Na-feldspar: temperature, pressure and the state of order

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Abstract. In feldspars, mean tetrahedral T–O bond lengths (\(T = Al,Si\)) are the standard measure of the tetrahedral Al content. However, for a sophisticated assessment of the Al, Si distribution, factors have to be accounted for (1) that cause individual T–O bond lengths to deviate from their tetrahedral means and (2) that cause mean tetrahedral lengths to deviate from values specified by the Al content. We investigated low albite, Na[AlSi₃O₈], from six X-ray crystal structure refinements available in the literature. The Al, Si distribution of low albite is fully ordered so that Al, Si–O bond length variations result only from bond perturbing factors. For the intra-tetrahedral variation \(\Delta T–O = T–O – \langle T–O \rangle\), only two factors turned out to be effective: (1) the sum of bond critical point electron densities in the Na–O and T–O bonds neighbouring the T–O bond under consideration and (2) the fractional s-bond character of the bridging oxygen atom. This model resulted in a root mean square (rms) value for \(\Delta T–O\) of only 0.002 Å, comparable to the estimated standard deviations (esd’s) routinely quoted in X-ray and neutron structure refinements. In the second step, the inter-tetrahedral differences \(\Delta \langle T–O \rangle = \langle T–O \rangle – \langle \langle T–O \rangle \rangle\) were considered. Here, apart from the tetrahedral Al content, the only size-perturbing factor is the difference between the tetrahedral and the grand mean fractional s-characters. The resulting rms value was as small as 0.0003 Å.

From this analysis, Al site occupancies, \(t\), can be derived from observed mean tetrahedral distances, \(\langle T–O \rangle_{\text{obs}}\), as

\[
t = 0.25(1 + n_{\text{An}}) + \left(\langle T–O \rangle_{\text{adj}} – \langle \langle T–O \rangle \rangle\right)/0.12466 (17),
\]

with the observed distance \(\langle T–O \rangle_{\text{obs}}\) adjusted for the influence of the fractional s-character, \(\langle T–O \rangle_{\text{adj}} = \langle T–O \rangle_{\text{obs}} + 0.1907(51)\(\langle f_s(O) \rangle – \langle f_s(O) \rangle\)). This equation served to determine the site occupancies of 16 intermediate to high albites and one analbite from their mean tetrahedral distances. It was found that the individual site occupancies \(t_1, t_1m\) and \(t_2, t_2m\) all vary linearly with the difference \(\Delta t_1 = t_1 – t_1m\). \(\Delta t_1\), in turn, varies linearly with the length difference, \(\Delta t_r[110]\), between the unit cell repeat distances [1/2a, 1/2b, 0] and [1/2a, –1/2b, 0]. Then, from the \(\Delta t_r[110]\) indicator, values of \(t\) were obtained as

\[
t_1 = (1 – b_0) + b_0 (b_1 + b_2 \Delta t_r[110])
\]

\[
t_1m = (1 – b_0) – (1 – b_0) (b_1 + b_2 \Delta t_r[110])
\]

\[
t_2 = t_2m = (b_0 – 0.5) – (b_0 – 0.5) (b_1 + b_2 \Delta t_r[110]),
\]

with \(b_0 = 0.7288(16), b_1 = 0.1103(59)\) and \(b_2 = 3.234(32) Å^{-1}\).

Finally, from an expression that converts the \(\Delta 2\theta(131)\) measure of order into \(\Delta t_r[110]\) and thus into site occupancies, it was possible to obtain from the unique suite of bracketed high-pressure experiments performed on albites by Goldsmith and Jenkins (1985) the evolution with equilibrium temperature of the thermodynamic order parameter \(Q_{od}\) and of the individual Al site occupancies \(t\) at a pressure of 1 bar. For that purpose, since the
Goldsmith and Jenkins experiments were performed at \(\approx 18\) kbar, a procedure was devised that accounts for the effect of pressure on the state of order. At 1 bar, low albite is stable up to 590 °C, where it begins to disorder, turning into high albite above 720 °C. The highly though not fully disordered monoclinic state (monalbite) is reached at 980 °C, 1 bar, and 1055 °C, 18 kbar, respectively. Eventually, when applying the determinative equations given above to low microcline, full order is predicted as in low albite.

