HOW TO RECOGNIZE O^{2-}, OH^-, AND H_2O IN CRYSTAL STRUCTURES DETERMINED BY X-RAYS

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ABSTRACT

A double-entry table of cation-to-anion bond lengths and associated bond valences leads to valence sums for the oxygen anions. Such a sum is approximately equal to 2 for an oxygen ion, 1 for a hydroxyl ion, and 0 for a water molecule. The deviation from the integral value gives information about hydrogen bonding. An empirical curve expresses bond valence v in terms of bond length L. It is based on two equations:

$$(1) \quad \text{For } L \leq \overline{L}, \quad v = v_i\left(\frac{\overline{L}}{L}\right)^p; \qquad (2) \quad \text{for } \overline{L} \leq L \leq L_{max}, \quad v = v_i\left(\frac{L_{max} - L}{L_{max} - \overline{L}}\right),$$

where $\overline{L}$ is the mean bond length of the cation polyhedron found in the structure under consideration; L_{max} is the largest cation-anion distance that will still be considered a bond; v_i is the ideal bond valence, i.e. formal cationic charge divided by coordination number. Values of L_{max} for common cation-oxygen distances are tabulated. By imposing the condition that the two curve segments have equal slope at their common point ($L=\overline{L}$, $v=v_i$), p is found to be equal to $\overline{L}/(L_{max}-\overline{L})$. The procedure is applied to sonoraite, grunerite and bultfonteinite.

INTRODUCTION

It frequently happens that the chemical analysis of a new mineral cannot distinguish hydroxyl groups from water molecules incorporated in the crystal structure. A crystal-structure determination will locate all oxygen ions, but unless extreme care is taken in data collecting, will not detect protons. Neutron-diffraction data will give hydrogen positions, but are not readily available. This paper draws attention to the fact that Pauling's principle of local neutralization of charge (Pauling, 1929) can solve the problem at hand. Evans and Mrose (1960), Evans (1960), Zachariasen (1963), and Pant and Cruickshank (1967) have described similar approaches for vanadates, borates, and silicates. Our procedure is applicable to all but molecular structures.

PROCEDURE

Sonoraite (Gaines, Donnay, and Hey, 1968), whose structure determination was recently completed (Donnay, Stewart, and Preston, 1970), will be used first to illustrate the principles. The chemical analysis of sonoraite shows that the only cations, Fe^{3+} and Te^{4+}, are present in the

Dedicated to Professor James D. McCullough for his 65th birthday

atomic ratio 1:1. The only other product of the analysis is water. The electron-density map reveals eight Fe and eight Te ions in the fourfold general position of space group $P2_1/c$ and, in addition, forty oxygen ions, also in general position. With $Z=4$ the chemical formula must thus be written $Fe_2Te_2O_{10}H_6$, the six protons being needed to balance the charges. We now have to choose between the structural formulae $Fe_2Te_2O_4(OH)_6$, $Fe_2Te_2O_5(OH)_4 \cdot H_2O$, $Fe_2Te_2O_6(OH)_2 \cdot 2H_2O$, and $Fe_2Te_2O_7 \cdot 3H_2O$. With the structure determination completed, with residual R for 1884 reflections equal to 6.2 percent and bond lengths known to better than 1 percent (Table 1), we proceed on the reasonable assumption that the bond length L uniquely determines the bond valence v, and we estimate the bond valences from observed bond lengths.

Pauling (1947) gave the equation $D(n) = D(1) - 0.600 \log n$, with $D(1)$ denoting the sum of single-bond radii of the two atoms plus the correction for the difference in electronegativity and n the fractional bond number. It has been applied successfully mainly to metallic and metallic-covalent bonds as in sulfide minerals (Pauling, 1970). The following two empirical equations represent approximations to Pauling's equation; we have found them easy to use and satisfactory for mineral crystal structures. The relation between L and v is given by two curve segments:

$$\text{For } L \leq \overline{L}, \qquad v = v_i \left(\frac{\overline{L}}{L} \right)^p \qquad (1)$$

