Zeitschrift für Kristallographie 154, 189–198 (1981)

The crystal structure of the 11 Å natural tobermorite $Ca_{2.25}[Si_3O_{7.5}(OH)_{1.5}] \cdot 1\,H_2O$

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Received: December 10, 1979; in revised form: March 21, 1980

Abstract. The crystal structure of a natural tobermorite from Zeilberg, Maroldsweisach, Germany (average formula $Ca_{2.25}[Si_3O_{7.5}(OH)_{1.5}]\cdot 1\,H_2O$), is solved using the data obtained from an automatic diffractometer. For the structure determination only the sharp main reflexions are considered. The crystal data of the chosen subcell are: $a' = 5.586(4)$ Å, $b' = 3.696(2)$ Å, $c = 22.779(7)$ Å, S.G. *Imm*2, $V = 470.25$ Å^3, $D_x = 2.39$ g/cm^3, $D_{exp.} = 2.43$ g/cm^3, and $Z = 2$. The disordered superposed structure is refined to a weighted R-value of 0.085. From the average structure the superposed chains are resolved and the tobermorite structure is then developed. One of the possible ordered tobermorite structures is monoclinic, space group $P2_1$, with the unit cell dimensions: $a_m = 6.69$ Å, $b_m = 7.39$ Å, $c_m = 22.779$ Å, and $\gamma = 123.49°$. The tobermorite has infinite $Si_3(O/OH)_9$ chains running parallel b. The calcium atoms are coordinated by seven oxygen atoms.

Introduction

Tobermorite is a rare mineral, but synthetic minerals of the tobermorite group are the main components in cement and lime-silica products and are produced during the binding process.

Powder and single crystals of tobermorite were investigated by Taylor (1953) and McConnell (1954) using X-ray methods. These authors gave the following lattice parameters: $a = 11.3$ Å, $b = 7.3$ Å, and $c = 22.6$ Å. McConnell (1954) reported that a pseudo cell of $a/2$ and $b/2$ can be chosen because all the reflexions, with either h or k odd, are very weak and diffuse. He suggested the space group $C222_1$ for the above mentioned unit cell and for the pseudo cell the following possibilities: *Immm*, *Imm* (?), *I*222, and

$I222_1$. A first structure determination was attempted by Megaw and Kelsey (1956) who presented an incomplete (001) projection. These authors reported also that tobermorite shows a similar disorder phenomenon like wollastonite (Jeffery, 1953) (wollastonite possesses also "Dreierketten"). Belov (1958) suggested the possibility of the existence of double chains in tobermorite like those in xonotlite.

Experimental

Selected single crystals from Zeilberg, Maroldsweisach, Germany (Jakob, 1977) were mounted on Weissenberg and Precession cameras. Photographs of the zones $h01$, $h1l$, $h2l$, $h3l$, $0k1$, $1kl$, $hk0$, $hk1$, and $hk2$ were taken with MoK_α, or CuK_α radiation. Rotation photographs about the b-axis show weak streaks for layers with k odd. Weissenberg photographs of such layers give very weak, broad and diffuse discs shaped reflexions (about 7 mm diameter), and a high background at low Bragg angles. These observations support the presence of a two-dimensional disorder mechanism. Taking the streaks into account (by the odd k-layers) the true lattice constant in the b-direction is 7.3 Å which is characteristic for the period of the "Dreierketten". For the structure determination the weak and diffuse reflexions of the odd layers were neglected and a subcell with the following lattice constants is chosen:

$a' = a/2 = 5.586(4)$ Å, $b' = b/2 = 3.69(2)$ Å,
and $c = 22.779(7)$ Å.

For the subcell the observed systematic absences are: $h + k + l = 2n + 1$, Laue class mmm. The following orthorhombic space groups are considered possible: $I222$, $I2_12_12_1$, $Imm2$, and $Immm$.

Intensities were collected with a Stoe two circle diffractometer using a crystal of the dimensions $0.06 \times 0.1 \times 0.07$ mm mounted on the b-axis. An absorption correction was not applied. Altogether 1380 reflexions were measured and reduced to 513 independent reflexions. The calculations were carried out with the programm L.S. in SHELX.

