Silanol groups in minerals and inorganic compounds

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Abstract

The Inorganic Crystal Structure Database (ICSD) was searched for Si-OH groups with ordered H positions leading to 31 structures with 46 Si-OH groups. The geometrical characteristics of these partly hydroxylated SiO_4 tetrahedra were analyzed. Depending on the condensation of the tetrahedra, the protonization of one tetrahedral apex allows variations in Si-O bond lengths and distorts the tetrahedron. The Si-OH distance decreases with the number of bridging O atoms (Si-O-Si) from average values of 1.668 Å for orthosilicates to 1.604 Å for tetrahedra with three bridging O atoms, whereas the ⟨Si-O⟩ distances of the non-hydroxylated Si-O bonds remain constant at 1.62 Å. This behavior was modeled by differences in bond strength sums of the tetrahedral O atoms. In the orthosilicates, the non-hydroxylated tetrahedral apices tend to be underbonded and the O of the silanol group is overbonded to satisfy the charge requirements of Si^{4+}. In contrast, an Si-OH bearing tetrahedron with three bridging O atoms is characterized by a more regular bond strength distribution consistent with minor bond length distortion.

Introduction

The SiO_4 tetrahedron is the most important and prevalent structural moiety in mineralogy (Gibbs 1982; Liebau 1985). Several mineral classifications are based on the SiO_4 unit and its manifold ways of condensation. Extensive work has been carried out on silicates and their structural and geometrical principles and properties (Kostov 1975; Liebau 1985; Pauling 1980; Zoltai 1960). To understand, quantify, and even predict (Gibbs 1982; Mortier et al. 1984) the geometry of silicate structures, some selected physico-chemical parameters such as bond lengths, degree of condensation, bond strengths, and bond valences appear to be important (Baur 1970; Brown 1976a; Brown 1976b; Brown and Altermatt 1985; Ferraris et al. 1987; Liebau 1985; Pauling 1980).

H is the most abundant cosmic element. In the lithosphere, it appears mostly as H_2O and OH^- either stoichiometrically or in trace amounts in minerals (Mason and Moore 1982). Trace amounts of water have been shown to exist in mantle minerals by Bell and Rossman (1992). The hydrogen bond is one of the most important chemical linkages in nature (Brown 1992).

In spite of the abundance and the spatial proximity of SiO_4 and H in minerals, they rarely bond to each other to form an SiOH group, a so-called silanol group. H atoms usually bond to an O atom of a higher-coordinated cation. Amphiboles, sheet silicates, and epidotes are examples of mineral groups where OH groups are linked to six- and higher-coordinated cations such as K, Na, Ca, Mg, Fe, Al, etc. (Deer et al. 1966). These 1+ to 3+ valent cations are characterized by weak bonds and low individual bond strengths (Pauling 1980), often yielding under-

bonded O atoms that are preferred sites for protonization. In contrast, the SiO_4 tetrahedron is characterized by strong bonds and a rigid geometry (Liebau 1985). In addition, silicates exhibit a wide variety of differently condensed silicate groups (Gibbs 1982). Linkage of individual SiO_4 units produces bridging O atoms, the latter obtaining a sufficient bond-strength sum of equal or nearly 2.0 v.u., inhibiting any additional strong bonds. However, the three-dimensional framework of a crystal structure produces steric and electronic constraints resulting in stress (Brown 1992). Possible stress factors are increasing degree of SiO_4-condensation, cation properties such as valence and size, etc. (Liebau 1985). Competition between Si and other cations for the available bonding space around the O atoms makes compromises necessary between the steric requirements of the silicate anions and the other cation-O polyhedra. These influences can lead to deviations of the regular coordination-sphere geometry (Brown 1992; Liebau 1985). Following the concept of Brown and Altermatt (1985) bond valences depend on bond lengths, and lengthened bonds result in underbonded O atoms. Thus, protonization of the SiO_4 tetrahedron occasionally occurs.