$$\text{For } \overline{L} \leq L \leq L_{\max}, \qquad v = v_i \frac{L_{\max} - L}{L_{\max} - \overline{L}} \qquad (2)$$

where v_i is the ideal bond valence, defined as the quotient of the cationic charge by the coordination number (CN), and $L_{\max}$ (see Table 2) is the upper limit of an atomic approach that will still be counted as an interatomic bond, so that CN is the number of anions at distances smaller than $L_{\max}$ from the cation. The average bond length, $\overline{L}$, is the mean value determined for each coordination polyhedron in the structure at hand, so that its use enables us to adapt the curve to the bonding actually encountered. Should $\overline{L}$ differ appreciably for two or more chemically identical but crystallographically different cations, a distinct curve is constructed and used for each one to obtain its bond valences.

For Fe—O in sonoraite (Table 1) $\overline{L}$ has the values 2.013 and 2.017 Å for Fe(1) and Fe(2), so that a mean of 2.015 Å is well within the experimental error of each, and only one curve of bond valence vs Fe—O bond length is needed. The ideal bond valence v_i is equal to 3/6 for $^{vi}Fe^{3+}$. (The Roman numeral denotes the coordination number.) The value of p in (1) is obtained by imposing the condition that the slope dv/dL be the same

TABLE 1. BOND LENGTHS (Å) AND ESTIMATED BOND VALENCES (V.U.)
IN SONORAITE, $FE_2TE_2O_6(OH)_2 \cdot 2H_2O$

Anions numbered	^{iii}Te(1)	^{iii}Te(2)	^{vi}Fe(1)	^{vi}Fe(2)	Σ_{Cv}	Anion chemistry	Σ_{Cv} for H bonds
^{iii}O(1)				2.163 (15)		H_2O	
				0.31	0.31		−0.10
^{iv}O(2)				⎛2.015 (11)		OH^-	
				⎜0.50	1.01		0.95
				⎜2.009 (12)			
				⎝0.51			
^{iii}O(3)	1.888 (13)			1.943 (14)		O^{2-}	
	1.33			0.61	1.94		2.11
^{iii}O(4)			2.000 (12)	1.983 (10)		OH^-	
			0.52	0.54	1.06		1.06
^{ii}O(5)		1.857 (12)	1.938 (11)			O^{2-}	
		1.42	0.61		2.03		2.03
^{iii}O(6)	1.893 (10)			1.990 (12)		O^{2-}	
	1.32			0.53	1.85		2.09
^{iii}O(7)					0	H_2O	−0.08
^{iii}O(8)		1.905 (11)	2.061 (11) ⎞			O^{2-}	
		1.28	0.44 ⎟		2.17		2.17
			2.055 (12) ⎟				
			0.45 ⎠				
^{iii}O(9)	1.895 (13)		2.040 (12)			O^{2-}	
	1.31		0.47		1.78		1.92
^{ii}O(10)		1.890 (11)	1.983 (11)			O^{2-}	
		1.33	0.54		1.87		1.87
Average bond length $\overline{L}$	1.892	1.884	2.013	2.017			
Σ_{Av}	3.96	4.03	3.03	3.00			

Σ_{Av} = valences of bonds emanating from cation summed over the bonded anions.
Σ_{Cv} = valences of bonds reaching anion.
Standard deviation between parentheses in units of the third decimal.
The coordination numbers of the anions include the hydrogen bonds of Table 3.

for both curve segments (1) and (2) at their common point $L = \overline{L}$, $v = v_i$. It follows that

$$p = \frac{\overline{L}}{L_{max} - \overline{L}}. \tag{3}$$

Finally, the valence is set equal to zero for all L values larger than the chosen L_{max}, which is obtained as follows. When two or more "effective ionic radii" are available, one for each observed CN (Shannon and Prewitt, 1969), we plot the v_i values against the ionic radii and extrapolate the curve to $v = 0$, which corresponds to the *maximum radius* r_{max} of the cation. With few exceptions (Ag^+, Cd^{2+}, Tl^+, and Pb^{2+}), r_{max} is less than the corresponding metallic radius (Evans, 1966) or "atomic radius" (Slater, 1964) by $0.1 - 0.5$ Å. To r_{max} of the cation we add the maximum radius of the anion (for oxygen $r_{max} = 1.45$ Å, for fluorine $r_{max} = 1.38$ Å, values obtained by extrapolation from the radii given in Table 2 of Shan-

