

## The crystal structure of taramellite

FIorenzo MAZZI AND GIUSEPPE ROSSI

C.N.R. Centro di Studio per la Cristallografia Strutturale  
Istituto di Mineralogia, Via Bassi 4, I-27100 Pavia, Italy

### Abstract

The crystal structure of taramellite has been redetermined on the basis of new chemical analyses which revealed the presence of boron and chlorine.

The X-ray diffraction data were measured with a single-crystal automatic diffractometer. The electron density maps computed using the new structure factors and the coordinates of the previous structure allowed location of the atoms of boron, chlorine, and oxygen which had been overlooked. The coordinates of all the atoms were refined anisotropically: the final conventional R factor was 0.028 for taramellite from Rush Creek, California and 0.033 for taramellite from the type locality of Candoglia, Italy.

The main structural feature of taramellite is a borosilicate radical  $(B_2Si_8O_{27})^{16-}$ , which is formed by two rings of four Si tetrahedra connected by a  $B_2O_7$  group sharing two oxygen atoms with each ring. Chlorine atoms occur, with incomplete occupancy, between adjacent borosilicate groups.

The chemical formula derived from the new analytical and structural data is:  $Ba_4Me_x(B_2Si_8O_{27})O_2Cl_x$  where  $0 \leq x \leq 1$ . In the Rush Creek sample the principal octahedral Me cation is  $Ti^{4+}$ , in the Candoglia sample  $Fe^{3+}$ .

### Introduction

The crystal structure of taramellite was determined (Mazzi and Rossi, 1965) on the basis of the stoichiometric unit  $Ba_2(Fe,Ti,Mg)_2H_2(Si_4O_{12})O_2$ ; this determination was started on poor crystals from the type locality (Candoglia, Italy) and was completed on a crystal from Rush Creek (Fresno County, California). The lattice parameters reported in that paper are:  $a = 13.95$ ;  $b = 12.21$ ;  $c = 7.15A$ ;  $Z = 4$ ; space group  $Pmmn$ .

According to that structural research, taramellite is a cyclosilicate with rings of four  $SiO_4$  tetrahedra; chains of (Fe,Ti) octahedra are formed by having opposite edges of each octahedron shared with two adjacent ones: such chains connect the tetrahedral rings and Ba atoms lie in cavities among the rings. As it was impossible to locate the hydrogen atoms in the unit cell, doubt remained as to whether they were linked to the oxygens of the tetrahedral framework or to the "free" oxygens.

Subsequent chemical analyses by the U.S. Geological Survey and recent preliminary analyses at the California Division of Mines and Geology (Pabst and Alfors, private communication) showed that bo-

ron and chlorine are also essential components of taramellite. Matsubara and Kato (1977) described a vanadium-rich taramellite from the Mogurazawa mine (Kiryu, Japan). These authors, as well as Alfors and Pabst, suggested the following new formula unit:  $Ba_4Me_4^{3+}B_2Si_8O_{28}Cl(OH)$  and  $Z = 2$ , where  $Me^{3+}$  would be prevalingly iron in the specimens from Candoglia, titanium in those from California, and vanadium in the Japanese taramellite.

Following these new results, the present re-examination of the crystal structure of taramellite was carried out on specimens from Candoglia and from Rush Creek.

### Experimental

Data were collected with a Philips PW 1100 single-crystal diffractometer. The lattice parameters were determined with one of the standard programs (LAT) of the instrument: the profiles of the four most intense reflections (as weighted by  $\tan \theta$ ) of a row of the reciprocal lattice are scanned in the positive and in the negative  $\theta$  regions, and the centers of gravity of these eight profiles are used in a least-squares refinement of  $\lambda/d$ . Rows  $a^*$ ,  $b^*$ , and  $c^*$  were investigated

Table 1. Crystallographic and refinement data

	Candoglia	Rush Creek
$a$ (Å)	12.150 (3)	12.200 (2)
$b$ "	13.946 (3)	13.952 (2)
$c$ "	7.129 (2)	7.128 (1)
Dimensions of the crystal (mm)	0.03x0.04x0.12	0.32x0.40x0.53
Scan range ( $\theta^\circ$ )	3.0	1.5
Scan rate ( $^\circ/\text{sec.}$ )	0.033	0.1
Measured reflections:		
total	3646	7292
independent	1896	1902
with $Int. > 3\sigma(Int)$	1059	1751
R (obs.)	0.033	0.028
R (all)	0.086	0.033

in the range  $3^\circ \leq \theta \leq 50^\circ$  (MoK $\alpha$ ) to obtain the lattice parameters of taramellite. Table 1 shows the newly determined lattice parameters together with other experimental data. Parameters  $a$  and  $b$  have been interchanged with respect to the previous structural determination to obtain the conventional  $a < b$ . The systematic extinctions are in agreement with those of the already known space group  $Pmmn$ .