Structure determination

In order to test the correctness of Megaw's and Kelsey's (1956) proposal, a three-dimensional Patterson map was calculated. At the outset two independent calcium and oxygen atoms could be identified with the help of the expected Ca–O bond length and Ca–O–Ca bond angles. These atomic coordinates are Ca(1) (0, 0, 0), Ca(2) (0, 0, 0.42), O(1) (0.26, 0.5, 0), and O(2) (0.26, 0.5, 0.42). They were used to phase the structure factors in the succeeding Fourier or difference Fourier and least-square calculations. While attempting to locate the maxima caused by $Si_3(O/OH)_9$-chains, in the

Fourier map, almost all the peaks due to $Si_3(O/OH)_9$-chains were found to occur twice, as if two such chains ("Dreierketten") have been superposed, but displaced relative to each other by $b/2$. Atoms which are affected by the statistical displacement by $b/2$ were taken into consideration during calculation by giving them the suitable occupation factors. The last difference Fourier map shows a maximum at (0.24, 0.5, 0.19). By crystal-chemical rules this maximum is considered as a calcium position with a lower occupation factor than for other calcium atoms. In the same way two equivalent positions of one tetrahedron from each chain was found. These tetrahedra containing Si(1) and Si(2) (Table 1) are statistically tilted by a mirror-plane m_a. On the same time they are influenced by the staking disorder of chains (displacement by $b/2$). The symmetry of the Fourier map can be interpreted as *Imm*2 or *Immm* so that the remaining space groups can be neglected. This observation is important because it means that the various subcells scatter quasi-coherently resulting in an average symmetry *mm*2 or *mmm* of a superposed structure. (This is likely due to the statistical stacking of the chains as found by Tolliday (1958) and Gard et al. (1960) in the case of β-wollastonite and foshagite respectively). The final least-squares refinement was undertaken for both space groups *Imm*2 and *Immm*. The final weighted R_w-values $\left(R_w = \Sigma\sqrt{w}\cdot\left||F_o| - |F_c|\right|/\Sigma F_o\cdot\sqrt{w},\ w = \frac{1}{\sigma^2 F_o}\right)$ for *Imm*2 and *Immm* are

Table 1. Atomic positional parameters, isotropic thermal parameters $U = B/8\pi^2$ and the occupancy factors K for the superposed structure in space group *Imm*2

	Position	x	y	z	U [Å^2]	K
Ca(1)	2(a)	0.0	0.0	0.0	0.017(8)	1
Ca(2)	2(a)	0.0	0.0	0.4135(3)	0.017(8)	1
Ca(3)	4(c)	0.244(7)	0.5	0.198(2)	0.06(1)	0.125
Si(1)	4(c)	0.322(5)	0.0	0.141(1)	0.035(4)	0.25
Si(2)	4(c)	0.344(6)	0.0	0.282(2)	0.035(4)	0.25
Si(3)	4(d)	0.5	0.414(4)	0.373(1)	0.015(2)	0.5
Si(4)	4(d)	0.5	0.425(4)	0.057(1)	0.015(2)	0.5
O(1)	8(e)	0.265	0.49(1)	0.019(1)	0.017(2)	0.5
O(2)	8(e)	0.265	0.48(1)	0.411(1)	0.017(2)	0.5
OH/O(3)	4(c)	0.32(1)	0.0	0.211(1)	0.08(1)	0.25
O/OH(4)	4(c)	0.070(5)	0.0	0.113(3)	0.08(1)	0.25
O(5)	2(b)	0.5	0.0	0.077(2)	0.024(5)	0.5
O(6)	2(b)	0.5	0.0	0.348(1)	0.024(5)	0.5
O(7)	4(d)	0.5	0.33(1)	0.311(1)	0.053(5)	0.5
O(8)	4(d)	0.5	0.34(1)	0.119(1)	0.053(5)	0.5
O/OH(9)	4(c)	0.076(5)	0.0	0.307(3)	0.08(1)	0.25
OH/O(10)	4(c)	0.35(1)	0.0	0.213(1)	0.08(1)	0.25
$H_2O(1)$	2(a)	0.0	0.0	0.112(1)	0.04(1)	0.5
$H_2O(2)$	2(a)	0.0	0.0	0.303(1)	0.04(1)	0.5