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TABLE 2. MAXIMUM BOND LENGTHS, L_{max} (Å), FOR Me—(O,OH) BONDS

H							
1.47							

Li	Be	B					
2.48	2.02	1.87					

Na	Mg	Al		Si			
3.13	2.85	2.26		2.13			

K	Ca	Sc	Ti	V	Cr	Mn	
						II　III	
3.33	3.25	2.74	2.43	2.36	~2.40	2.65　2.45	

	Cu II	Zn	Ga	Ge	As		
	2.50	2.50	2.40	2.29	2.28		

Rb	Sr	Y	Zr	Nb	Mo		
3.43	3.27	3.05	2.65	2.56	2.70		

	Ag I	Cd	In	Sn	Sb III	Te IV	
	3.15	3.00	2.77	~2.70	~2.65	~2.35	

Cs	Ba	La	Hf	Ta	W		
3.63	3.43	3.05	2.65	~2.60	~2.70		

		Tl		Pb		Bi III	
		I　　III		II　　IV			
		3.50　2.81		3.35　2.78		2.83	

Ce III: 3.02　IV: 2.93　Th IV: 2.75, U IV, VI: 2.75,　Fe II: 2.50 III: 2.40　Co II: ~2.45, Ni II: ~2.40

Estimated values obtained by extrapolating the *effective ionic radii* of Shannon and Prewitt (1969) to r_{max} and adding 1.45 Å for oxygen radius.

To get maximum bond length of Me-F subtract 0.07 Å from that of Me-(O,OH).

non and Prewitt, 1969) to obtain L_{max} (Table 2). These values are less than the sums of the van der Waals radii by about 0.25 Å on the average. We have observed that our L_{max} values appear too large, for example, when d-p π bonding strengthens a Si—O bond (Brown, Gibbs, and Ribbe, 1969). However, for the present purpose of finding protons, accurate L_{max} values are not required.

In the case of Fe^{3+} with high spin, Shannon and Prewitt give 0.49 Å for the effective ionic radius of $^{iv}Fe^{3+}$ and 0.645 Å for that of $^{vi}Fe^{3+}$. These being the only two available radii, the extrapolation must necessarily be linear; it gives an r_{max} for Fe^{3+} of 0.955 Å and an L_{max} for Fe^{3+}—O of 2.40 Å. Substituting in (3) gives

$$p(\text{Fe}-\text{O}) = \frac{2.015}{2.405 - 2.015} = 5.17 \cdot$$

The curve of v *vs* L can now be constructed for Fe—O (Fig. 1) using
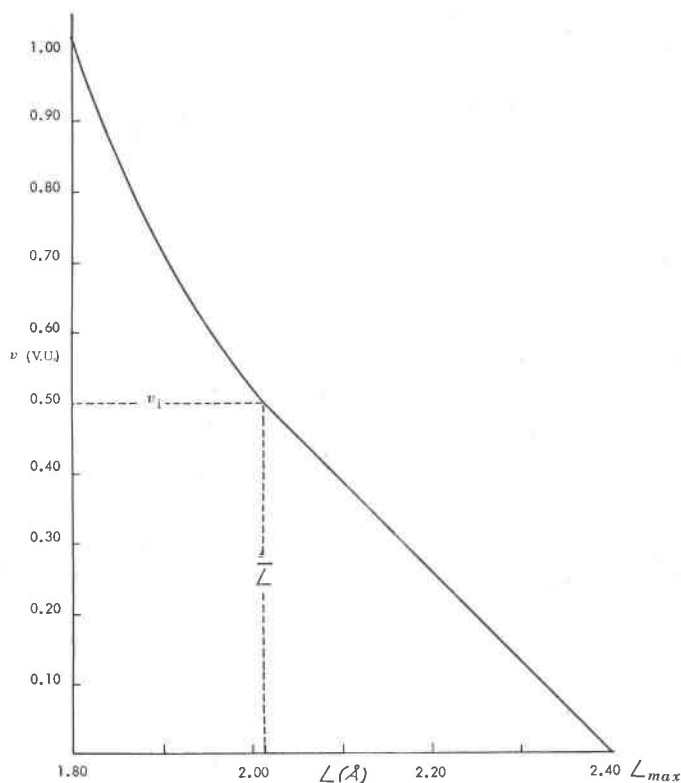
FIG. 1. Bond valence v vs bond length L for Fe^{3+}—O^{2-} in sonoraite.