Non-empirical quantum-chemical calculations have become an important tool for determining the structure of molecules and predicting the geometry of small moieties in crystals (Gibbs et al. 1981; Gibbs 1982). Such calculations (also called ab initio calculations) were performed by Gibbs et al. (1981), who investigated the bond lengths of $SiO_3(OH)$ and $SiO_2(OH)_2$ groups and compared observed structures with calculated data. A corresponding approach was chosen by Mortier et al. (1984), who pre-

TABLE 1. Selected interatomic distances, angles, and bond strengths for atoms involved in silanol groups

Structure	Ref. no.	Method*	Si-OH	⟨Si-O⟩	s_{OH}	Δs	Δl
0 bridging O atoms							
Mozartite	1	X, D, R	1.647(2)	1.634(1)	2.330	0.469	0.013
α-Uranophan	2	X, D	1.64(1)	1.615(5)	2.116	0.393	0.025
			1.64(1)	1.615(5)	2.000	0.277	0.025
Afwillite	3	X, D, C	1.674(2)	1.618(1)	2.402	0.622	0.056
			1.688(2)	1.622(1)	2.286	0.506	0.066
Poldervaartite	4	X, D, R	1.696(2)	1.616(1)	2.735	0.948	0.080
$Na_2SiO_2(OD)_2 \cdot 8D_2O$	5	N, D, R	1.672(3)	1.593(3)	2.170	0.490	0.079
$Na_2SiO_2(OD)_2 \cdot 7D_2O$	6	N, R	1.676(3)	1.601(2)	2.000	0.405	0.075
			1.654(4)	1.601(2)	2.164	0.572	0.053
$Na_2SiO_2(OH)_2 \cdot 5H_2O$	7	N, D, R	1.682(4)	1.606(3)	2.163	0.483	0.076
			1.648(4)	1.606(3)	1.997	0.317	0.042
$Na_2SiO_2(OH)_2 \cdot 4H_2O$	8	N, D, R	1.667(1)	1.6055(7)	2.170	0.475	0.062
			1.656(1)	1.6055(7)	2.230	0.535	0.051
$Na_3SiO_3(OH) \cdot H_2O$	9	X, D, R	1.690(2)	1.619(1)	2.397	0.594	0.071
$Na_3SiO_3(OH) \cdot 2H_2O$	10	X, D	1.685(3)	1.615(2)	2.160	0.400	0.070
$Na_3SiO_3(OH) \cdot 2H_2O$	11	X, D, R	1.703(2)	1.618(1)	2.163	0.503	0.085
$Na_3SiO_3(OH) \cdot 5H_2O$	12	X, D, R	1.677(2)	1.621(1)	2.306	0.693	0.056
Average			⟨1.668⟩	⟨1.615⟩	⟨2.234⟩	⟨0.506⟩	⟨0.054⟩
1 bridging O atom							
$Mn_4AsSi_3O_{12}(OH)$	13	X, D	1.650(8)	1.622(5)	2.163	0.211	0.028
Medaite	14	X, D	1.669(4)	1.621(2)	2.160	0.192	0.048
Rosenhahnite	15	X, D, R	1.648(2)	1.614(1)	2.116	0.100	0.034
			1.676(2)	1.624(1)	2.286	0.334	0.052
Average			⟨1.661⟩	⟨1.620⟩	⟨2.181⟩	⟨0.209⟩	⟨0.041⟩
2 bridging O atoms							
$Na_4K_3(M^{2+})_2Si_8O_{22} \cdot 7H_2O$	16	X, D, R	1.630(3)	1.626(2)	2.130	0.117	0.004
Tinaksite-type	17	X, D, R	1.621(4)	1.616(2)	2.021	0.042	0.005
$Na_{16}K_2Si_{18}O_{36}(OH)_{18} \cdot 38H_2O$	18	X, D	1.661(6)	1.625(4)	2.030	0.190	0.028
			1.648(6)	1.618(4)	2.030	0.190	0.031
			1.637(7)	1.610(4)	2.200	0.420	0.031
			1.651(7)	1.618(4)	2.030	0.190	0.027
			1.651(7)	1.611(4)	2.200	0.420	0.041
			1.645(7)	1.623(4)	2.030	0.250	−0.005
			1.654(6)	1.625(4)	2.170	0.330	0.025
			1.657(7)	1.619(4)	2.230	0.390	0.024
			1.625(6)	1.629(4)	2.250	0.470	0.037
Krauskopfite	19	X, D, R	1.625(7)	1.609(4)	2.050	0.030	0.015
			1.644(7)	1.627(4)	2.220	0.210	0.014
$KHSiO_3$	20	X, D, R	1.628(5)	1.616(2)	2.080	0.079	0.018
Tinaksite	21	X, D, R	1.620(3)	1.623(2)	2.030	−0.020	−0.003
Babingtonite	22	N, C	1.623(3)	1.628(2)	2.080	−0.009	−0.005
Kvanefjeldite	23	X, D, R	1.649(2)	1.618(1)	2.283	0.186	0.031
Santaclaraite	24	X, D	1.624(2)	1.616(1)	2.163	0.110	0.008
Cascandite	25	X, D	1.629(4)	1.623(2)	2.163	0.110	0.006
Tokkoite	26	X, D, R	1.628	1.624	2.052	−0.022	0.004
Amstallite	27	X, D	1.649(3)	1.605(1)	2.330	0.200	0.044
Average			⟨1.638⟩	⟨1.619⟩	⟨2.132⟩	⟨0.185⟩	⟨0.018⟩
3 bridging O atoms							
$KHSi_2O_5$	28	X, D	1.586(3)	1.627(1)	1.833	−0.278	−0.041
Grumantite	29	X, D	1.608(4)	1.628(3)	1.997	−0.171	−0.021
Ussingite	30	X, D, R	1.626(2)	1.620(1)	2.164	0.137	0.006
$Si_8O_{18}(OH)_2$-complex	31	X, D, R	1.594(6)	1.602(4)	1.830	−0.170	−0.006
Average			⟨1.604⟩	⟨1.619⟩	⟨1.956⟩	⟨−0.121⟩	⟨−0.016⟩
Average (all data)			1.643	1.618	2.126	0.195	0.024