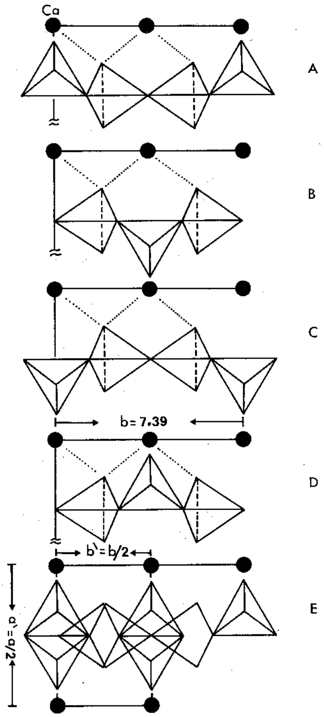

Fig. 1. A–D: The various chain positions relative to Ca atoms at (0, 0, 0). The pointed lines represent the Ca–O bonds. The two alternative chain positions can be seen in A and C or B and D. E: The superposition of one chain with the different possibilities shown in A–D

0.085 and 0.14 respectively. The atom parameters, isotropic thermal parameters, and the occupancy factors for the superposed structure in *Imm*2 are given in Table 1.

From the refined superposed disordered structure, the existence of the "Dreierketten" in tobermorite and the disorder mechanisms the ordered structure may be obtained. The disorder in tobermorite may be described as due to the following three mechanisms:

(1) The statistical displacement of the $Si_3(O/OH)_9$ chains by $b/2$ into two equivalent positions (Fig. 1, A and D or B and C). This type of disorder was also found by Gard and Taylor (1960) in foshagite.

(2) One tetrahedron from each chain is tilted statistically in two alternative positions (Fig. 1, A and C or B and D).

(3) The Ca(3) position is statistically occupied (Hamid, 1979) and is influenced by the tilting direction of the tetrahedra. The $H_2O(1)$ and $H_2O(2)$ are also influenced in the same way.

The statistical displacement of the $Si_3(O/OH)_9$ chains by $b/2$ or b' and the statistical tilting of one tetrahedron from each chain is illustrated in Figure 1 A–D. From the same Figure it can also be seen that the Ca–O bonds (pointed lines) are not affected by the two alternative chain positions. The two different chain positions (stacking disorder) and the two possible tilting directions agree with the site occupation factors obtained from the least-squares calculations (Table 1). The average chemical formula for the disordered crystal is calculated from the occupancy factors-*K* (Table 1) to be $Ca_{4.5}[Si_6O_{15}(OH)_3] \cdot 2\,H_2O$.

Electron diffraction and the structure of one of the possible ordered phases

Selected area electron diffraction of some synthetic thin tobermorite crystals show *hk*0 reflexions without streaks parallel a^*. The lattice constants of such patterns are $a = 2a'$ and $b = 2b'$ and the visual intensity distribution is monoclinic. *h*0*l* reflexions from crystals with electron beam parallel to *a* show the systematic absences 00*l* with $l = 2n + 1$ (Kurczyk and Schwiete, 1960). On the basis of this observation and by resolving the superposition (Fig. 1) of chains and doubling the lattice constants a' and b' to $a = 11.17$ Å and $b = 7.39$ Å *a* C-centred pseudo orthorhombic cell results ($C2_1$). This cell contains four primitive subcells with lower symmetry than the disordered superposed subcell (*Imm*2). In the case of the existence of 2_1 parallel *c* (electron diffraction) and by removing the superposition, a monoclinic ordered cell can be transformed from the pseudo orthorhombic one. The transformation matrix is

$$\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The space group of the ordered monoclinic cell is $P2_1$ and the lattice constants are:

$a_m = 6.69$ Å, $b_m = 7.39$ Å, $c_m = 22.77$ Å, and $\gamma = 123.49°$.

A (001) projection of the monoclinic cell together with the C-centred geometrically orthorhombic cell is shown in Figure 2. The atom coordinate of the monoclinic cell and some interatomic distances are given in Table 2 and Table 3 respectively. A three dimensional view of the tobermorite structure is given in Figure 3. In this view only that part of the geometrically orthorhombic cell is drawn which is limited by $a/2$, *b* and $c/2$.