equations (1) and (2). The desired valences for the Fe—O bonds in the sonoraite structure (Table 1) are read from this curve or calculated from equations (1) and (2).

For $^{iii}Te^{4+}$—O the two observed $\overline{L}$ values, 1.892 and 1.884 Å (Table 1), are also close enough so that their average (1.888 Å) can be used in the construction of one curve of bond valence vs bond length. The magnitude of L_{max} is 2.35 Å (Table 2), and the resulting p is 4.09.

The valence sum, $\Sigma_C v$, of bonds reaching each anion (Table 1) gives the answer to our question of the hydrogen distribution in the sonoraite structure: O(1) and O(7) belong to water molecules; O(2) and O(4) belong to hydroxyl groups; the remaining anions are oxygen ions. The formula is thus found to be $Fe_2Te_2O_6(OH)_2 \cdot 2H_2O$, with 4 formula units per cell.

The substantial deviations of $\Sigma_C v$ values from the integers 0, 1 and 2 indicate the presence of hydrogen bonding, which is borne out by

TABLE 3. SHORT OXYGEN—OXYGEN DISTANCES (Å) AND ESTIMATED
HYDROGEN-BOND VALENCES (V.U.) IN SONORAITE

Acceptor \ Donor	$H_2O(1)$		$H_2O(7)$		$\Sigma_H v$
O(2) H			3.03;	0.09 ⎫	−0.06
O(2)‴H			2.85;	−0.15 ⎭	
O(3)″	2.80;	0.17			0.17
O(6)‴	2.62;	0.24			0.24
O(9)″			2.87;	0.14	0.14
$\Sigma_A v$	0.41		0.08		

$\Sigma_H v$ = sum of valences donated by hydrogen ions of water molecules.
$\Sigma_A v$ = sum of valences accepted by oxygen ions.
Estimated bond valences based on Table 4.

Unprimed atoms with coordinates x, y, z belong to the chosen asymmetric unit. The primed atoms have coordinates $\bar{x}$, $\bar{y}$, $\bar{z}$; the doubly primed atoms, $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; the triply primed atoms, x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

oxygen-oxygen approaches of less than 3.2 Å between oxygen ions that are not bonded to the same cation (Table 3). The values of hydrogen-bond valence vs oxygen-oxygen separation (Table 4) are taken equal to the effective fractional charge on non-equivalent oxygen atoms in a linear hydrogen bond, as calculated by Lippincott and Schroeder (1955, Fig. 5). The v values for H—O_2 thus obtained tend to be too high when the bond is bent, rather than linear, which is the rule rather than the exception. If one of the two oxygen ions in a pair does not belong to either a hydroxyl group or a water molecule, then it can only be an acceptor ion. Thus, its valence sum must be increased by the amount due

TABLE 4. H—O_2 BOND VALENCE OF ASYMMETRIC, LINEAR O_1—H—O_2 BOND.
(AFTER LIPPINCOTT AND SCHROEDER, 1955, FIG. 5)

O_1—O_2 distance (Å)	H—O_2 valence (v.u.)
3.2	0.060
3.1	0.080
3.0	0.100
2.9	0.130
2.8	0.165
2.7	0.210
2.6	0.255
2.5	0.310

to the hydrogen bond, and the valence sum of the donor oxygen ion must be decreased by the same amount. This is the case for O(3), O(6), and O(9) (Table 3), which would receive 0.17, 0.24, and 0.14 v.u. respectively, if their hydrogen bonds were linear. A close approach involving only hydroxyl and water oxygen ions does not permit a straightforward decision on the donor and acceptor roles, since each oxygen ion could play either role. The decision can usually be reached on the basis of local charge neutralization, in view of the fact that the maximum number of hydrogen bonds per oxygen ion is four. In the case of sonoraite, O(7), which can only be the donor ion for O(9)″, should be the donor for O(2) and the acceptor for O(2)‴H. Thus $H_2O(7)$ is involved in three hydrogen bonds; if these were all linear bonds, O(7) would show a slight excess valence of 0.08 unit.

