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A reconsideration of the structure of datolite, $CaBSiO_4(OH)$

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Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday

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Auszug

Der bisherige Kristallstrukturvorschlag des Datoliths, $CaBSiO_4(OH)$ wurde durch die Anwendung von „kleinsten Quadratmethoden“ und der Berücksichtigung anisotroper Schwingungen verfeinert. Hierfür wurden die drei-dimensionalen Daten von Ito und Mori (1953) benutzt. Die Verfeinerung ergab einen R-Wert $= 12{,}8\,^0/_0$, wobei 525 Intensitäten benutzt wurden. Die Resultate sind: $Si–O_{bridg.} = 1{,}668 \pm 0{,}007$, $Si–O_{periph.} = 1{,}563 \pm 0{,}012$ Å und $Si–O_{bridg.}–B = 125°$; B—O-Längen in den BO_4-Tetraedern variieren von $1{,}449 \pm 0{,}022$ bis $1{,}561 \pm 0{,}027$ Å. Die Ca—O-Bindungen sind strukturell bedeutungsvoll. Die Pauling-Zachariasen-Vorstellungen über den Einfluß von Wertigkeiten auf Ionenabstände werden bestens bestätigt durch die gefundenen Größen der Si—O-, B—O- und Ca—O-Abstände. Die Variabilität der Si—O-Längen mag durch π-Bindungen erklärt werden. — Die isotypen Strukturen des Herderit ($CaBePO_4 \cdot F$) und Gadolinit [$\sim$(Y,Fe)$BeSiO_4 \cdot O$, wahrscheinlich mit Kationen-Fehlstellen] werden in diesem Zusammenhang diskutiert.

Abstract

The crystal structure of datolite, $CaBSiO_4(OH)$, has been refined by the method of least squares with allowance for anisotropic vibrations using Ito and Mori's (1953) three-dimensional data. Refinement to an R of $12.8\,^0/_0$ with 525 reflections has led to the mean dimensions: $Si–O(br) = 1.668 \pm 0.007$, $Si–O(per) = 1.563 \pm 0.012$ Å and $Si–O(br)–B = 125°$; bond lengths in the boron tetrahedra vary from 1.449 ± 0.022 to 1.561 ± 0.027 Å. The $Ca \cdots O$ links play a significant role in the structure. The Pauling-Zachariasen method of the balancing of valences gives an excellent qualitative description of the variations in the Si—O, B—O and $Ca \cdots O$ lengths. π bonding may be the mechanism for the variations in the Si—O lengths. The structures of herderite, $CaBePO_4F$ which is isotypic with datolite, and gadolinite are also discussed on the basis of the balancing of valences.

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Introduction

The analogies in the series of perchlorates, polysulphates, polyphosphates and silicates suggest (Cruickshank, 1961) that there may be some degree of d—p π bonding in silicates. Though the differences between the shortest and longest X—O bonds are about 0.25 Å for each of the perchlorate, sulphate and phosphate series, the differences between short and long Si—O bonds are much less (McDonald and Cruickshank, 1967); indeed in 1961 it was possible to note that practically all the accurate Si—O distances then known were within 0.03 Å of 1.63 Å. The small spread of Si—O distances is due to two factors: (*a*) X—O—X angles are generally larger for silicates than for phosphates and sulphates; this causes bridging bonds to gain strength at the expense of peripheral bonds, and (*b*) owing to the low electronegativity of silicon, the cation-oxygen bonds are more significant.

In the molecule P_4O_{10} (Beagley, Cruickshank, Hewitt and Haaland, 1967) the peripheral P—O bonds of 1.429 ± 0.004 Å are much shorter than the bridging bonds of 1.604 ± 0.003 Å. The P—O—P angles bridging the tetrahedra are 124°. By analogy, a silicate with the hypothetical $Si_4O_{10}^{4-}$ anion and with cations of low electronegativity should show a substantial difference between the peripheral and bridging bonds, because the Si—O—Si angles would be constrained to be near 120°. (No large differences in bond lengths in $(Si_2O_5^{2-})_\infty$ structures have yet been reported, partly because the Si—O—Si angles are 140° or greater.)