X-ray diffraction data were collected using MoK $\alpha$  radiation monochromatized by a flat graphite crystal. The intensities of equivalent reflections within two (Candoglia) or four (Rush Creek) octants of the reciprocal sphere were measured up to  $\theta = 30^\circ$ , by the  $\theta$ -scan mode. Three standard reflections, monitored at three-hour intervals, showed no variation in intensity greater than 4.6 percent (Candoglia) and 1.8 percent (Rush Creek). Processing of the data was carried out with a program specifically written for the PW 1100 diffractometer by Hornstra and Stubbe (1972). A preliminary absorption correction to account for the shape of the crystals was applied to all reflections according to the empirical procedure described by North *et al.* (1968); an absorption correction for spherical crystals was subsequently applied and the intensities of the equivalent reflections were averaged. Reflections with  $F^2 > 3\sigma(F^2)$  were considered as observed and used in the refinements of the crystal structures. The different numbers of observed reflections (Table 1) for the two specimens follow from the poor quality of the Candoglia crystals, which occur in aggregates of fine needles, whereas crystals from Rush Creek are massive and well formed.

## Structure analyses and refinements

Fourier syntheses were computed starting from the atomic positions previously determined (Mazzi and Rossi, 1965); all the preceding atomic sites were confirmed and new sites were identified for boron, chlorine, and one more oxygen, O(10). Isotropic and anisotropic refinements were then carried out with the program ORFLS (Busing *et al.*, 1962) until convergence was achieved. Scattering factor curves for neutral atoms were used (*International Tables for X-ray Crystallography*, 1974, vol. 4, p. 99–101); the curves for the octahedral Me atoms were obtained by the combination of 0.75 Fe and 0.25 Ti (Candoglia), or 0.25 Fe and 0.75 Ti (Rush Creek) to account for the different chemical compositions.<sup>1</sup> The comparable temperature factors for octahedral cations obtained at the end of the refinements support the choice of the above Fe/Ti ratios for the two specimens.

Positional and thermal parameters are given in Tables 2 and 3. Observed and calculated structure factors are compared in Table 4.<sup>2</sup>

## Description of the structure

Figure 1 shows the revised crystal structure of taramellite. The main difference from the previously determined structure is the presence of B<sub>2</sub>O<sub>7</sub> groups of two tetrahedra: they connect two four-fold rings of SiO<sub>4</sub> tetrahedra to form the anionic radical (B<sub>2</sub>Si<sub>8</sub>O<sub>27</sub>)<sup>16-</sup>. Boron is coordinated by two O(8) oxygens belonging to two different four-fold rings, by one of the "free" oxygens, O(3), of the old structure, and by a new oxygen, O(10), which bridges the two tetrahedra of the B<sub>2</sub>O<sub>7</sub> group. The anionic groups are superposed along  $a$ , with the planes of the four-fold rings roughly parallel to (100).

Barium atoms lie between the four-fold rings, together with chlorine, which is surrounded by three Ba atoms (Ba–Cl = 3.14–3.38Å) and by one more Ba at a longer distance (3.74Å).

<sup>1</sup> The Fe/Ti ratio for the Californian taramellite has been merely assumed as indicative of the total number of electrons in the octahedral sites, irrespective of the actual chemical composition, which, according to the preliminary analyses, also includes magnesium and some manganese. Professor Pabst and coworkers have in progress a new complete chemical analysis, which will be published.

<sup>2</sup> To obtain a copy of Table 4, order Document AM-79-119 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 2. Atomic positional and thermal parameters ( $B_{eq}$  in  $\text{Å}^2$ )

