

## A Comparison of Bonding Effects in Ussingite and Low Albite

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### Abstract

The ordered structures of ussingite,  $\text{Na}_2\text{AlSi}_3\text{O}_8(\text{OH})$  (Rossi, Tazzoli, and Ungaretti, 1974) and low albite,  $\text{NaAlSi}_3\text{O}_8$ , are remarkably similar. The equation

$$T\text{-O} = 1.568 + [0.122 \times (\text{Al content of the } T \text{ site})] - [0.037 \times (\Delta\text{Al}_{\text{br}})] \\ + [0.063 \times (\Sigma[1/(\text{Na, H-O})^2])] + [0.029 \times (-1/\cos(T\text{-O-T}))],$$

whose constants were derived by multiple linear regression analysis for sodic plagioclases (Phillips and Ribbe, 1973a), gives an excellent estimation of the 16 individual Al-O, Si-O, and Si-(OH) bond lengths in ussingite. Respectively, the independent variables take account of (1) the aluminum content of the individual tetrahedral (*T*) sites—ussingite is assumed to be ordered; (2) the effects of linkage—*e.g.*, the Si-O(→Si) bonds in ussingite are 0.026 Å longer on the average than Si-O(→Al) bonds; (3) inductive effects of the non-tetrahedrally coordinated Na and H cations as well as oxygen coordination number effects—*e.g.*, the Si-O bonds to 3-coordinated oxygens are 0.021 Å longer on the average than those to 2-coordinated oxygens; and (4) the inter-tetrahedral *T*-O-*T* angles.

Using this equation the values 1.588 and 1.626 Å are estimated for the two non-bridging Si-(OH) bonds in ussingite: observed values are 1.584 and 1.626 Å, respectively. The overall correlation coefficient for observed and estimated distances is 0.987.

### Introduction

There are certain obvious chemical and structural similarities in ussingite,  $\text{Na}_2\text{AlSi}_3\text{O}_8(\text{OH})$ , and low albite, the ordered polymorph of  $\text{NaAlSi}_3\text{O}_8$ . A recent neutron diffraction refinement by Harlow, Brown, and Hamilton (1973) indicated that, within estimated errors, all the aluminum in low albite is concentrated in the  $T_1\text{O}$  site ( $\langle T_1\text{O-O} \rangle = 1.743$  Å) and that silicon occupies the three other tetrahedral sites ( $\langle T_1m\text{-O} \rangle = 1.608$  Å;  $\langle T_2\text{O-O} \rangle = 1.614$  Å;  $\langle T_2m\text{-O} \rangle = 1.615$  Å). Rossi, Tazzoli, and Ungaretti (1974) have shown that ussingite has an “interrupted” framework structure whose sharing coefficient (Zoltai, 1960) is 1.875. There are 4-, 6-, and 8-membered tetrahedral rings in ussingite (as in the feldspars), and Al is concentrated in one of the four tetrahedral sites ( $\langle T(1)\text{-O} \rangle = 1.734$  Å) whereas the others are Si-rich ( $\langle T(2)\text{-O} \rangle = 1.619$  Å;  $\langle T(3)\text{-O} \rangle = 1.620$  Å;  $\langle T(4)\text{-O} \rangle = 1.621$  Å).

The two Na atoms in ussingite are located in irregular coordination polyhedra, one with 6 and the other with 5 oxygen atoms at less than 2.75 Å; the next shortest Na-O bond is >3.15 Å. In low albite the Na atom is also irregularly coordinated with 5 oxygen neighbors closer than 2.7 Å and 2 oxygens at

3.0 Å (Wainwright and Starkey, personal communication).

The conspicuous similarities of these mineral structures suggests that the regression equation derived by Phillips and Ribbe (1973a) to account for the variation of individual *T*-O bond lengths in sodic plagioclases might be appropriately tested on ussingite. The equation was derived by the application of multiple linear regression analysis “. . . to the geometric and chemical variables in sodic plagioclases in order to determine their relative effects on individual *T*-O bond lengths in the  $\text{Al}_{1+z}\text{Si}_{3-z}\text{O}_8$  tetrahedral framework” (Phillips and Ribbe, 1973a, p. 327). The equation, simplified for the case of ussingite, is:

$$T\text{-O} = 1.568 \\ + [0.122 \times (\text{Al content of the } T \text{ site})] \\ - [0.037 \times (\Delta\text{Al}_{\text{br}})] \\ + [0.063 \times (\Sigma[1/(\text{Na, H-O})^2])] \\ + [0.029 \times (-1/\cos(T\text{-O-T}))]$$

where the Al content of a particular tetrahedral (*T*) site is estimated from the mean *T*-O bond lengths, where  $\Delta\text{Al}_{\text{br}}$  is a linkage factor to account for the

