2(1)	135.25'		
Si(2)—O(8)—Si(3)	139.3(1)	136.32'		
Mean	143.2			

The structure of wollastonite-1T has been proposed by Dornberger-Schiff et al. (1954) and determined by Mamedov and Belov (1956), refined by Buerger and Prewitt (1961) and Ohashi and Finger (1978), that of wollastonite-2M by Tolliday (1958), and Trojer (1968). The structures of the higher polytypes 3T, 4T, 5T and 7T of wollastonite have been described by Henmi et al. (1983) and Henmi et al. (1978).

The aim of this refinement of wollastonite-2M is to comment on the large differences in Si–O distances and O–Si–O angles of Trojer's structure determination.

Experimental

A specimen of parawollastonite crystals from Death Valley, California, was kindly provided by H.-R. Wenk. A crystal measuring $0.125 \times 0.175 \times 0.275$ mm was used for data collection on an automatic Philips PW 1100 four-circle diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.7107$) and $\omega - 2\theta$ ($\theta_{\max} = 50^\circ$). The intensities of 9122 non-equivalent reflections were measured; 3886 of these had $I > 3\sigma(I)$ and were implied in the subsequent refinement. The standard deviations, $\sigma(I)$, were estimated using the formula of Stout and Jensen (1968). Refined cell dimensions were determined with the program LAT written by Hornstra and Vossers (1973/74). Lorentz, polarization and absorption corrections (Busing et al., 1957) were applied [$\mu(\text{MoK}\alpha) = 24.56 \text{ cm}^{-1}$]. The structure was refined by full-matrix least-squares analysis with the program SHELX-76 (Sheldrick, 1976), starting with the atomic coordinates given by Trojer (1968). The atomic scattering factors were taken from the International Tables for X-ray Crystallography, Vol. IV, 1974, for neutral atoms. Anisotropic refinements of the crystal structure converged at $R(\text{unweighted}) = 0.038$ and $R(\text{weighted}) = 0.031$ $\{R(\text{weighted}) = \Sigma \sqrt{w} [|F_o| - |F_c|] / \Sigma \sqrt{w} |F_o|, w = 1/\sigma^2\}$. Final atomic parameters are given in Table 1, bond lengths and angles in Table 2. A list of observed and calculated structure factors can be obtained from the author.

Results

In Table 2 the bond lengths $d(\text{Si}-\text{O})$ and $d(\text{Ca}-\text{O})$ and the bond angles O–Si–O and Si–O–Si obtained are compared with those reported by Trojer. The ranges $\Delta d = d_{\max} - d_{\min}$ and $\Delta \angle = \angle_{\max} - \angle_{\min}$ obtained (0.084 Å, 0.416 Å and 19.8°) are considerably smaller than the corresponding ranges given by Trojer (0.234 Å, 0.727 Å and 33.3° respectively) and indicate that the $[\text{SiO}_4]$ tetrahedra and $[\text{CaO}_6]$ polyhedra are less distorted than reported.

Acknowledgement. I thank H. H. Jensen for helpful technical assistance. Computations were carried out at the Rechenzentrum der Universität Kiel. I thank H.-R. Wenk for supplying a sample of the Death Valley parawollastonite. A critical review of the manuscript by F. Liebau is appreciated.

References

- Buerger, M. J., Prewitt, C. T.: The crystal structure of wollastonite and pectolite. Proc. Natl. Acad. Sci. **47**, 1884–1888 (1961)
- Busing, W. R., Levi, H. B.: High-speed computation of the absorption correction for single crystal diffraction measurements. Acta Crystallogr. **10**, 180–182 (1957)
- Dornberger-Schiff, K., Liebau, F., Thilo, E.: Über die Kristallstruktur des $(\text{NaAsO}_3)_x$, des Maddrellschen Salzes und des β -Wollastonits. Naturwissenschaften **41**, 551 (1954)
- Henmi, Ch., Kawahara, A., Henmi, K., Kusachi, I., Takeuchi, Y.: The 3T, 4T and 5T polytypes of wollastonite from Kushiro, Hiroshima Prefecture, Japan. Am. Mineral. **68**, 156–163 (1983)
- Henmi, Ch., Kusachi, I., Kawahara, A., Henmi, K.: 7T wollastonite from Fuka, Okayama Prefecture. Mineral J. **9**, Nr. 3, 169–181 (1978)
- Hornstra, J., Vossers, H.: Das Philips Einkristalldiffraktometer. Philips Tech. Rundsch. **33**, Nr. 3, 65–78 (1973/74)
- International tables for X-ray crystallography*, Vol. IV. The Kynoch Press, Birmingham (1974)
- Jeffery, J. W., Heller, L.: Preliminary X-ray investigation of pseudo-wollastonite. Acta Crystallogr. **6**, 807–808 (1953)
- Mamedov, K.H. S., Belov, N. V.: The crystalline structure of wollastonite. Dokl. Acad. Sci. USSR **107**, 463–466 (1956)
- Ohashi, Y., Finger, L. W.: The role of octahedral cations in pyroxenoid crystal chemistry. I. Bustamite, wollastonite, and the pectolite-schizolite-serandite series. Am. Mineral. **63**, 274–288 (1978)
- Sheldrick, G. M.: SHELX-76. Program for crystal structure determination. Univ. of Cambridge, England (1976)
- Stout, G. H., Jensen, L. H.: *X-ray structure determination*. New York: Macmillan (1968), p. 457
- Tolliday, J.: Crystal structure of β -wollastonite. Nature **182**, 1012–1013 (1958)
- Trojer, F. J.: The crystal structure of parawollastonite. Z. Kristallogr. **127**, 291–308 (1968)
- Wenk, H.-R.: Polymorphism of Wollastonite. Contrib. Mineral. Petrol. **22**, 238–247 (1969)
- Yamanaka, B. T., Mori, H.: The Structure and Polytypes of α -CaSiO₃ (Pseudowollastonite). Acta Crystallogr. **37**, 1010–1017 (1981)