To our knowledge, no example of an $A_4Si_4O_{10}$ structure exists, but the reasons which suggest that it would show a considerable bond-length variation also apply to structures of the type $ASiO(OR)_3$. Datolite, $CaBSiO_4(OH)$, (Ito and Mori, 1953; Pavlov and Belov, 1959) might be regarded as an example of this sort. This is a sheet structure built up from silicate and borate tetrahedra. Of the oxygens in each SiO_4^{4-} group, three act as bridges between silicon and boron, and the fourth is unshared except through weaker links to calcium. In the boron tetrahedra, three oxygens bridge the silicon tetrahedra and the fourth forms an OH group. In terms of the percentage ionic character of bonds, estimated through electronegativities by Pauling's method (1960), the Ca—O links are 79% ionic and the B—O links 44% ionic, as compared with 51% for Si—O bonds. Because of the very different attachments to the four oxygens, it is therefore unreasonable to regard the SiO_4 group as an isolated entity. Thus datolite in some sense contains a group of the type $SiO(OR)_3$, and it is not surprising that ITO and MORI (1953) reported bond lengths of 1.52 Å for the peripheral Si—O bond and 1.69 Å for the bridging bonds, accurate to 0.03 Å.

Although ITO and MORI (1953) reported the values of 525 three-dimensional $F(hkl)$, they refined the structure mainly by two-dimensional Fourier syntheses supplemented by a line synthesis for the x parameters of two overlapping atoms. The final discrepancy index R for all the 525 observed reflections was $\sim 22\%$. The paper by PAVLOV and BELOV (1959) reported the use of comparatively extensive projection data obtained with Mo radiation, but unfortunately no lists of structure factors were given. PAVLOV and BELOV seem not to have expected any significant irregularity in the silicon tetrahedra, for they remark that the two kinds of tetrahedra are much more regular at the end of their analysis.

The present study was undertaken to clarify this anomaly by making use of ITO and MORI's three-dimensional data, and to give a fuller description of the crystal structure and of the various bond lengths and angles.

Crystal data

The space group of datolite, $CaBSiO_4(OH)$, is $P2_1/c$ with cell dimensions $a = 4.84 \pm 0.005$, $b = 7.60 \pm 0.01$, $c = 9.62 \pm 0.01$ Å and $\beta = 90°9'$. There are four units of $CaBSiO_4(OH)$ in each cell. The linear absorption coefficient is $\sim 171\ \mathrm{cm}^{-1}$ for Cu$K\alpha$ and $\sim 19\ \mathrm{cm}^{-1}$ for Mo$K\alpha$ radiation.

Least-squares refinement

The data used in the refinement were the 525 independent non-zero $|F_0|$ given by ITO and MORI. These had been collected from zero-layer Weissenberg photographs about all the three crystallographic axes using Cu$K\alpha$ radiation, and from oscillation photographs about the a axis ($h = 1, 2, 3, 4$ and 5) using Mo$K\alpha$ radiation. Corrections for Lorentz and polarisation factors were applied but absorption was neglected. As the crystal dimensions are not stated, absorption had to be neglected also in the present refinement.