Note: $s_{OH} = \Sigma z_i/CN$; $\Delta s = s_{OH} - \langle s_O \rangle$; $\Delta l = $ Si-OH $- \langle$Si-O$\rangle$. Bond lengths are in Å, bond angles in °.
  * The letters denote the mode of data acquisition and the quality of the hydrogen localization: N = neutron diffraction data; X = X-ray diffraction data; D = H localized by difference-Fourier methods; R = H position refined; C = H position or O-H bond lengths constraint.
  (1) Nyfeler et al. 1997; (2) Ginderow 1988; (3) Malik and Jeffery 1976; (4) Dai et al. 1993; (5) Schmid et al. 1984; (6) Felsche et al. 1987; (7) Williams and Dent Glasser 1971; (8) Schmid et al. 1985; (9) Schmid and Felsche 1990; (10) Schmid et al. 1981; (11) Schmid et al. 1979; (12) Smolin et al. 1973; (13) Gramaccioli et al. 1979; (14) Gramaccioli et al. 1981; (15) Wan et al. 1977; (16) Rastsvetaeva et al. 1991; (17) Rozhdestvenskaya et al. 1991; (18) Yamnova et al. 1992; (19) Coda et al. 1967; (20) Dent Glasser et al. 1984; (21) Bissert 1980; (22) Tagai et al. 1990; (23) Johnsen et al. 1983; (24) Ohashi and Finger 1981; (25) Mellini and Merlino 1982; (26) Rozhdestvenskaya et al. 1989; (27) Quint 1987; (28) Malinovskii and Belov 1979; (29) Yamnova et al. 1989; (30) Rossi et al. 1974; (31) Smolin et al. 1976.