There are three other symmetry possibilities for the choice of the ordered tobermorite cell. This possibilities depend upon the choice of the tilting direction of the tetrahedra (2_1 or *n* is present), stacking periodicity and Ca distribution and will be discussed elsewhere.

As the above mentioned disorder phenomena in tobermorite are more complex than those in wollastonite (Tolliday, 1958) and foshagite (Gard and Taylor, 1960), they affect the intensity of the reflections considerably. Hence, a high degree of precision cannot be expected. The departure from the *Immm*

Table 2. Atom coordinates in space group $P2_1$ (Ca denoted with $^{+)}$ are statistically distributed)

	x	y	z		x	y	z
Ca(1)	0.75	0.75	0	Ca(4)	0.75	0.25	0.413
Ca(2)	0.75	0.25	0	$^{+)}$Ca(5)	0.506	0.38	0.198
Ca(3)	0.75	0.75	0.413	$^{+)}$Ca(6)	0.506	0.88	0.198
Si(1)	0.25	0.287	0.056	Si(4)	0.25	0.207	0.373
Si(2)	0.25	0.707	0.056	Si(5)	0.084	0.417	0.282
Si(3)	0.068	0.909	0.141	Si(6)	0.25	0.787	0.373
O(1)	0.25	0.17	0.12	O(10)	0.25	0.0	0.348
O(2)	0.015	0.137	0.0189	O(11)	0.015	0.122	0.4108
O(3)	0.484	0.372	0.0189	O(12)	0.484	0.357	0.4108
O(4)	0.25	0.50	0.077	O(13)	0.25	0.335	0.31
O(5)	0.015	0.622	0.0189	OH/O(14)	0.1	0.425	0.213
O(6)	0.484	0.856	0.0189	O(15)	0.25	0.645	0.31
O(7)	0.25	0.83	0.12	O(16)	0.015	0.638	0.4108
OH/O(8)	0.068	0.909	0.211	O(17)	0.484	0.872	0.4108
O/OH(9)	−0.18	0.785	0.113	O/OH(18)	−0.175	0.288	0.306
$H_2O(1)$	0.75	0.75	0.303	$H_2O(2)$	0.75	0.25	0.11

symmetry is small; on the other hand *Imm*2 gave the best *R*-value. Application of physical methods (piezoelectric test) to detect the presence of the inversion centre for tobermorite is difficult because of the lack of single crystals with suitable size without imperfections.

The tobermorite structure (Figs. 2 and 3) has infinite $Si_3(O/OH)_9$ chains running parallel to *b* which are linked together by calcium atoms. The mean Si—O distance is 1.62 Å and the average value of the O—O distances in the $Si_3(O/OH)_9$ chains is 2.64 Å (Table 3). The environments of Ca(1) and Ca(2) are fairly similar. Both of them are coordinated with seven oxygens. In the case of Ca(1) two oxygens are in the range of 2.35—2.38 Å [O(6) and O(3)], four oxygen atoms in the range 2.42—2.46 Å [O(5), O(2), O(11′), and O(12′)]. The seventh oxygen OH(9) has a distance of 2.6 Å. Ca(3) and Ca(4) are also coordinated by seven oxygens but with a slightly different arrangement as Ca(1) and Ca(2) (Table 3). In general Ca(1), Ca(2), Ca(3), and Ca(4) are coordinated with four co-planar oxygen atoms, two oxygens above or below forming a dome and the seventh oxygen below or above the co-planar oxygen group forming a tetragonal pyramid (Figs. 2 and 3). The octahedral coordination of Ca(5) and Ca(6) (if they are present) is similar and is very distorted (weak Ca—O interaction).

The tobermorite formula can be written for various Ca/Si ratio as follows:

$Ca_4[Si_6O_{14}(OH)_4]\cdot 2\,H_2O$, Ca/Si = 0.667;

$Ca_5[Si_6O_{16}(OH)_2]\cdot 2\,H_2O$, Ca/Si = 0.83, [Ca(5) or Ca(6) is present;