The structure-factor least-squares programme of J. G. F. SMITH and D. W. J. CRUICKSHANK for the KDF 9 computer was used. ITO and MORI's parameters were used as starting values for least-squares refinement. The form-factors were taken from *International tables* *for x-ray crystallography*, Vol. III (1962), and the weighting scheme was

$$w = 1/(4 + |F_o| + 0.024\, |F_o|^2).$$

After three full-matrix isotropic least-squares cycles with eight individual scale factors, R was 13.6%. Anisotropy for the thermal motion of the atoms was assumed at this stage and two sets of calculations were carried out simultaneously: (i) with eight scale factors as in the isotropic case, and (ii) with a single overall scale factor, the relative layer scales being taken as those derived from the isotropic refinement. After three anisotropic least-squares cycles R fell to 12.79% and 12.83% for the first and second sets respectively. HAMILTON's significance test (1965) then showed that the anisotropy was significant, but that no significance at all could be attached to the differences in the results from the two sets of anisotropic calculations. This was quite obvious even by looking at the two sets of parameters; differences were well inside the e.s.d.'s for the thermal parameters and were much less for the coordinates. In spite of the fact that there were four marginally negative U_{ii} in the first set as against two in the second set, the final atomic parameters have been taken as those of the first set. This is because, out of the eight layers of data, three were collected with Cu$K\alpha$ radiation and five with Mo$K\alpha$; and it is to be expected that errors due to the difference in absorption of the two radiations will be partly compensated by the individual scale factors.

An attempt to locate the hydrogen atom by computing a three-dimensional difference synthesis was rather unsuccessful. A least-squares cycle was also carried out with the hydrogen atom at an initial position suggested by SAHL (1966) on the basis of his measurement of the pleochroism of the OH stretching frequencies in datolite. Although the position suggested by him appears to be very reasonable, no useful results were obtained.

Results and discussion

The revised coordinates and their e.s.d.'s are given in Table 1. There have been changes of up to 0.06 Å as compared with the results of ITO and MORI, the maximum change being to the boron atom. The e.s.d.'s are those given by the inversion of the full matrix. The anisotropic vibration parameters are not given as they seem to be considerably affected by the neglect of absorption; the apparent

Table 1. *Final fractional coordinates and estimated standard deviations*

	x	y	z
Ca	0.9926(6)	0.1049(4)	0.3365(3)
Si	0.4707(8)	0.2663(6)	0.0845(4)
B	0.5874(52)	0.4060(27)	0.3442(20)
O(1)	0.2411(24)	0.3991(16)	0.0395(13)
O(2)	0.6840(20)	0.2956(18)	0.4573(11)
O(3)	0.6903(23)	0.3305(17)	0.2101(11)
O(4)	0.3193(25)	0.0865(14)	0.1439(13)
O(5)	0.2655(23)	0.4133(15)	0.3361(11)

Table 2. *Bond lengths and angles*

Si —O(1)	1.563 ± 0.012 Å	O(1) —Si—O(2′)	114.81 ± 0.65°
Si —O(2′)	1.671 ± 0.011	O(1) —Si—O(3)	117.42 ± 0.67
Si —O(3)	1.679 ± 0.011	O(1) —Si—O(4)	108.32 ± 0.64
Si —O(4)	1.653 ± 0.011	O(2′)—Si—O(3)	102.58 ± 0.56
O(1) —O(2′)	2.724	O(2′)—Si—O(4)	107.17 ± 0.67
O(1) —O(3)	2.770	O(3) —Si—O(4)	105.77 ± 0.63
O(1) —O(4)	2.607		
O(2′)—O(3)	2.614		
O(2′)—O(4)	2.675		
O(3) —O(4)	2.658		
B —O(2)	1.450 ± 0.022	O(2) —B—O(3)	108.51 ± 1.53
B —O(3)	1.499 ± 0.022	O(2) —B—O(4′)	112.86 ± 1.57
B —O(4′)	1.449 ± 0.022	O(2) —B—O(5)	112.24 ± 1.49
B —O(5)	1.561 ± 0.027	O(3) —B—O(4′)	109.04 ± 1.51
O(2) —O(3)	2.393	O(3) —B—O(5)	107.72 ± 1.41
O(2) —O(4′)	2.415	O(4′)—B—O(5)	106.32 ± 1.50
O(2) —O(5)	2.500		
O(3) —O(4′)	2.401		
O(3) —O(5)	2.471		
O(4′)—O(5)	2.410		
Ca—O(1′)	2.271	Si—O(3) —B	121.30 ± 1.17
Ca—O(1″)	2.291	Si—O(2′)—B	120.92 ± 1.17
Ca—O(2)	2.386	Si—O(4) —B	132.19 ± 1.21
Ca—O(3)	2.559		
Ca—O(3′)	2.628		
Ca—O(4″)	2.443		
Ca—O(5′)	2.691		
Ca—O(5″)	2.535		