TABLE 1—_EXTENDED_

O-H	H...O	O...O	O-H...O angle
0.91(4)	1.638	2.501(3)	158(5)
0.87	2.04	2.88	163
0.86	2.2	3.02	160
1.193	1.39	2.583	177
1.059	1.52	2.54	161
0.84(4)	1.81(4)	2.636	168.03
0.977(3)	1.799(3)	2.755(3)	164.6(2)
0.975(4)	1.847(4)	2.816(4)	171.8(4)
1.011(4)	1.608(4)	2.618(4)	176.2(4)
0.95(1)	1.93(1)	2.882	170(1)
0.93(1)	1.68(1)	2.628	175(1)
1.000(2)	1.684(2)	2.683	176.3(2)
0.990(2)	1.745(2)	2.726	170.5(2)
0.83(5)	1.78(5)	2.597	172(4)
0.877	1.776	2.639(4)	167.3
0.97(3)	1.95(3)	2.917(2)	171(3)
1.06	1.51(5)	2.698(3)	170.82
⟨0.96⟩	⟨1.74⟩	⟨2.690⟩	⟨168⟩
0.98	1.91	2.753	142.0(4)
0.98	1.811	2.788	180.0(2)
0.74(5)	1.94(5)	2.681(2)	172(6)
0.99	1.58(4)	2.575(2)	176(4)
⟨0.92⟩	⟨1.81⟩	⟨2.699⟩	⟨167⟩
0.81(8)	1.75(8)	2.527	161(8)
0.85(5)	1.88(5)	2.714(4)	163.12
0.9(1)	1.9(1)	2.563(8)	131(5)
0.9(1)	1.8(1)	2.557(8)	142(6)
0.9(1)	1.8(1)	2.602(8)	151(3)
0.9(1)	1.7(1)	2.520(8)	150(9)
1	1.6	2.565(9)	168
0.9(1)	1.8(1)	2.641(8)	173(6)
1.0(1)	1.9(1)	2.843(9)	147(7)
0.9(1)	1.9(1)	2.724(9)	159(9)
0.9(1)	1.7(1)	2.581(1)	158(8)
1.048	1.671	2.72(1)	179.29
1.051	1.553	2.60(1)	179.78
0.9(1)	1.6(1)	2.517	170(8)
0.72(6)	2.00(6)	2.716	174.71
1.010(4)	1.571(4)	2.579	174.5(3)
0.78(4)	1.83(4)	2.603	180
0.88	1.668	2.491	156
0.877	1.729	2.597	170.1
0.65	2.36	2.95	152.48
0.73(4)	2.18(4)	2.91(1)	176(1)
⟨0.89⟩	⟨1.80⟩	⟨2.644⟩	⟨163⟩
0.62(5)	1.83(5)	2.460(3)	168.5
0.9(1)	1.6(1)	2.513(6)	166
0.97(5)	1.54(5)	2.507(3)	171(3)
1.0(1)	1.6(1)	2.508(8)	162.82
⟨0.87⟩	⟨1.64⟩	⟨2.497⟩	⟨167⟩
0.91	1.75	2.633	166

FIGURE 1. Plot of the Si-OH bond length vs. ⟨Si-O⟩ from the structures compiled in Table 1. See text for explanation.

dicted the geometry of both bridging and terminal silanol groups. Fischer et al. (1988) performed a compilation of structures with silanol groups and described the observed geometries of 23 terminal OH groups.

A recent study on mozartite (Nyfeler et al. 1997) describes how the orientation of the Jahn-Teller distortion strains the entire structure, causing protonization of the SiO_4 tetrahedron. This investigation triggered the search for other structures containing Si-OH groups. This study provides an overview on the geometric characteristics and structural features of silanol groups.
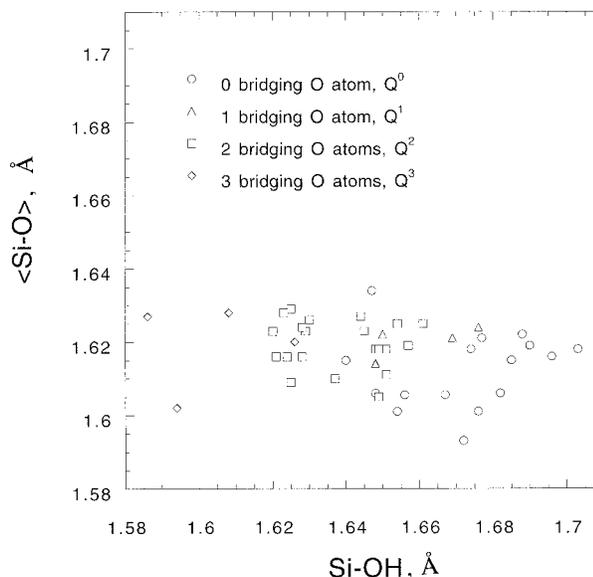
EXPERIMENTAL METHODS