Bond-valence considerations can thus be used not only to identify the number of protons associated with the anions, but to obtain information on the asymmetric hydrogen bonding in the crystal structure.

Bond-valence tables for two other examples, grunerite (Finger, 1969) and bultfonteinite (McIver, 1963), will illustrate complications frequently encountered in mineral structures, such as cation and anion substitutions and symmetrical hydrogen bonding.

Grunerite

The grunerite specimen studied by Finger (1969) has a chemically analyzed composition approximated by $(Fe_{6.2}Mg_{0.8})Si_8O_{22}((OH)_{1.5}F_{0.5})$. Grunerite crystallizes in $C2/m$ with two formula units per cell. The cations distribute themselves among four positions—$M(1)$, $M(2)$, $M(3)$, $M(4)$—of which the last contains only ferrous iron, whereas the other three contain some magnesium in addition to iron. The Fe:Mg ratios were evaluated from least-squares refinement coupled with chemical restraints (Finger, 1968). The published bond lengths show that the cations in $M(1)$, $M(2)$, and $M(3)$ have six nearest anion neighbors within L_{max} (2.6 Å) for (Fe, Mg)—O (Table 2), but Fe^{2+} in M(4) has only four neighbors at distances less than 2.50 Å, which is the L_{max} value for Fe^{2+}—O (Table 2). Two more bonds, $M(4)$—O(6), of 2.757(5) Å each, are included in Finger's Table 4 and play a role in his discussion of the structure. In the present treatment, however, since they exceed L_{max}, they cannot be considered bonds.

When we speak of the valence of an (Fe, Mg)—(O, OH, F) bond, we mean, of course, the weighted average of the valence contributions of Fe—(O, OH), Fe—F, Mg—(O, OH), and Mg—F. To obtain the proper L_{max} we accept the occupancies found from the X-ray results and weight the various L_{max} of Table 2 accordingly. The L_{max} of a bond issuing from

TABLE 5. BOND LENGTHS (Å) AND ESTIMATED BOND VALENCES (V.U.)
IN GRUNERITE, $(Fe_{6.2}Mg_{0.8})Si_8O_{22}[(OH)_{1.5}F_{0.5}]$

Anions (numbered)	$^{vi}M(1)$	$^{vi}M(2)$	$^{vi}M3)$	$^{iv}M(4)$	$^{iv}Si(1)$	$^{iv}Si(2)$	$\Sigma_C v$	Anion chemistry
		At. % Mg						
	15.2 (8)	22.7 (7)	11.2 (12)	1.5 (8) ~0				
$^{iv}O(1)$	2x 2.082 (5)	2x 2.161 (5)	4x 2.118 (5)		1.637 (4)			
	0.36	0.30	0.33		0.97		1.96	O^{2-}
$^{iv}O(2)$	2x 2.160 (4)	2x 2.128 (4)		2x 2.135 (5)		1.633 (4)		
	0.30	0.33		0.42		0.98	2.03	O^{2-}
$^{iii}O(3)$	2x 2x 2.122 (4)		2x 2.103 (6)					75 at. % OH
	0.33		0.34				1.00	25 at. % F
$^{iii}O(4)$		2x 2.075 (4)		2x 1.988 (4)		1.604 (4)		
		0.37		0.59		1.04	2.00	O^{2-}
$^{ii}O(5)$					1.627 (5)	1.611 (5)		
					0.99	1.03	2.02	O^{2-}
$^{ii}O(6)$					1.630 (4)	1.638 (5)		
					0.99	0.97	1.96	O^{2-}
$^{ii}O(7)$					2x 1.613 (2)			
					1.02		2.04	O^{2-}
Average bond length $\bar{L}$	2.121	2.121	2.113	2.062	1.627	1.622		
$\Sigma_A v$	1.98	2.00	2.00	2.02	3.97	4.02		

The numbers in the upper left corners give the number of identical bonds reaching the anion; the numbers in the upper right corners give the number of identical bonds emanating from the cation.