TABLE 1. Mean Observed and Predicted Bond Lengths and Bond Strengths for Ussingite (Us) and Low Albite (Ab)

Mineral	Atom	Mean observed bond lengths (Å)*	Mean predicted T-O distances (Å)**	Brown-Shannon(1973) bond strength sums
Us	Na(1)	2.539[6]		0.866
	Na(2)	2.435[5]		0.876
Ab	Na	2.633[7]		0.885
Us	H	0.97[1], 1.54[1]		1.055
Us	Al in T(1)	1.734	1.741 (1.734)	3.229
Ab	Al in T <sub>2</sub> O	1.740	1.739	3.179
Us	Si in T(2)	1.619	1.616	4.065
	Si in T(3)	1.620	1.608 (1.615)	4.062
	Si in T(4)	1.621	1.620	4.050
Ab	Si in T <sub>2</sub> m	1.609	1.609	4.184
	Si in T <sub>2</sub> O	1.614	1.614	4.131
	Si in T <sub>2</sub> m	1.615	1.615	4.121
		Mean Si-O(→Al)	Mean Si-O(II(→Si))	Mean Si-O(III(→Si))
Us		1.608[4]	1.620[2]	1.641[4]
Ab		1.598[4]	1.613[4]	1.627[4]

\* Numbers in brackets indicate number of bonds. Data for ussingite (Us) from Rossi *et al* (1974); data for low albite (Ab) from Wainwright and Starkey (pers. comm.).

\*\* The means of four individual T-O distances predicted using the equations of Phillips and Ribbe (1973a). See Figure 1. Numbers in parentheses result from a transfer of 5% Al from T(1) to T(3).

Al content of adjacent *T* sites in the framework, and where *T-O-T* is the inter-tetrahedral angle involving the *T-O* bond. Since this equation can be used successfully in estimating the individual *T-O* distances in ussingite, especially the non-bridging Si-(OH) bonds of which there are no analogues in feldspars, it was thought that it might provide a substantive basis for a discussion of the bonding effects in ussingite.

### Discussion

Inasmuch as the linear model for predicting aluminum contents of tetrahedral sites in feldspars (Smith and Bailey, 1963) is demonstrably limited in its usefulness, especially for highly ordered structures (see Ribbe, Phillips, and Gibbs, 1973), it was decided to assume a perfectly ordered Al/Si distribution in the first test of the regression equation for ussingite. The parameter  $\Delta Al_{br} \equiv Al_{br} - \langle Al_{br} \rangle$ , as defined for feldspars, was introduced by Phillips and Ribbe (1973a) to account for the tendency of tetrahedra to maintain constant tetrahedral bond

strengths and for the fact that Si-O bonds of the type Si-O(→Si) are 0.02–0.03 Å longer than those of the type Si-O(→Al) (Clark and Papike, 1967). This linkage factor is also important in ussingite: the mean Si-O(→Si) bond is 1.634 Å and the mean Si-O(→Al) bond is 1.608 Å (Table 1).  $\Delta Al_{br}$  has been calculated by way of example for four *T-O* bonds in ussingite in Table 2 with reference to Figure 1.

The third variable in the regression equation takes into consideration the inductive effects of the non-tetrahedral cations, Na and H, on the *T-O* bond. Because it is a summation of the inverse squares of the distances to all of the non-tetrahedrally coordinated cations considered to be bonded to the oxygen of the *T-O* bond, this term also accounts for oxygen coordination number effects which were first shown to be of importance in feldspars by Megaw, Kempster, and Radoslovich (1962)<sup>1</sup>. The coordination number effect is demonstrated for ussingite and low albite in Table 1 (bottom). For example, Si-O bonds to 2-coordinated oxygens are 0.01 to 0.02 Å shorter than those to 3-coordinated oxygens (see the analysis of these effects in framework structures by Phillips, Gibbs, and Ribbe, 1974).