Atom	<i>M</i>	<i>PS</i>	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ba(1)	2	<i>mm</i>	0.75	0.25	0.2394(1)	1.10	14(0)	11(0)	78(2)	0	0	0
			0.75	0.25	0.2362(1)	1.47	12(0)	11(0)	141(1)	0	0	0
Ba(2)	2	<i>mm</i>	0.25	0.25	0.4659(2)	1.94	26(1)	8(0)	129(2)	0	0	0
			0.25	0.75	0.4671(1)	1.37	22(0)	7(0)	108(1)	0	0	0
Ba(3)	4	<i>m</i>	0.25	0.4749(0)	0.0070(1)	0.81	14(0)	12(0)	35(1)	0	0	-3(0)
			0.25	0.4716(0)	0.0078(1)	0.82	13(0)	11(0)	39(1)	0	0	-2(0)
Me	8°	1	0.6295(1)	0.5020(1)	0.4765(1)	0.75	15(1)	9(0)	31(2)	0(0)	-3(1)	-2(1)
			0.6285(1)	0.5026(1)	0.4758(1)	0.76	14(0)	10(0)	35(1)	1(0)	-2(1)	-3(1)
Si(1)	8	1	0.4894(1)	0.3662(1)	0.2048(3)	0.52	9(1)	6(1)	29(4)	0(1)	0(1)	0(1)
			0.4896(1)	0.3659(1)	0.2062(2)	0.46	8(1)	5(1)	24(2)	0(1)	0(1)	-2(1)
Si(2)	8	1	0.4736(2)	0.6441(1)	0.2073(2)	0.45	8(1)	7(1)	17(3)	-1(1)	0(1)	-1(1)
			0.4736(1)	0.6441(1)	0.2051(2)	0.49	10(1)	5(1)	25(2)	0(1)	1(1)	1(1)
B	4	<i>m</i>	0.25	0.6593(7)	0.2773(15)	0.64	18(6)	0(4)	41(17)	0	0	-2(7)
			0.25	0.6585(5)	0.2787(10)	0.17	4(4)	0(3)	13(11)	0	0	0(4)
O(1)	4	<i>m</i>	0.5062(6)	0.25	0.2212(10)	0.81	27(5)	2(3)	35(13)	0	-14(6)	0
			0.5087(5)	0.25	0.2217(8)	1.14	29(4)	5(2)	64(10)	0	-13(5)	0
O(2)	4	<i>m</i>	0.5207(5)	0.75	0.2684(10)	0.76	17(4)	5(3)	44(13)	0	-8(6)	0
			0.5191(4)	0.75	0.2656(7)	0.81	20(3)	4(2)	47(9)	0	-5(5)	0
O(3)	4	<i>m</i>	0.25	0.5767(4)	0.4088(9)	0.72	29(4)	3(3)	10(11)	0	0	0(4)
			0.25	0.5754(4)	0.4094(8)	1.11	28(3)	8(2)	49(9)	0	0	6(4)
O(4)	4	<i>m</i>	0.75	0.5715(4)	0.3623(10)	1.24	52(6)	0(3)	33(12)	0	0	-1(5)
			0.75	0.5711(4)	0.3609(9)	2.11	78(6)	10(3)	45(10)	0	0	-5(4)
O(5)	8	1	0.5388(4)	0.6092(3)	0.0167(7)	0.86	15(3)	14(2)	30(8)	0(2)	3(4)	-2(4)
			0.5383(3)	0.6090(3)	0.0162(5)	0.76	13(2)	12(1)	28(6)	3(1)	2(3)	1(3)
O(6)	8	1	0.3798(4)	0.4001(3)	0.3135(6)	0.83	18(3)	11(2)	28(8)	5(2)	-1(4)	-9(3)
			0.3810(3)	0.3994(3)	0.3149(5)	0.78	12(2)	12(2)	33(6)	1(1)	4(3)	-6(3)
O(7)	8	1	0.6073(3)	0.4110(3)	0.2617(7)	0.78	12(3)	9(2)	47(8)	-4(2)	-4(4)	-2(4)
			0.6068(3)	0.4118(3)	0.2628(5)	0.86	13(2)	11(2)	46(6)	0(2)	-3(3)	-6(3)
O(8)	8	1	0.3456(4)	0.6482(3)	0.1479(6)	0.74	9(2)	14(2)	28(8)	6(2)	9(4)	-8(4)
			0.3453(3)	0.6477(3)	0.1458(5)	0.80	7(2)	12(2)	53(6)	0(1)	3(3)	-6(3)
O(9)	8	1	0.4946(4)	0.5722(3)	0.3763(7)	0.95	17(3)	12(2)	44(9)	3(2)	-4(4)	3(4)
			0.4938(3)	0.5718(3)	0.3741(5)	0.92	25(2)	9(2)	27(6)	-2(2)	2(3)	6(3)
O(10)	2	<i>mm</i>	0.25	0.75	0.3803(11)	0.65	16(5)	13(4)	0(15)	0	0	0
			0.25	0.75	0.3780(10)	0.90	20(5)	14(3)	22(12)	0	0	0
Cl	2°°	<i>mm</i>	0.25	0.25	-0.0088(9)	2.24	36(3)	20(2)	149(10)	0	0	0
			0.25	0.25	-0.0049(5)	1.64	23(2)	11(1)	33(6)	0	0	0

*M* multiplicity; *PS* point symmetry.

Roman figures refer to the specimen from Candoglia (Italy); italic figures refer to the specimen from Rush Creek (California). Standard deviations are in parentheses in terms of last significant figures.

° site population: 0.75 *Fe* and 0.25 *Ti* (Candoglia); 0.25 *Fe* and 0.75 *Ti* (Rush Creek).

°° site occupancy: 0.89 (Candoglia); 0.95 (Rush Creek).