average mean-square vibration amplitudes were approximately 0.005 Å^2 for calcium and silicon, 0.011 Å^2 for oxygen and 0.017 Å^2 for boron. Table 2 shows the revised distances and angles. They are not significantly different from the values of Ito and Mori and, as such, confirm their results rather than those of Pavlov and Belov.

(*a*) Description of the structure

Datolite is a sheet structure built up from alternating silicate and borate tetrahedra (see Fig. 1). As pointed out by Ito and Mori, and later classified by Zoltai (1960), datolite belongs to the apophyllite structure family. In each tetrahedron one oxygen is one coordinate, and three oxygens are two coordinate, giving a mean oxygen coordination of 1.75 — the sharing coefficient in Zoltai's classification. The tetrahedra form rings, or loops, of four and eight tetrahedra. Each sheet extends parallel to (100) and is held to the adjacent sheets through Ca atoms, each of which is surrounded by six oxygens and two hydroxyl oxygens. The Ca atom lies almost in the (100) plane

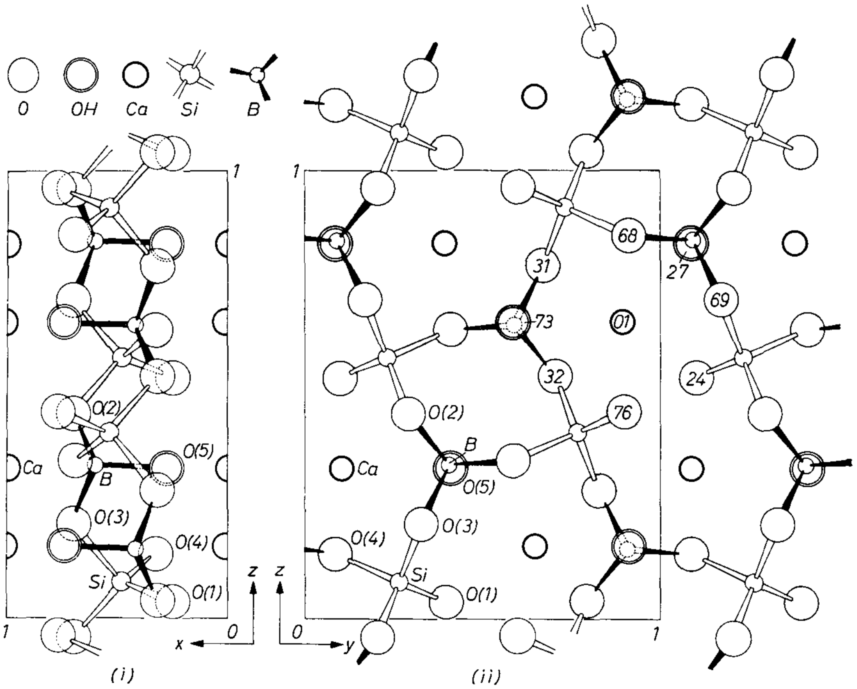

Fig. 1. Projection of the structure, (i) along [010] showing the linking of the sheets through the calcium atoms, and (ii) along [100] showing alternating silicon and boron tetrahedra. Numbers give the heights of the atoms in hundredths of the cell dimension

through the origin; three oxygens and one hydroxyl oxygen lie at an average fractional height of 0.28 in an almost square configuration, whereas the other three oxygens and the other hydroxyl oxygen lie at —0.28, also in an almost square configuration, but twisted with respect to the first by about 45°. The individual Ca···O distances vary between 2.27 and 2.63 Å, while the two Ca···O(H) distances are 2.69 and 2.53 Å. Two of the Ca···O distances (2.27 and 2.29 Å) are slightly less than the expected sum of ionic radii, 0.99 + 1.40 = 2.39 Å.