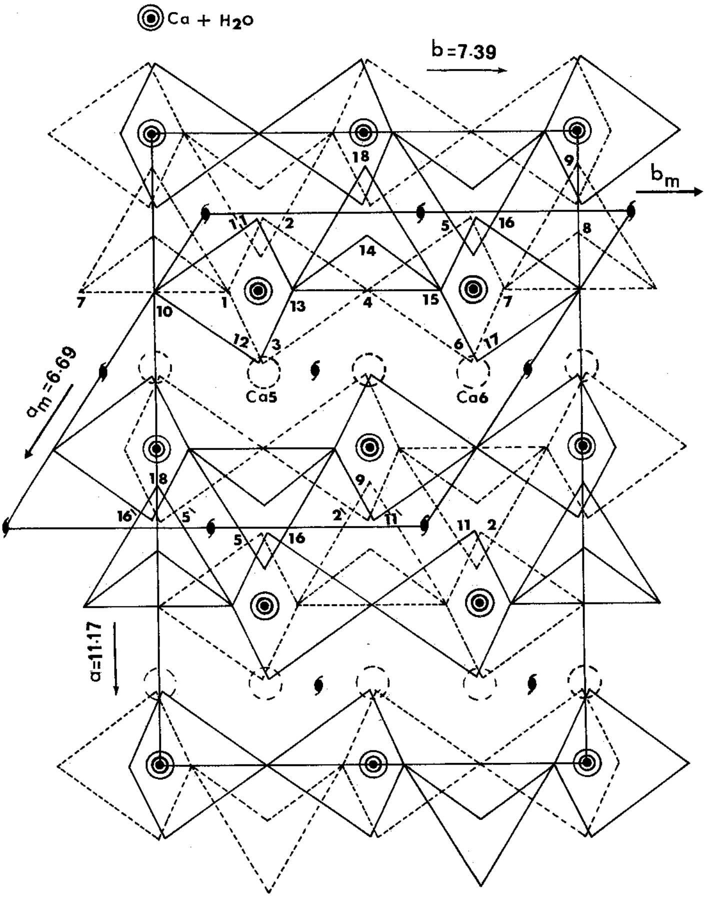

Fig. 2. (001) projection of the pseudo orthorhombic cell ($C2_1$) together with the monoclinic cell. Only the oxygen atoms are numbered. For other atoms see Table 2. The dotted Ca atoms are statistically distributed. The atom symbols are identical with those in Tables 2 and 3

$Ca_6[Si_6O_{18}] \cdot 2\,H_2O$, $Ca/Si = 1.0$, [Ca(5) and Ca(6) are present only in synthetic crystals].

The average formula obtained from the subcell is:

$Ca_{4.5}[Si_6O_{15}(OH)_3] \cdot 2\,H_2O$.

This means that the fifth Ca (in the case of natural tobermorite) is statistically distributed among the cells.

Like other calcium silicate hydrates tobermorite has many stacking modifications with multiple values of *a* and *c*. These modifications will also be discussed elsewhere.