The anisotropic thermal parameters are defined by:  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})] \times 10^{-4}$   
 $B_{eq}$  is the equivalent isotropic temperature factor.

The octahedral coordination of Me atoms is formed by four oxygens—O(6), O(7), and two O(9)—of the SiO<sub>4</sub> tetrahedra, by the O(3) oxygen of a BO<sub>4</sub> tetrahedron, and by one more oxygen, O(4), which, as in the earlier structure, does not participate in any tetrahedral coordination. Each Me octahedron shares two edges, O(3)–O(4) or O(9)–O(9), with two opposite adjacent octahedra; a chain of octahedra is thus formed along [100], and it connects four different anionic groups in the unit cell.

Table 5 gives the interatomic distances in all polyhedra, and the bond angles in tetrahedra and in the

Me octahedron. The values obtained from both refinements are practically identical: in particular, the mean distance in each Me octahedron is the same in spite of the different ratios between iron and titanium. This mean distance (2.021 Å) agrees well with the sum of the ionic radii (Shannon, 1976) of Fe<sup>3+</sup> and O<sup>2-</sup> (2.025 Å); furthermore it is halfway between the distances Ti<sup>3+</sup>–O = 2.05 and Ti<sup>4+</sup>–O = 1.985 Å, suggesting the possible simultaneous presence of Ti<sup>3+</sup> and Ti<sup>4+</sup>. On the other hand, a comparable Me–O distance could also be attained with a combination of Ti<sup>4+</sup>, Fe<sup>2+</sup>, and Mg in addition to Fe<sup>3+</sup>, without any