The fourth term involves the inter-tetrahedral angle *T-O-T*. Gibbs *et al* (1972) showed that the functional relationship between this angle and *T-O* bond length could best be linearized by using the negative inverse cosine of the angle, and for that reason the parameter  $-1/\cos(T-O-T)$  was used by Phillips and Ribbe (1973a) in the multiple linear regression analysis. Ribbe *et al* (1973; Figs. 3 and 4, pp. 34–35) have shown graphically that “when linkage factors and coordination effects are isolated, there are distinct patterns [in feldspar

<sup>1</sup> Phillips, Ribbe, and Gibbs (1973) found that in anorthite 82 and 70 percent of the variations in the Si-O and Al-O bond lengths, respectively, could be explained in terms of the factor,  $\Sigma[1/(M-O)^2]$ . Also see Phillips and Ribbe (1973a, b) for its importance in sodic plagioclases and potassium-rich feldspars.

TABLE 2. Sample Calculations of  $\Delta Al_{br}$  for Four *T-O* Bonds in Ussingite\*

Bond	$Al_{br}$	$\langle Al_{br} \rangle$	$\Delta Al_{br}$
T(2)-O(1)	1.0 Al in T(1)	0.25[1 Al in T(1) + 0 Al in other 3 sites]	1.0 - 0.25 = +0.75
T(2)-O(6)	0.0 Al in T(3)	0.25[1 Al in T(1) + 0 Al in other 3 sites]	0.0 - 0.25 = -0.25
T(4)-O(3)	0.0 Al in T(2)	0.33[2.0 Al in two T(1) sites + 0 Al in T(2)]	0.0 - 0.67 = -0.67
T(4)-O(5)	1.0 Al in T(1)	0.33[2.0 Al in two T(1) sites + 0 Al in T(2)]	1.0 - 0.67 = +0.33

\*Refer to Figure 1.

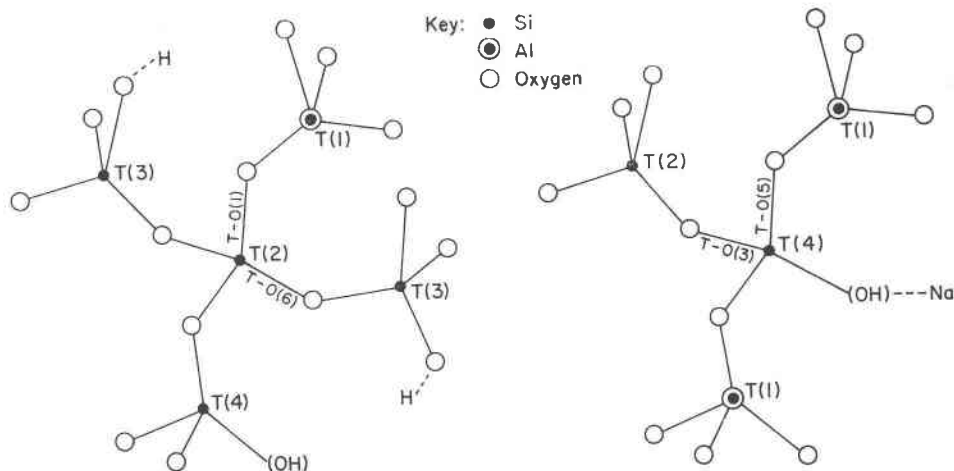


FIG. 1. Schematic drawings of the linkages in ussingite used to illustrate the calculations of  $\Delta Al_{br}$  for the  $T(2)$ -O(1), O(6) and  $T(4)$ -O(3), O(5) bonds in Table 2.

data] showing that wider  $T$ -O- $T$  angles are associated with shorter  $T$ -O bonds as predicted by Cruickshank (1961).” The same is true of ussingite.

In contrast to feldspars, in which the Zoltai sharing coefficient is 2.0, ussingite has two of nine oxygens which are non-bridging. Both of these are bonded to hydrogen, O(2) ... H = 1.54 Å, O(8)-H = 0.97 Å (see Table 1), and both are coordinated by two Na atoms in addition to Si. Using the feldspar regression equation to estimate the non-bridging  $T(3)$ -O(2) and  $T(4)$ -O(8) bond lengths was remarkably successful. The calculated values, 1.588 and 1.626 Å, agree well with the respective observed distances, 1.584 and 1.626 Å. (In these calculations both the  $\Delta Al_{br}$  and the  $T$ -O- $T$  values were assumed to be zero.) The 16 individual observed and calculated  $T$ -O distances for ussingite are plotted in Figure 2 and show rather good agreement, especially considering that these Si-O bonds range from 1.584 to 1.660 Å. Observed and calculated mean  $T$ -O distances are compared in Table 1 with those from low albite.