(*b*) Bond lengths and angles in the SiO_4 and $BO_3O(H)$ tetrahedra

The bond lengths and angles in the silicon and boron tetrahedra are given in Table 2. The bridging Si—O bonds, of mean length 1.668 ± 0.007 Å, and the peripheral ones, of length 1.563 ± 0.012 Å, show an unusually large difference, perhaps the largest known so far in any silicate structure, suggesting thereby appreciable π bonding. Although such large differences are not normally observed in silicate structures for reasons already discussed in the introduction, similar trends have been observed in some structures with relatively small values for the angles at the bridging oxygens. As also remarked earlier, large differences are to be expected in datolite, where the Si—O(br)—B angles average 125°. For Na_2SiO_3 (McDonald and Cruickshank, 1967) corresponding dimensions are 1.672 ± 0.005, 1.592 ± 0.004 Å and ~134° and for α $Na_2Si_2O_5$ (Pant and Cruickshank, 1967) the means are 1.630 ± 0.002, 1.578 ± 0.004 Å and ~ 146°. These results show the correlation between the angle at the bridging oxygen and the difference in length between the two types of bonds.

There is a marked distortion of the angles at Si from the tetrahedral value; the largest, O(1)—Si—O(3) = 117.4°, involves O(1), the non-bridging oxygen, while the smallest, O(2′)—Si—O(3) = 102.6°, does not. These distortions are in the same directions as in Na_2SiO_3 and α $Na_2Si_2O_5$; plots of the mean lengths of any pair of bonds forming an angle at Si against O···O fit the general curve given by McDonald and Cruickshank (1967).

In the $BO_3O(H)$ tetrahedra the B—O(5) bond of length 1.561 ± 0.027 Å is significantly longer than the average, 1.466 ± 0.013 Å, of the other three almost equal lengths. In a number of accurate borate structures {$K[B_5O_6(OH)_4]\cdot 2H_2O$ by Zachariasen and Plettinger

(1963); γ HBO_2 by ZACHARIASEN (1963*a*); β HBO_2 by ZACHARIASEN (1963*b*); CaB_2O_4 by MAREZIO, PLETTINGER and ZACHARIASEN (1963)} B—O bonds have been shown to be very variable in length, although the mean lengths of 1.365 Å in the triangles, and 1.475 Å in the tetrahedra, are good constants. One can regard the borates as a class where the bond orders at any boron must add up to 3, whereas in aromatic hydrocarbons the bond orders must add up to 4 at any carbon. In the hydrocarbons the variability is in the π-bond strengths, in the borates the variability is in the σ-bond strengths (and with triangular boron possibly also in the π-bond strengths).

ZACHARIASEN's (1963*b*) paper on monoclinic metaboric acid, β HBO_2, discusses the structure in terms of PAULING's bond strengths (1929), which are based on the idea of the balance of electrostatic valences (as required by lines of force). ZACHARIASEN suggested that the observed bond lengths r_{ij} uniquely determine the bond strengths v_{ij}. On the basis of a number of boron-oxygen and hydrogen-oxygen bond lengths, he has given a table correlating these lengths and their bond strengths.