Table 3. Parameters for the ellipsoids of vibration

Atom	rmsd	$U^a$	$U^b$	$U^c$	rmsd	$U^a$	$U^b$	$U^c$	rmsd	$U^a$	$U^b$	$U^c$
Ba(1)	103 (2) <i>94 (1)</i>	0	90	90	105 (2) <i>104 (1)</i>	90	0	90	141 (2) <i>190 (1)</i>	90	90	0
Ba(2)	90 (2) <i>85 (2)</i>	90	0	90	140 (2) <i>130 (1)</i>	0	90	90	215 (2) <i>187 (1)</i>	90	90	0
Ba(3)	91 (1) <i>97 (1)</i>	90	116 (3) <i>121 (3)</i>	154 (3) <i>149 (3)</i>	103 (1) <i>99 (1)</i>	0	90	90	110 (1) <i>108 (1)</i>	90	154 (3) <i>149 (4)</i>	64 (3) <i>59 (4)</i>
Me	85 (3) <i>88 (2)</i>	104 (5) <i>95 (6)</i>	110 (9) <i>130 (5)</i>	155 (7) <i>40 (5)</i>	97 (2) <i>98 (2)</i>	107 (8) <i>41 (8)</i>	24 (9) <i>123 (7)</i>	106 (9) <i>68 (7)</i>	109 (2) <i>108 (2)</i>	157 (7) <i>137 (8)</i>	102 (7) <i>124 (6)</i>	71 (5) <i>58 (5)</i>
Si(1)	75 (5) <i>69 (4)</i>	71(41) <i>89(20)</i>	161(41) <i>151(13)</i>	90(19) <i>119(13)</i>	81 (5) <i>78 (3)</i>	19(41) <i>16(37)</i>	71(41) <i>97(24)</i>	92(34) <i>78(33)</i>	87 (5) <i>82 (3)</i>	92(33) <i>106(37)</i>	90(22) <i>117(14)</i>	178(34) <i>32(20)</i>
Si(2)	65 (6) <i>69 (4)</i>	94(27) <i>95(10)</i>	106(21) <i>169(16)</i>	164(26) <i>80(15)</i>	73 (5) <i>79 (4)</i>	36(16) <i>112(17)</i>	60(19) <i>79(16)</i>	102(33) <i>25(17)</i>	86 (5) <i>88 (3)</i>	55(16) <i>157(17)</i>	142(15) <i>89 (9)</i>	79(12) <i>113(17)</i>
B	- <i>-</i>	90 <i>90</i>	174(20) <i>80(40)</i>	96(20) <i>90(40)</i>	103(22) <i>57(24)</i>	90 <i>90</i>	96(20) <i>90(40)</i>	6(20) <i>0(40)</i>	116(19) <i>55(24)</i>	0 <i>0</i>	90 <i>90</i>	90 <i>90</i>
O(1)	42(32) <i>70(15)</i>	90 <i>90</i>	0 <i>0</i>	90 <i>90</i>	80(20) <i>113(11)</i>	66(10) <i>58 (9)</i>	90 <i>90</i>	24(10) <i>32 (9)</i>	151(12) <i>181 (9)</i>	156(10) <i>148 (9)</i>	90 <i>90</i>	66(10) <i>58 (9)</i>
O(2)	70(21) <i>62(16)</i>	90 <i>90</i>	0 <i>0</i>	90 <i>90</i>	93(18) <i>104(11)</i>	51(21) <i>59(20)</i>	90 <i>90</i>	39(21) <i>31(20)</i>	124(14) <i>127(10)</i>	141(21) <i>149(20)</i>	90 <i>90</i>	51(21) <i>59(20)</i>
O(3)	51(28) <i>82(14)</i>	90 <i>90</i>	- <i>152(14)</i>	- <i>62(14)</i>	58(25) <i>120(11)</i>	90 <i>90</i>	- <i>62(14)</i>	- <i>28(14)</i>	146(12) <i>146 (9)</i>	0 <i>0</i>	90 <i>90</i>	90 <i>90</i>
O(4)	- <i>89(14)</i>	90 <i>90</i>	178(18) <i>146(22)</i>	92(18) <i>124(22)</i>	93(17) <i>115(12)</i>	90 <i>90</i>	92(18) <i>56(22)</i>	2(18) <i>146(22)</i>	196(11) <i>242 (9)</i>	0 <i>0</i>	90 <i>90</i>	90 <i>90</i>
O(5)	85(12) <i>83 (9)</i>	71(21) <i>74(49)</i>	100(16) <i>95(38)</i>	159(20) <i>163(58)</i>	109 (9) <i>90 (9)</i>	19(22) <i>41(28)</i>	86(53) <i>127(13)</i>	72(22) <i>74(61)</i>	117 (9) <i>118 (7)</i>	89(51) <i>127(11)</i>	169(28) <i>143(11)</i>	80(24) <i>96(11)</i>
O(6)	61(17) <i>75(10)</i>	77(11) <i>63(14)</i>	127(10) <i>117 (9)</i>	140(13) <i>140(10)</i>	101(11) <i>101 (8)</i>	46(14) <i>27(15)</i>	118(13) <i>72(20)</i>	56(14) <i>70(17)</i>	133 (9) <i>117 (7)</i>	134(13) <i>85( 9)</i>	131(10) <i>147(13)</i>	72(10) <i>57(11)</i>
O(7)	68(15) <i>89 (9)</i>	132(11) <i>116(31)</i>	133(12) <i>129(20)</i>	106(12) <i>130(12)</i>	110(10) <i>101 (8)</i>	118(68) <i>29(30)</i>	47(38) <i>118(26)</i>	124(99) <i>98(23)</i>	114(10) <i>121 (7)</i>	125(60) <i>102(16)</i>	76(75) <i>129(12)</i>	39(94) <i>41 (10)</i>
O(8)	- <i>72(10)</i>	132(11) <i>188(15)</i>	66 (6) <i>84(13)</i>	52(10) <i>79(10)</i>	105(11) <i>98 (8)</i>	48(10) <i>79(16)</i>	92(16) <i>36(12)</i>	42(10) <i>57(12)</i>	131 (9) <i>126 (7)</i>	109(12) <i>85 (7)</i>	156 (6) <i>125(12)</i>	75(14) <i>38(11)</i>
O(9)	90(13) <i>66(11)</i>	56(16) <i>35 (5)</i>	125(17) <i>128(10)</i>	54(21) <i>39(10)</i>	114(11) <i>105 (8)</i>	110(44) <i>85(10)</i>	61(40) <i>39(10)</i>	37(22) <i>51(10)</i>	123 (9) <i>139 (6)</i>	138(29) <i>173 (7)</i>	131(34) <i>83 (8)</i>	85(43) <i>91 (7)</i>
O(10)	- <i>75(20)</i>	90 <i>90</i>	0 <i>0</i>	0 <i>0</i>	109(20) <i>122(14)</i>	0 <i>0</i>	90 <i>90</i>	90 <i>90</i>	113(14) <i>118(14)</i>	90 <i>90</i>	0 <i>0</i>	90 <i>90</i>
Cl	141 (7) <i>105 (6)</i>	90 <i>90</i>	0 <i>0</i>	90 <i>90</i>	163 (7) <i>132 (5)</i>	0 <i>0</i>	90 <i>90</i>	90 <i>90</i>	196 (7) <i>185 (4)</i>	90 <i>90</i>	90 <i>90</i>	0 <i>0</i>

Root-mean-square displacements along principal axes are in Å: Rmsd values approaching zero and showing an abnormally high standard deviation have been omitted. Angles between crystallographic axes ( $a$ ,  $b$ ,  $c$ ) and principal axes ( $U$ ) of the thermal ellipsoids are in degrees: values with abnormally high standard deviations (about 180°) have been omitted.

Standard deviations are indicated in parentheses in terms of the last significant figures.

Roman figures refer to the specimen from Candoglia; italic figures refer to the specimen from Rush Creek.