A search in the ICS-Database (Bergerhoff et al. 1983) was performed extracting all structures with an Si....H separation (linked by O) less than 2.8 Å. All structures fitting this search scheme were checked according to a proper Si-OH group. Because of their disordered character zeolites and hydrogarnets were excluded, just as structures with partial substitution of other tetrahedrally coordinated cations in the OH-bearing tetrahedron [e.g., $HAlSi_2O_6$ (Vogt et al. 1990)]. Structures with disordered H [e.g., pectolite (Takeuchi et al. 1976)] and cement-phases (e.g., tobermorite) were also omitted, as were structures where H could not be properly located [e.g., ellenbergite, $NaCaHSiO_4$, nambulite (Comodi and Zanazzi 1993; Cooksley and Taylor 1974; Narita et al. 1975]. Only one study per structure was considered. Some structures had to be rejected because of inconsistencies of the atomic coordinates. This stringent procedure yielded 31 structures with 46 silanol groups for further analyses. In some investigations the actual H position was not refined but only located by means of difference-Fourier maps. In other structures the O-H distance was constrained to a fixed value. Furthermore, data sets were collected at a wide range of temperatures, and several investigations are based on neutron diffraction data (Felsche et al. 1987; Schmid et al. 1984, 1985; Tagai et al. 1990; Williams and Dent Glasser 1971) that more reliably localize H or D.

Bond strengths (including H) of the O atoms engaged in the tetrahedron are calculated using the method proposed by Pauling (1980). An electrostatic bond strength received by an anion X from a cation is

$$s = \frac{z}{CN} \tag{1}$$

where z is the formal charge of the cation and CN is the coordination number of the cation. The anion receives from all the surrounding i cations a sum of electrostatic bond strengths (e.g., Baur 1970).

$$\sum_i s_i = \sum_i \frac{z_i}{CN_i} \qquad (2)$$

The coordination numbers, CN_i, were established considering all O atoms around the respective cation within 3.0 Å (3.5 Å for K and Ba). Because of the irregular coordination geometry of U^{6+} in α-uranophane (Ginderow 1988) with two U-O bonds of 1.8 Å and five additional U-O distances between 2.24 and 2.46 Å, a bond strength of 2.0 v.u. was assigned to the short U-O bonds, and 0.4 v.u. to the five long bonds. The bond strength for a short O-H bond was considered 0.83 v.u. and 0.17 v.u. for a long (<2.5 Å) H...O hydrogen bond (Baur 1970). The parameter Δs is defined as the difference of the Pauling bond-strength sum between O of the OH group (s_{OH}) and the average of the remaining O atoms of the tetrahedron ($\langle s_O \rangle$): $\Delta s = s_{OH} - \langle s_O \rangle$. The parameter Δl represents the difference between the Si-OH bond length and the average of the non-hydroxylated Si-O bond length ($\langle Si\text{-}O \rangle$): $\Delta l = Si\text{-}OH - \langle Si\text{-}O \rangle$.

RESULTS

The geometrical characteristics of the Si-OH...O groups of the extracted structures are listed in Table 1. Some information is provided on the mode of diffraction-data acquisition and on the quality of H localization. The structures are listed according to the connectivity of the SiO$_4$ tetrahedron. Each O atom of the SiO$_4$ tetrahedron that is part of another tetrahedron is considered a bridging O. Tetrahedra with no bridging O, orthosilicates (labeled Q^0), are followed by structures with one bridging O. The next group with two bridging O atoms mostly comprises inosilicates. The structures listed under Q^3 contain tetrahedra with three O atoms bridging to other tetrahedra.

The average bond length of the non-hydroxylated Si-O bonds ($\langle Si\text{-}O \rangle$) is 1.618 Å, in contrast to the more expanded average Si-O bond length of the silanol group (Si-OH) of 1.643 Å. In tetrahedra with two or three bridging O atoms, $\langle Si\text{-}O \rangle$ was found to reach or even exceed Si-OH. Figure 1 shows a plot of the Si-OH bond length vs. $\langle Si\text{-}O \rangle$ from the structures compiled in Table 1. Only a small spread from 1.593 to 1.637 Å is found for $\langle Si\text{-}O \rangle$, whereas the Si-OH distances range from 1.586 Å up to 1.703 Å. The Si-OH distance decreases with the number of bridging O atoms from average values of 1.668 Å for orthosilicates to 1.604 Å for tetrahedra with three bridging O atoms, whereas the $\langle Si\text{-}O \rangle$ distance remains constant at 1.62 Å.