Because the mean  $T(1)$ -O distance of 1.73 Å in ussingite is significantly shorter than the 1.740 Å and 1.743 Å reported for the Al-containing  $T_1O$  sites in two low albites (Wainwright and Starkey, 1968; Harlow *et al.*, 1973), a second calculation was made for ussingite in which ~5 percent Al was assumed to be transferred from  $T(1)$  to  $T(3)$ . The result was a better agreement between individual observed and predicted values (see Table 1 and Figure 2).

Bond strengths calculated by the method of Brown

and Shannon (1973) for both ussingite and low albite have been included in Table 1. Values were calculated using the constants in their Table 1, p. 269. Except for the Na atoms in both structures, agreement of the bond strengths with the formal charges is within ~5 percent. According to Brown

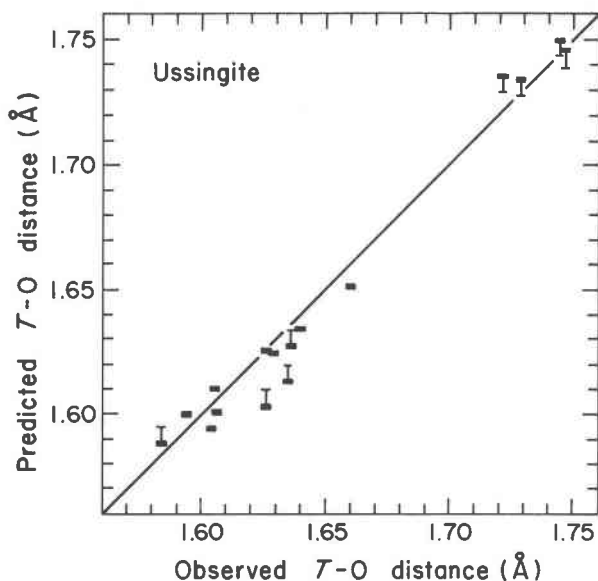


FIG. 2. Observed  $T$ -O values for ussingite plotted against those calculated from the regression equation of Phillips and Ribbe (1973a). The line shown is at 45°; the rectangles are  $2\sigma$  long,  $1\sigma$  wide. The narrow horizontal bars indicate calculated values of  $T(1)$ -O and  $T(3)$ -O distances when the Al occupancy is assumed to be 0.95 in  $T(1)$  and 0.05 in  $T(3)$ . A regression line for the completely ordered model has the equation  $y = 1.012x - 0.024$ ; the correlation coefficient is 0.987.

and Shannon, this is of particular significance in confirming the H<sup>+</sup> positions, although the method of Donnay and Allmann (1970) is equally successful (see Rossi *et al.*, 1974). The 12–13 percent discrepancy in the bond strength sums for Na with formal charge would indicate possible misjudgments in assigning coordination numbers for Na. This may be true for presumed 6-coordinated Na(1) in ussingite whose seventh oxygen neighbor at 3.153 Å would contribute an additional 0.040 to  $S(\text{Na}(1))$ . But inclusion of further oxygens in the coordination sphere is somewhat unrealistic because the eighth nearest neighbor (excluding two H<sup>+</sup> atoms) is silicon at 3.193 Å. The sixth nearest neighbor of Na(2) (also excluding two H<sup>+</sup>) is an aluminum atom at 3.144 Å, so the assumed 5-fold coordination of Na(2) is quite realistic.

As Rossi *et al.* (1974) pointed out, the electrostatic charge balance in ussingite, computed by the method of Donnay and Allmann (1970), is "satisfactory," each oxygen atom receiving 1.84 to 2.14 e.s.u. The corresponding values calculated by the method of Brown and Shannon (1973) are 1.81 to 2.13 e.s.u., whereas the classic Pauling bond strengths range from 1.83 to 2.20.

### Summary

The crystal chemical principles influencing the steric details of ussingite and the sodic feldspars are remarkably similar, and the regression equation derived by Phillips and Ribbe (1973a) for feldspars gives very reasonable estimates of the T–O distances in ussingite, even for the non-bridging bonds involving hydrogen. The Si–O(→Si) bonds in ussingite are 0.026 Å longer on the average than Si–O(→Al) bonds, and Si–O bonds to 3-coordinated oxygens are 0.021 Å longer on the average than those to 2-coordinated oxygens.

The position of the hydrogen atom in ussingite determined by Rossi *et al.* (1974) is confirmed by the methods of both Donnay and Allmann (1970) and Brown and Shannon (1973), and the coordination number assignments for Na (and thus for oxygen) are likewise upheld.

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