Ti<sup>3+</sup> atoms. Actually, Fe<sup>3+</sup> dominates over Fe<sup>2+</sup> and Ti in the iron-rich taramellite from Candoglia (Mazzi, 1957), whereas divalent cations (Fe<sup>2+</sup>, Mg) and little Fe<sup>3+</sup> are present in the titanium-rich taramellite from Rush Creek (Pabst and Alfors, private communication). The sum of the ionic radii of V<sup>3+</sup> and O<sup>2-</sup> (2.02 Å) is also comparable with the above Me-O distance, so that the occurrence of a vanadian taramellite is easily explainable from a crystal-chemical point of view.

Table 3 gives the analysis of the anisotropic thermal parameters: the trend is analogous in both structures, even if the actual values of the amplitudes of the thermal ellipsoid axes and their ratios differ to

some extent. For instance, the thermal ellipsoid of boron is very flattened, with the shortest axis nearly in the  $b$  direction; the thermal vibrations of Ba(3), Me, and Si atoms are almost isotropic, whereas the thermal ellipsoids of Ba(1) and Ba(2) are elongated in the  $c$  direction.

The atomic content of the unit cell given in the introduction should be rewritten in the following way, to account for the actual anionic group: Ba<sub>8</sub>Me<sub>8</sub><sup>3+</sup>(B<sub>2</sub>Si<sub>8</sub>O<sub>27</sub>)<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>Cl<sub>2</sub>. However, according to the structural results, the presence of H atoms is rather unlikely: atomic sites with multiplicity 2 occur in the space group  $Pm\bar{m}n$  only on two-fold axes, and, from a purely geometrical point of view, the only

way to accommodate two hydrogens in this structure would be to link them to chlorine. Furthermore, both  $O_2$  and  $(OH)_2$  of the formula unit correspond to four equivalent  $O(4)$  atoms, lying on symmetry planes parallel to  $(100)$ ; therefore, if the two hydrogens are linked to these oxygens, they would occupy statistically one-half of the sites with four-fold multiplicity. On the other hand no plausible hydrogen sites were detected on the difference Fourier syntheses, and no other evidence was found to describe taramellite in a space group with lower symmetry. Also the balance of the electrostatic charges supports the absence of H atoms: Table 6 shows such balance for the Candoglia taramellite computed following two completely different methods (Brown and Kang Kun Wu, 1976; Donnay and Allman, 1970); the presence of chlorine is irrelevant in the calculation after Brown and Kang Kun Wu, and the calculation after Donnay and Allman was done in both the absence and presence of chlorine. All the calculated balances are comparable and in any case no oxygen shows a sharp tendency to be a hydroxyl.

The best balance is obtained without the H atoms, assuming 3.25+ as the charge of the Me atoms. This fact suggests that the average charge of Me atoms is greater than 3+, and therefore  $Ti^{4+}$  is probably present, in accordance with the preceding considerations about the mean Me-O distance.

Indications are given by the refinements for incomplete occupancy of the chlorine sites (Table 2). This element should not be considered a really essential component of the crystal structure: it merely balances the surplus of charge (over 3+) of the Me atoms: the occupancy of chlorine sites in the Candoglia iron-rich taramellite is in fact slightly lower than that in the Californian titanium-rich taramellite (0.89 and 0.95 respectively). Complete occupancy of the chlorine sites corresponds to a charge of 3.25+ for the Me atoms. In conclusion  $Ti^{3+}$  is likely absent in all taramellites. The excess charge of  $Ti^{4+}$  is balanced both by divalent cations ( $Fe^{2+}$ ,  $Mg$ ) in the octahedral Me sites and by the variable amounts of chlorine.

The general stoichiometric unit for all taramellites, obtained from this structural study, is therefore as follows:



where  $0 \leq x \leq 1$ ;  $Z = 2$ .

#### Acknowledgments

The authors are much indebted to Professor A. Pabst, who suggested the revision of the crystal structure of taramellite, and sent