The CN of O(3) does not include the H atom.

$M(1)$, for instance, is calculated as follows. The cation is $(Fe^{2+}_{0.848} Mg_{0.162})$ and it is bonded to 11/2 (O, OH) ions and 1/2 F^- ion. The appropriate weighting gives

$$L_{max} = \frac{11}{12} \left[0.152 \times (Mg–O)_{max} + 0.848(Fe–O)_{max} \right]$$

$$+ \frac{1}{12} \left[0.152 \times (Mg–F)_{max} + 0.848(Fe–F)_{max} \right] = 2.547 \text{ Å}.$$

$M(3)$ is analogous to $M(1)$, except for a change in fractional occupancies.

TABLE 6. PARAMETERS USED TO CONSTRUCT CURVES OF BOND
VALENCE *vs* BOND LENGTH FOR GRUNERITE

Cation-Anion	$\bar{L}$(Å)	v_i (v.u.)	L_{max}(Å)	p
$^{vi}M(1)$—(O, OH, F)	2.121	0.33	2.547	4.98
$^{vi}M(2)$—O	2.121	0.33	2.579	4.63
$^{vi}M(3)$—(O, OH, F)⎰	2.113	0.33	2.533	5.03
$^{iv}M(4)$—O	2.062	0.50	2.50	4.71
^{iv}Si—O	1.624	1.00	2.13	3.21

In $M(2)$ the fluorine complication does not enter. The parameters used
to construct the necessary curves for grunerite (Table 6) are so similar
for $M(1)$, $M(2)$, and $M(3)$ that the valences read for the observed dis-
tances are practically indistinguishable. This will not generally be the
case, of course, for positions that differ in occupancy, especially if the
observed bond lengths depart more from $\bar{L}$ than they do here. Only one
curve is needed for the two Si positions, because their $\bar{L}$ values, 1.627
and 1.622 Å, are close enough to be replaced by the average value of
1.624 Å.

The valence sums $\Sigma_C v$ (Table 5) are satisfactory: the maximum devia-
tion from the formal valence is 0.04 v.u. There is, thus, no indication
of any hydrogen bonding between $O(3)$, the (OH^-, F^-) ion, and any other
oxygen ion; indeed no O—O approaches of less than 3.2 Å occur between
oxygen ions that are not bonded to the same cation.

BULTFONTEINITE

The chemical formula of bultfonteinite closely approximates
$Ca_2SiH_3O_5F$. During the structure determination (McIver, 1963), no
assumptions were made concerning the presence of H_2O or anions F^-,
$(OH)^-$, $(OH_{\frac{1}{2}})^{1.5-}$ (Table 7, column 1). The triclinic cell contains four
formula units; all but two hydrogen ions occupy the general 2-fold posi-
tion. There are seven Ca—O distances shorter than $(Ca-O)_{max}$ for each
of the four Ca positions. The preliminary parameters for the curves of
Ca—O and Si—O bond valence *vs* bond length (Table 8) lead to valence
sums $\Sigma_C v$ that are significantly different from the ideal values: 0, 1, 1.5,
2, indicating the presence of extensive hydrogen bonding. Nevertheless,
it is already apparent that $O(1)$ and $O(2)$ are univalent anions, that
$O(3)$ through $O(6)$ are $OH_{\frac{1}{2}}$, that $O(9)$ and $O(10)$ are H_2O molecules, and
that the remaining four anions must be bivalent O; the formula must be
written: $Ca_2Si(OH_{\frac{1}{2}})_2O_2F \cdot H_2O$.