Applied to datolite these bond-strength considerations explain qualitatively not only the various B—O distances, but also quite elegantly the Si—O distances and the large differences in the various Ca···O distances. If we assign bond strengths of 0.75 to a tetrahedral B—O bond, 1.00 to a H—O bond, 1.00 to a Si—O bond and 0.25 to a Ca···O link, then O(1) is highly 'underbonded' and O(3) and O(5) are 'overbonded' (Table 3). These get balanced in the actual structure by: (i) the shortening of the Si—O(1) (1.563 ± 0.012 Å) and the two Ca···O(1) (2.27 and 2.29 Å) distances, (ii) the slight lengthening of the two Ca···O(3) (2.56 and 2.63 Å) distances, and (iii) the increases in the B—O(5) (1.561 ± 0.027 Å) and the two Ca···O(5) (2.69 and 2.54 Å) distances.

There could be possibly two objections to an explanation of this sort if it is regarded in purely electrostatic terms. First B—O and Si—O bonds are typically only 44% and 51% ionic respectively, and second, such an explanation would fail completely in a compound with X—X bonds. In the present type of heteroatom problem the electrostatic valences are exactly equal to the typical covalences (Si = 4, B = 3, O = 2, H = 1), so we should expect a balancing of valences whether the bonds are ionic or covalent or a mixture. Thus the success of ZACHARIASEN's descriptive method does not compel us to regard any bonds as ionic.

Table 3. *Valence balance in* $CaBSiO_4(OH)$

(*a*) Unbalanced

	Si	B	H	Ca	$\Sigma_i v_{ij}$
O(1)	1.00	—	—	$2 \times \frac{1}{4}$	1.50
O(2)	1.00	0.75	—	$\frac{1}{4}$	2.00
O(3)	1.00	0.75	—	$2 \times \frac{1}{4}$	2.25
O(4)	1.00	0.75	—	$\frac{1}{4}$	2.00
O(5)	—	0.75	1.00	$2 \times \frac{1}{4}$	2.25
$\Sigma_j v_{ij}$	4.00	3.00	1.00	2.00	10.00

(*b*) Suggested balance

	Si	B	H	Ca	$\Sigma_i v_{ij}$
O(1)	1.30	—	—	2×0.35	2.00
O(2)	0.90	0.80	—	0.25	1.95
O(3)	0.90	0.74	—	2×0.20	2.04
O(4)	0.90	0.80	—	0.25	1.95
O(5)	—	0.66	1.00	2×0.20	2.06
$\Sigma_j v_{ij}$	4.00	3.00	1.00	2.00	10.00

In short, the above discussion regarding the variation of Si—O and B—O lengths in datolite amounts to: (i) variable B—O σ-bond strengths, which may be part covalent and part ionic; (ii) variable Si—O bond strengths; (iii) appreciable sharing of the oxygen valences with the calcium atoms. Since we have to introduce variable σ-bond strengths for the B—O bonds, the question arises as to whether the Si—O lengths could be explained in terms solely of variable σ-bond strengths without any introduction of the idea of π-bonding contributions. This question was also discussed for Na_2SiO_3 by McDONALD and CRUICKSHANK (1967) who concluded that the π-bonding theory could be retained as a working hypothesis. This theory has the merit of suggesting, without consideration of the cations, which Si—O bonds are likely to be short and which long; and it provides a mechanism for the variations in length. However, the correctness of the π-bonding idea is certainly not proved, and further investigations are needed, particularly on sets of similar compounds with different cations.

A very obvious conclusion from the present study is that the cations have an important effect on the Si—O bonds, even though the individual Ca···O links are weak compared with the Si—O and B—O bonds. McDONALD and CRUICKSHANK noted that silicate 'ions' have a tendency to shed their negative charge through the formation of partial covalent bonds to cations, particularly to those of low electropositive character. However they do not seem to have appreciated that the cation links would retain their importance in the balance of bond strengths in a structure such as datolite with cations of high electropositive character. In fact, ITO and MORI (1953) noted that datolite, in spite of its sheet-like structure, has no conspicuous cleavage. It appears that the Ca···O links play a significant role in this property, as these are the only links holding the sheets together (see Fig. 1). It may be pertinent that the shortest Ca···O distances of 2.27 and 2.29 Å are shorter than the usual sum of ionic radii.