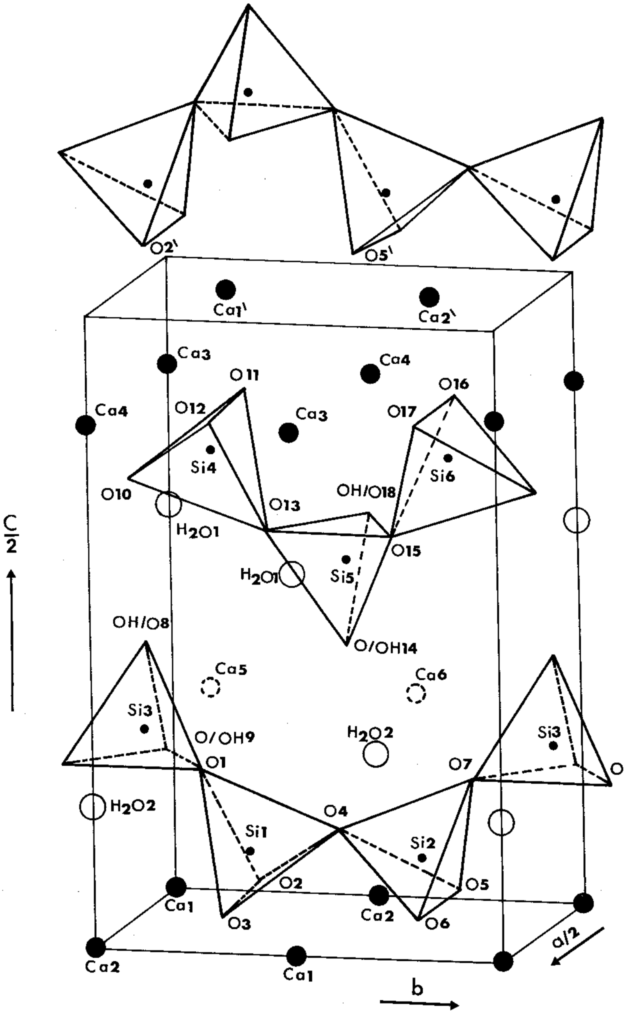

Fig. 3. A three dimensional view of the tobermorite structure using the orthorhombic axis $a/2 = 5.58$ Å, $b = 7.39$ Å, and $c/2 = 11.389$ Å. The atom symbols are identical with those in Tables 2 and 3. The dotted Ca-atoms are statistically distributed

Wieker (1968, 1979) reported the existence of double chain tobermorite in natural and synthetic specimens (chromatographic method). But tobermorite from Zeilberg is formed by single chains because the sum of the occupancy factors of O/OH(3) and O/OH(10) (Table 1) is 2 thereby giving the single chain formula. On the other hand the existence of double chain tobermorite (at least at higher temperature than single chain tobermorite) is possible if

Table 3. Interatomic distances [Å] in space group $P2_1$. Atoms signed with (′) are equivalent by symmetry to those with the same No. (Table 2). Atoms signed with ^{a} are O or OH. W(1) and W(2) represent oxygen from $H_2O(1)$ and $H_2O(2)$ (Table 2)

Si–O					
Si(1)–O(1)	1.68	Si(2)–O(4)	1.60	Si(3)–O(1)	1.67
–O(2)	1.59	–O(5)	1.59	–O(7)	1.67
–O(3)	1.58	–O(6)	1.58	–^{a}O(8)	1.59
–O(4)	1.64	–O(7)	1.69	–^{a}O(9)	1.55
	1.62		1.62		1.62
O–O					
O(1)–O(2)	2.72	O(7)–O(1)	2.51	O(4)–O(5)	2.57
O(1)–O(3)	2.71	O(7)–^{a}O(8)	2.63	O(4)–O(6)	2.57
O(1)–O(4)	2.63	O(7)–^{a}O(9)	2.72	O(4)–O(7)	2.63
O(2)–O(3)	2.62	O(1)–^{a}O(8)	2.63	O(5)–O(7)	2.73
O(2)–O(4)	2.60	^{a}O(9)–^{a}O(8)	2.63	O(5)–O(6)	2.62
O(3)–O(4)	2.60	O(1)–^{a}O(9)	2.72	O(6)–O(7)	2.72
	2.64		2.64		2.64
Ca–O					
Ca(1)–O(2)	2.43	Ca(3)–W(1)	2.51	Ca(5)–O(1)	2.35
–O(3)	2.38	–O(2′)	2.75	–W(1)	3.31
–O(5)	2.46	–O(3′)	2.74	–W(2)	3.05
–O(6)	2.35	–O(11)	2.31	–^{a}O(8′)	3.05
–^{a}O(9)	2.60	–O(12)	2.43	–O(9)	3.19
–O(11′)	2.42	–O(16)	2.33	–O(13)	2.98
–O(12′)	2.42	–O(17)	2.40	–^{a}O(14)	2.93
	2.44		2.49		2.98

O/OH(8) and O/OH(14) (Fig. 3) are joined together [in this case the chain containing O/OH(14) must be displaced by $b/2$] forming a double chain tobermorite. The chemical formula will be

$$Ca_4[Si_6O_{15}(OH)_2]\cdot 2\,H_2O \text{ or } Ca_5[Si_6O_{15}(OH)_2]\cdot(OH)_2.$$

I would like to thank Professor E. Eberhard for many useful discussions and his interest during these investigations and Dr. H. Jakob for providing us with tobermorite from Zeilberg. I thank Professor Berthold for the opportunity to measure the scattered X-ray intensities and Dr. Wartchow (Institut für Anorganische Chemie, Universität Hannover) for his help during the measurements and the use of his program library. I would also like to thank the RRZN Hannover for cooperation during computing.

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