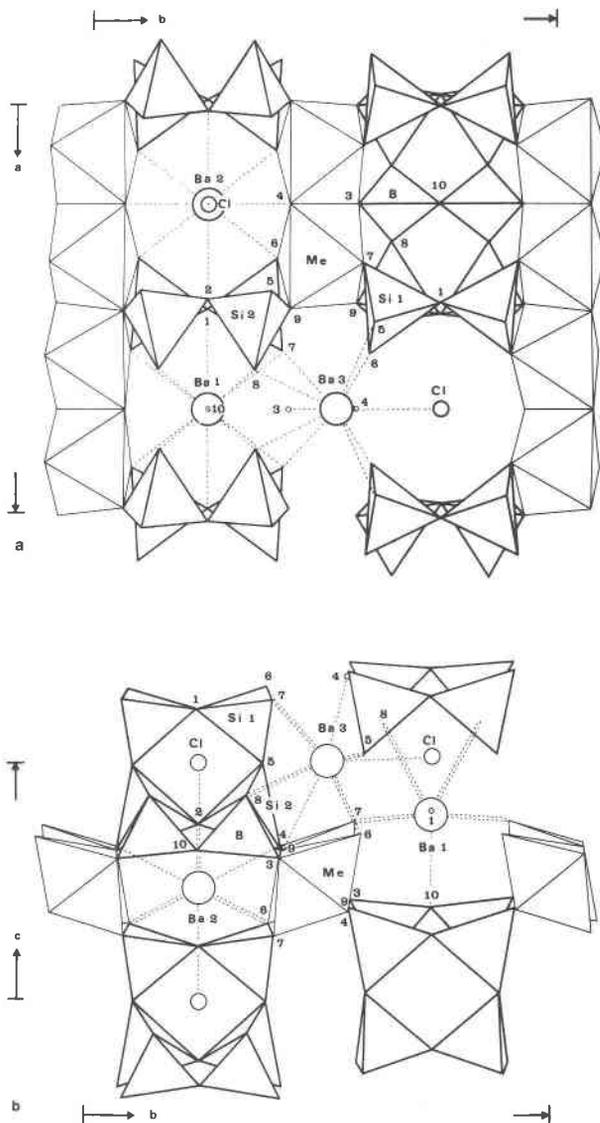


Fig. 1. Projection of the structure of taramellite along  $[001]$  (a) and  $[100]$  (b). Some atoms and polyhedra have been omitted for clarity.

us fine specimens of taramellite from Rush Creek, together with the results of the preliminary chemical analyses.

#### References

- Brown, I. D. and Kang Kun Wu (1976) Empirical parameters for calculating cation-oxygen bond valences. *Acta Crystallogr.*, B32, 1957-1959.
- Busing, W. R., K. O. Martin and H. A. Levy (1962) ORFLS, a Fortran crystallographic least-squares program. *Oak Ridge National Laboratory, Doc. ORNL-TM-305*.
- Donnay, G. and R. Allmann (1970) How to recognize  $O^{2-}$ ,  $OH^-$

Table 5. Interatomic distances (Å) and angles (°)

Si(1) tetrahedron			Si(2) tetrahedron			B tetrahedron		
- O(6)	1.611(5)	1.604(4)	- O(9)	1.587(5)	1.591(4)	- O(10)	1.463(11)	1.459(8)
- O(7)	1.615(5)	1.616(4)	- O(8)	1.612(5)	1.623(4)	- O(3)	1.484(12)	1.487(8)
- O(1)	1.637(5)	1.637(2)	- O(2)	1.643(3)	1.635(3)	- O(8) × 2	1.492(8)	1.507(6)
- O(5)i	1.652(5)	1.658(4)	- O(5)	1.647(5)	1.636(4)			
Mean	1.629	1.629	Mean	1.622	1.621	Mean	1.483	1.490
O(6) ^ O(5)i	103.1(2)	103.3(2)	O(5) ^ O(8)	104.9(3)	105.1(2)	O(8) ^ O(8)iv	102.3(8)	100.9(5)
O(1) ^ O(7)	104.8(3)	104.4(3)	O(2) ^ O(9)	108.1(3)	108.7(2)	O(3) ^ O(8) × 2	108.1(5)	108.4(4)
O(1) ^ O(5)i	107.5(3)	107.6(2)	O(2) ^ O(5)	108.5(3)	108.9(2)	O(3) ^ O(10)	110.7(8)	112.2(5)
O(7) ^ O(5)i	110.1(3)	109.7(2)	O(5) ^ O(9)	111.2(3)	111.0(2)	O(8) ^ O(10) × 2	113.6(5)	113.1(4)
O(1) ^ O(6)	111.1(3)	111.9(3)	O(2) ^ O(8)	111.9(3)	111.6(2)			
O(6) ^ O(7)	119.9(3)	119.6(2)	O(8) ^ O(9)	112.2(3)	111.5(2)			
<b>Me octahedron</b>								
- O(4)	1.935(4)	1.945(4)	O(9) ^ O(9)ii	80.5(2)	81.0(2)	O(7) ^ O(3)ii	93.6(2)	93.7(2)
- O(7)	2.007(5)	1.995(4)	O(4) ^ O(3)ii	83.9(2)	82.9(2)	O(3)ii ^ O(6)ii	96.2(2)	96.2(2)
- O(3)ii	2.004(4)	2.012(4)	O(9) ^ O(6)ii	83.7(2)	84.0(2)	O(4) ^ O(7)	95.6(2)	95.4(2)
- O(6)ii	2.030(4)	2.027(4)	O(6)ii ^ O(9)ii	85.6(2)	85.3(2)	O(4) ^ O(9)	102.7(2)	103.4(2)
- O(9)	2.039(5)	2.039(4)	O(7) ^ O(9)	85.9(2)	85.6(2)	O(7) ^ O(6)ii	168.7(2)	168.7(2)
- O(9)ii	2.109(5)	2.109(4)	O(7) ^ O(9)ii	88.5(2)	88.8(2)	O(9) ^ O(3)ii	173.4(2)	173.8(2)
Mean	2.021	2.021	O(4) ^ O(6)ii	90.9(3)	91.3(2)	O(4) ^ O(9)ii	175.0(3)	174.2(2)
			O(3)ii ^ O(9)ii	92.9(3)	92.8(2)			
<b>Ba(1) polyhedron</b>			<b>Ba(2) polyhedron</b>			<b>Ba(3) polyhedron</b>		
- O(10)ii	2.711(8)	2.750(7)	- O(4)ii × 2	2.774(7)	2.781(6)	- O(4)i	2.711(7)	2.695(6)
- O(7) × 4	2.842(5)	2.862(4)	- O(6) × 4	2.837(5)	2.842(4)	- O(5)i × 2	2.827(4)	2.822(4)
- O(1) × 2	2.965(7)	2.948(6)	- O(2)ii × 2	3.369(7)	3.401(5)	- O(8) × 2	2.864(5)	2.890(4)
- O(8)i × 4	3.315(5)	3.288(4)				- O(6) × 2	2.890(5)	2.892(4)
Mean of 7	2.858	2.870	Mean of 6	2.816	2.822	- O(7)i × 2	3.034(5)	3.070(4)
Mean of 11	3.024	3.021	Mean of 8	2.954	2.967	- O(3)	3.197(6)	3.208(6)
						Mean of 7	2.839	2.843
						Mean of 10	2.914	2.925
			- Cl	3.385(6)	3.385(3)	- Cl	3.139(6)	3.094(5)
			- Cl iii	3.744(6)	3.763(3)			