The values for s_{OH} range from 1.830 v.u. to 2.735 v.u., with an average of 2.126 v.u. The bond-length differences (Δl) of Si-OH and $\langle Si\text{-}O \rangle$ and the difference bond-strength sums (Δs) correlate positively (Fig. 2). Linear-regression analysis yielded the equation $\Delta s = 0.058 + 6.997\Delta l$ with a correlation coefficient R = 0.831. The exceptionally high bond-strength sum (2.735 v.u.) for the H-bearing O

atom of poldervaartite (Dai et al. 1993) arises from the contribution of two long bonds of (5 + 2) - coordinated (Ca, Mn). This structure has also one of the longest Si-OH distances. Thus, the valence sum according to Brown and Altermatt (1985) is appropriate, though the bond-strength sum is high.

The compiled O-H bond lengths are between 0.62 and 1.19 Å, with an average of 0.91 Å. The H...O distances also show a wide spread from 1.39 to 2.36 Å, with a mean value of 1.75 Å. The O...O distances are all between 2.46 and 3.02 Å, with an average of 2.633 Å. With one exception (Yamnova et al. 1992), the values of the compiled O-H...O angles are wider than 140°, averaging 166°.

DISCUSSION

Hydroxylated and non-hydroxylated Si-O bonds

The average Si-O distance observed in silicate tetrahedra is 1.626 Å ranging from 1.55 to 1.76 Å (Gibbs 1982; Liebau 1985). Smith and Bailey (1963) found that the average Si-O distance increases from 1.61 Å (framework silicates) to 1.63 Å (orthosilicates). This observation was later explained by a linear dependence of the average Si-O distance from the mean O coordination number (Brown and Gibbs 1969) or from the sum of electrostatic bond strengths (Baur 1970). This topic is discussed in detail by Liebau (1985). The average Si-OH distance presented here (1.643 Å) is in good agreement with the value (1.65 Å) calculated by Newton and Gibbs (1980) for H_4SiO_4. Gibbs et al. (1981) compiled Si-OH bonds for the silanol group of tetrahedral $SiO_3(OH)$ and $SiO_2(OH)_2$ units ranging in length from 1.63 to 1.70 Å with a mean value of 1.67 Å. Similar calculations (Mortier et al. 1984) predict that the Si-O bond is lengthened by 0.04 Å on protonation, which is compared with values of 0.06 to 0.08 Å derived from some X-ray analyses.

Si-O bond lengths in relation to bond strengths

The tendency for the Si-OH distance (Fig. 1) to decrease with increasing number of tetrahedral bridging O atoms can be explained by local electrostatic requirements (Gibbs 1982; Baur 1970). We followed the concept of Baur (1970), who compared individual Si-O bond lengths with the corresponding O bond-strength sums. One extreme is the Si-OH-bearing tetrahedron with one tetrahedral apex terminated by OH and three bridging O atoms, the latter of which tend to be electrostatically balanced by accepting approximately 2.0 v.u. To satisfy 4 v.u., Si will accept a similar valence contribution from each coordinated O including the OH group. Thus, Si-OH and $\langle Si\text{-}O \rangle$ distances have approximately the same value. The other extreme is the orthosilicate group $[SiO_3OH]^{3-}$ wherein the non-hydroxylated tetrahedral apices tend to be underbonded (the average of O bond-strength sums is lower than 2.0 v.u.). In addition, the O atoms of silanol groups with an average bond strength of 2.234 v.u. tend to be overbonded to satisfy the charge requirements of Si^{4+}. Thus Δs values in orthosilicates are generally high ($\langle 0.506 \rangle$ v.u.). As a consequence of these
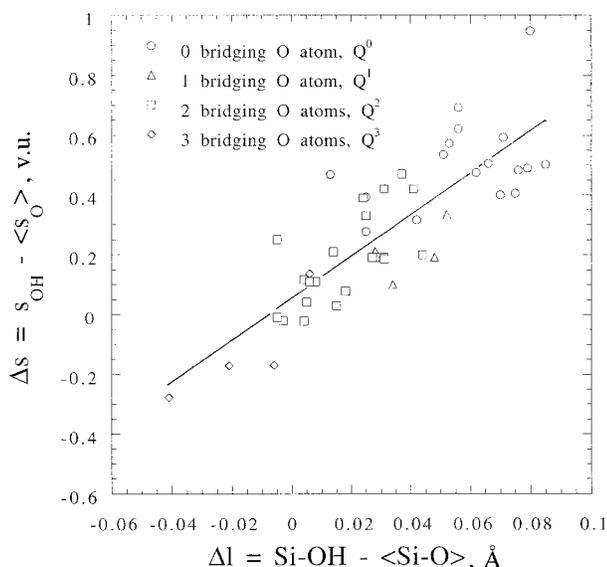
FIGURE 2. Plot of Δl vs. Δs, where Δl is the difference between the Si-OH distance and the average of the non-hydroxylated Si-O bond length, Δs is the difference of Pauling bond strength sum between O of the OH group and the average of the remaining O of the tetrahedron. The line represents a least-square fit. The outlier in the upper right corner represents poldervaartite (Dai et al. 1993) discussed in the text.