The stoichiometric amount of fluorine in the formula indicates, even
though it does not prove, an ordered distribution of this anion in the

Table 7. Bond Lengths (Å) and Estimated Bond Valences (v.u.) in Bultifonteinite, $Ca_2SiH_3O_5F$

Anions (numbered)	^{vii}Ca(1)	^{vii}Ca(2)	^{vii}Ca(3)	^{vii}Ca(4)	^{iv}Si(1)	^{iv}Si(2)	Σ_{Cv}	Anion chemistry	Σ_{Cv} corrected for H bonds
^{iv}O(1)	2.41;0.28[a]	2.37;0.30	2.31;0.32	2.40;0.29			1.19		
	0.27	0.28	0.30	0.27			1.12	F⁻	1.12
									(0.99)
^{iv}O(2)	2.39;0.29	2.36;0.30	2.30;0.32	2.37;0.30			1.21		
	0.28	0.29	0.31	0.28			1.16	F⁻	1.16
									(1.01)
^{i}O(3)	2.31;0.32					1.67	1.26		
	0.33					0.94	1.27	OH$_{1/2}$	1.46
									(1.47)
^{i}O(4)		2.31;0.32			1.69		1.22		
		0.33			0.90		1.23	OH$_{1/2}$	1.44
									(1.45)
^{iv}O(5)			2.46;0.27		1.64		1.27		
			0.27		1.00		1.27	OH$_{1/2}$	1.47
									(1.49)
^{iv}O(6)				2.49;0.26		1.66	1.22		
				0.26		0.96	1.22	OH$_{1/2}$	1.40
									(1.41)
^{iv}O(7)	2.42;0.28		2.24;0.35						
			0.36			1.67	1.80		
	0.29		2.58;0.23					O²⁻	1.84
			0.23			0.94	1.82		(1.86)
^{iv}O(8)	2.32;0.32		2.40;0.29						
			0.29			1.59	1.96	O²⁻	
			2.52;0.25						1.96
	0.32		0.25			1.10	1.96		(2.01)
^{iv}O(9)	2.53;0.24	2.45;0.27					0.51		
	0.25	0.27					0.52	H$_2$O	0.13
									(0.16)
^{i}O(10)	2.52;0.25	2.47;0.26					0.51		
	0.25	0.27					0.52	H$_2$O	0.13
									(0.15)
^{iv}O(11)		2.34;0.31		2.40;0.29					
		0.31		0.29	1.62		1.90		
				2.47;0.26					
				0.27	1.04		1.91	O²⁻	1.91
									(1.96)
^{iv}O(12)		2.38;0.30		2.28;0.33					
		0.30		0.34	1.60		1.93		
				2.59;0.22					
				0.23	1.08		1.95	O²⁻	1.95
									(2.00)
$\overline{L}$ for Me-(O, F)	2.41	2.38	2.40	2.43	1.64	1.65			
Σ_{Av}	1.99	2.06	2.02	1.95	4.02	3.94			
$\overline{L}$ for Me-F	2.40	2.36$_5$	2.30$_5$	2.38$_5$					
$\overline{L}$ for Me-O	2.42	2.39	2.44	2.45					
	1.99	2.05	2.01	1.94					
Σ_{Av}	(1.99)	(2.06)	(2.02)	(1.95)					

[a] The bond length is followed by the preliminary bond valence estimate.
The second line contains the bond valence which takes anion ordering into account. ($v_i = 2/7$ for Ca—F and Ca—O.)
In parentheses, values resulting from v_i (Ca—F) = 0.25 v.u. and v_i(Ca—O) = 0.30 v.u.

TABLE 8. PARAMETERS USED TO CONSTRUCT CURVES OF BOND
VALENCE *vs* BOND LENGTH FOR BULTFONTEINITE

Cation-Anion	$\overline{L}(\text{Å})$	v_i (v.u.)	$L_{\max}(\text{Å})$	p
^{vii}Ca—(O, F)	2.40_5	2/7	3.25	2.85
^{iv}Si—O	1.64	1.00	2.13	3.35
^{vii}Ca—F	2.36	2/7 (0.25)	3.18	2.88
^{vii}Ca—O	2.42	2/7 (0.30)	3.25	2.92

structure. As McIver (1963) points out, only in positions O(1) and O(2) will fluorine ions be surrounded by almost regular tetrahedra of calcium ions reminiscent of their environment in fluorite, where the Ca—F distance is 2.37 Å as compared with 2.36 Å for $\overline{L}$ of Ca—O(1)+Ca—O(2). The F—F distances are also of the same order of magnitude in the two structures. Accepting this assignment of fluorine ions, we can now plot the curve of bond valence *vs* bond length for Ca—F and reconstruct the one for Ca—O using the corrected $\overline{L}$ (Table 8) but keeping the value of of v_i equal to 2/7 for both types of bonds.