Roman numerals refer to the following equivalent positions:

i (1 - x)(1 - y) - z; ii (1 - x)(1 - y)(1 - z); iii x y (1 + z); iv (½ - x) y z.

Roman figures refer to the specimen from Candoglia; italic figures refer to the specimen from Rush Creek. Standard deviations are in parentheses in terms of last significant figures.

Table 6. Balance of the electrostatic valence

Anions	Bonded cations	Bond strengths		
		A	B	C
O(1)	Si(1), Si(1), Ba(1)	2.09	2.16	2.16
O(2)	Si(2), Si(2), Ba(2)	1.96	1.95	1.95
O(3)	Me, Me, B, Ba(3)	1.85	1.87	1.95
O(4)	Me, Me, Ba(2), Ba(3)	1.82	1.89	1.92
O(5)	Si(1), Si(2), Ba(3)	2.09	2.14	2.11
O(6)	Si(1), Me, Ba(2), Ba(3)	1.93	2.03	2.01
O(7)	Si(1), Me, Ba(1), Ba(3)	1.89	1.96	1.98
O(8)	Si(2), B, Ba(3), Ba(1)	2.04	2.02	1.99
O(9)	Si(2), Me, Me	1.93	1.93	2.00
O(10)	B, B, Ba(1)	1.88	1.95	1.95
	Mean unbalance	0.088	0.074	0.046
Cl	Ba(2), Ba(2), Ba(3), Ba(3)			0.73
A:	after Brown and Kang Kun Wu (1976): Me = Fe <sup>3+</sup> after Donnay and Allman (1970)			
B:	Me = Fe <sup>3+</sup> , Cl absent			
C:	Me = Me <sup>3.25+</sup> , Cl present. The Ba-Cl distances were assumed as Ba-O distances after having subtracted 0.41 Å (difference between the ionic radii of Cl and O)			

and H<sub>2</sub>O in crystal structures determined by X-rays. *Am. Mineral.*, 55, 1003-1015.

Hornstra, J. and B. Stubbe (1972) PW 1100 Data Processing Program. *Philips Research Laboratories, Eindhoven, Holland.*

Matsubara, S. and A. Kato (1977) An unknown Ba-V silicate mineral from the Mogurazawa mine, Kiryu. *Annual Meeting Mineral. Soc. Japan.*

Mazzi, F. (1957) Riesame della taramellite. *Atti Soc. Toscana Sci. Nat., Serie A*, 64, 237-245.

— and G. Rossi (1965) The crystal structure of taramellite. *Z. Kristallogr.*, 121, 243-257.

North, A. C., D. C. Phillips and F. S. Mathews (1968) A semi-empirical method of absorption correction. *Acta Crystallogr.*, A24, 351-359.

Shannon, R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, A32, 751-767.