differences the Si-O bond lengths of the silanol groups ($\langle 1.668 \rangle$ Å) are longer than the average $\langle$Si-O$\rangle$ distance of the non-hydroxylated tetrahedral apices ($\langle 1.615 \rangle$ Å).

The spread of the data around the regression line in Figure 2 is mainly caused by insufficiencies of the bond-strength approach in which a constant bond-strength value is assigned independently of the length of the bond.

Hydrogen bonded O-H...O

The average O-H bond length in this compilation is comparable to other studies. Ceccarelli (1981) compared one hundred O-H...O bonds in crystals determined by neutron diffraction yielding an average O-H bond length of 0.969 Å, slightly longer than that found by Ferraris and Ivaldi (1988) in a survey of 41 neutron diffraction structures (0.956 Å). Based on quantum mechanical calculations, Gibbs (1982) reported an O-H bond length of 0.98 Å for Si(OH)$_4$, whereas Mortier (1984) calculated 0.959 Å for Si-OH and 0.967 Å for OH at the bridging O of Si-O-Al. The O-H bond lengths compiled in Table 1 must be regarded with some restrictions. Not all data were generated in exactly the same way. Possible differences are discussed above. Because of its lightness, the H atom is affected to an especially high extent by such variations in the mode of data acquisition or structure determination procedure. Except for studies based on neutron diffraction data, the location of protons in crystalline structures is generally unsatisfactory (Ferraris and Ivaldi 1988). Despite these restrictions, the observed range of O-H bond lengths confirms the presence of proper hydroxyl groups.

The average H...O distance of 1.75 Å is comparable to the results of Ceccarelli et al. (1981) reporting an average of 1.818 Å. Partly, the observed scatter is because of the same reasons as for the O-H bond length variation discussed above. On the other hand, the variation of H...O distances is considered to be in closer accordance with the real structural situation. The weak bond strength of a H...O interaction is easily affected by other structural influences and therefore does not expose a well-defined and narrow range of bond lengths.

This study agrees with the average O...O distance of 2.767 Å compiled by Ceccarellis et al. (1981). Short O...O distances are the result of strong hydrogen bonds (Brown 1976a, 1976b; Brown and Altermatt 1985). Ferraris and Ivaldi (1988) compared bond valence and bond length for hydrogen bonded O...O and calculated an energetic minimal O...O distance of about 2.55 Å.

The average O-H...O angle determined in this study is very similar to an average of 167° in the compilation of Ceccarelli et al. (1981). Brown (1976b) believes that the angle O-H...O decreases from 180° when O...O distances are shorter than 2.73 Å. However, the data compiled in Table 1 do not support this relationship. The lack of agreement may be ascribed to uncertainties and differences in the mode and quality of data acquisition of the structures examined.

In general, hydrogen bonds from hydroxylated SiO$_4$ tetrahedra do not differ from those of OH groups attached to higher-coordinated cations.

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