We are ready to take hydrogen bonding into account by scrutinizing all the oxygen approaches that fall below 3.2 Å and are not edges of cation coordination polyhedra (McIver, 1963; Table 3C). Of seven such distances, four are equal to 2.73 ± 0.03 Å and three are equal to 2.48 ± 0.01 Å (Table 9). Distances of less than 2.50 Å shall be considered

TABLE 9. SHORT OXYGEN-OXYGEN DISTANCES (Å) AND ESTIMATED HYDROGEN-
BOND VALENCES (V.U.) IN BULTFONTEINITE

Acceptor \ Donor	$H_2O(9)$	$H_2O(10)$	$O(3)'H_{1/2}$	$O(4)'H_{1/2}$	$O(5)'H_{1/2}$	$O(6)'H_{1/2}$	$\Sigma_H v$
$O(3)H_{1/2}$	2.73 0.19		2.48 ±0.50				0.19
$O(4)H_{1/2}$		2.69 0.21		2.47 ±0.50			0.21
$O(5)H_{1/2}$	2.72 0.20					2.49 ±0.50	0.20
$O(6)H_{1/2}$		2.78 0.18			2.49 ±0.50		0.18
$\Sigma_A v$	0.39	0.39	—	—	—	—	

$\Sigma_A v$ = sum of valences donated by hydrogen ions of water molecules.
$\Sigma_H v$ = sum of valences accepted by oxygen ions.
Estimated bond valences based on Table 4.
Unprimed atoms with coordinates x, y, z belong to the chosen asymmetric unit. The primed atoms have coordinates $\bar{x}$, $\bar{y}$, $\bar{z}$.

symmetrical hydrogen bonds of strength 0.50 v.u. for the two oxygen ions involved in the bonding. This treatment is, of course, arbitrary and may have to be modified in special cases (Hamilton and Ibers, 1968). The necessary corrections for the valence sums $\Sigma_C v$ of Table 7 appear as $\Sigma_A v$ and $\Sigma_C v$ values in Table 9. They fall somewhat short of what would be needed to give the ideal values ($0, 1, 1\frac{1}{2}$, and 2) for the corrected $\Sigma_C v$ (Table 7, last column).

The strikingly regular arrangements of calcium ions about fluorine, mentioned above, may be used as the basis for an alternative definition of v_i for Ca—F as follows: let v_i be the quotient of the anionic charge by the coordination number of the anion, so that it becomes $\frac{1}{4}$ and the value for Ca—O is taken to be $\frac{1}{5} (2.00 - 2 \times \frac{1}{4})$ or 0.30 The resulting magnitudes of $\Sigma_C v$ (last column of Table 7) tend towards their ideal values for all but the water oxygen ions. The discrepancies which remain are not excessive, considering that the standard deviations reported for interatomic distances are ± 0.02 Å. It thus appears advisable to consider the two alternative v_i definitions whenever the anion environment approximates or exceeds the cation environment in regularity and when the chemical nature of the anion is known.

Conclusion

The given relationship between bond valence and bond length has turned out to be serviceable for allocating protons in the various mineral structures to which we have applied it. Admittedly it is a pragmatic approach without much theoretical foundation. It grew out of the observation that Pauling's principle of local neutralization of charge is remarkably well obeyed, regardless of bond type, in all the crystal structures where it can be tested quantitatively because the coordination polyhedra have high enough symmetry. A procedure that permits a general quantitative application of this principle and leads to inferences regarding hydrogen bonding should be worth trying.

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