In the following sections the structures of herderite and gadolinite, which are similar to datolite, are discussed on the basis of the balancing of valences.

(c) On the structure of herderite

PAVLOV and BELOV (1959) also reported a structure determination of herderite, $CaBePO_4F$, which is iso-typic with datolite. The replacement of "$Be^{2+}P^{5+}$" by "$B^{3+}Si^{4+}$" corresponds to a change from the smaller PO_4 tetrahedron (edge ~2.50 Å) to the larger SiO_4 group (edge ~2.61 Å), and this change is matched by the change from the larger BeO_3F tetrahedron (edge ~2.64 Å) to the smaller $BO_3(OH)$ group (edge ~2.45 Å). By simple analogy with datolite, one might expect that the phosphate tetrahedron would show bond-length inequalities towards those in triphenyl phosphate (SVETICH and CAUGHLAN, 1965) or P_4O_{10} (BEAGLEY, CRUICKSHANK, HEWITT and HAALAND, 1967). The level of refinement by PAVLOV and BELOV is insufficient to show whether this is true; however there are reasons for thinking that the phosphate tetrahedron in herderite may be more regular than the silicate tetrahedron in datolite. On PAULING's scale (1960) the Be—O bonds (63 %) ionic) in herderite are 24 % more ionic than the P—O bonds (39 %), whereas the B—O bonds (44 %) in datolite are 7 % less ionic than the Si—O bonds (51 %). Further, the Be—O bonds (63 %) are nearly as ionic as the Ca···O links, so that the four oxygens of the phosphate tetrahedron are subject to rather equal influences; and, therefore, relatively little difference is to be expected in the lengths of the two sorts of P—O bond.

If we assign bond strengths of 0.5 to tetrahedral Be—O and Be—F bonds, 1.25 to a P—O bond and 0.25 to a Ca···O link, then O(3) would be "overbonded" and O(1) "underbonded". In the actual structure the two Ca···O(1) are the shortest links (both are 2.40 Å), and P—O(1) (1.51 Å), although shortest, is equal to P—O(4) (1.51 Å, e.s.d.'s 0.015 Å); also the two Ca···O(3) distances (2.61 and 2.70 Å) and the P—O(3) bond (1.57 ± 0.015 Å) are the longest, thus balancing the bond strengths. P—O(3) certainly has the expected length but P—O(1) might have been shorter. However, it is hard to discuss the structure of herderite in more detail as the estimated standard deviations of the various bond lengths and angles are rather high.

(*d*) On the structure of gadolinite

As pointed out by Ito and Mori (1953), and later confirmed by Pavlov and Belov (1959), the structure of gadolinite may be derived from that of datolite simply by replacing calcium by yttrium, boron by beryllium and OH by oxygen, and placing in addition iron at (0 0 0) and ($0\ \frac{1}{2}\ \frac{1}{2}$). By assigning bond strengths of 0.5 to a tetrahedral Be—O bond, 1.0 to a tetrahedral Si—O bond and $\frac{3}{8}$ to Y—O and $\frac{1}{3}$ to Fe—O links, one finds that O(1), $1\frac{3}{4}$, and O(5), $1\frac{7}{12}$, would be 'underbonded', whereas O(2), $2\frac{5}{24}$, O(3), $2\frac{6}{24}$, and O(4), $2\frac{5}{24}$, would be 'overbonded'. We should, therefore, expect that the Si—O(1) and Be—O(5) bonds would be short in gadolinite also. Pavlov and Belov's suggestion that Fe—O(5) = 2.18 Å seems unlikely, since O(5) needs short Fe—O(5) bonds.

It is useful to add here that the variation of bond lengths in the structures of Na_2SiO_3 and α $Na_2Si_2O_5$, which have been discussed elsewhere (Pant and Cruickshank, 1967), can also be accounted for using the principle of the balancing of valences.

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