Dedicated by Herbert Kroll to Peter Baumgart for decades of caretaking

1 Introduction

The phase relations of alkali feldspars, \((\text{Na,K})[\text{AlSi}_3\text{O}_8]\), have been debated for several decades, although as early as 1960 in his salient paper \(\text{Al}/\text{Si} \ Verteilungen, \ Phasen-\) Transformationen und Namen der Alkali-Feldspäte (later on translated into English by the late Joseph V. Smith), Fritz Laves had already clarified the “confusion” (Laves and Goldsmith, 1961) about the stability and metastability of the Na- and K-feldspar polymorphs and varieties. For Na-feldspar, \(\text{Na}[\text{AlSi}_3\text{O}_8]\), two stable modifications are accepted to exist: monoclinic monalbite, \(\text{SG} \ C2/m \ (T > 980 \degree \text{C})\), and triclinic albite, \(\text{SG} \ C1 \ (T < 980 \degree \text{C})\). Laves, 1960; Winter et al., 1979; Kroll et al., 1980). Analbite is the triclinic quench product of monalbite, metastable at all \(P, T\) conditions. Sanidine, \(\text{SG} \ C2/m\), and low microcline, \(\text{SG} \ C1\), are the stable polymorphs of K-feldspar, \(\text{K}[\text{AlSi}_2\text{O}_8]\), the transition temperature lying somewhere between 450 and 480 °C (Bambauer et al., 2005). It took until 1994, when Carpenter and Salje asserted the first-order character of the sanidine to microcline transition, ending the dispute about the “stability” of so-called intermediate microcline.

In monalbite, similar to sanidine, there are two symmetrically non-equivalent tetrahedral sites, \(T_1\) and \(T_2\), onto which the \(\text{Al}\) and \(\text{Si}\) atoms are distributed in a highly disordered but not completely random manner. When judging from tetrahedral sizes, even at high temperatures the larger \(\text{Al}\) atom not completely random manner. When judging from tetrahedral sizes, even at high temperatures the larger \(\text{Al}\) atom

\[ \langle T-O \rangle_{\text{obs}} - \langle T-O \rangle \]

\[ \frac{1}{K} \]

\[ t = 0.25 (1 + n_{\text{An}}) + \left( \frac{\langle T-O \rangle_{\text{obs}} - \langle T-O \rangle}{K} \right) \]

where \(n_{\text{An}}\) is the mole fraction of the anorthite \((\text{CaAl}_2\text{Si}_2\text{O}_8)\) component, \(K\) is the size difference between pure \(\text{Al}\) and pure \(\text{Si}\) tetrahedra \((K = 0.127(3) \text{ Å}; \text{see below})\), and \(\langle T-O \rangle\) is the grand mean of the \(4 \times 4\) individual \(T-O\) distances corresponding to the formula unit. Ribbe derived \(t\) values from \(\langle T-O \rangle\) distances because direct refinement of site occupancies is hampered in X-ray structure work due to the similarity of \(\text{Al}\) and \(\text{Si}\) scattering powers.

When \(\langle T-O \rangle\) data are lacking, numerous models have been proposed to obtain site occupancies from unit cell dimensions and optic axial angles (Stewart and Ribbe, 1969; Kroll, 1971, 1973; Kroll and Ribbe, 1983, 1987; Hovis, 1986; Su et al., 1986).

It is our goal to utilise the equilibrated experiments of Goldsmith and Jenkins (1985) and Waterwiese et al. (1995)
to derive from reported diffraction peak positions and lattice parameters the Al site occupancies of Na-feldspar as a function of both temperature and pressure. From the unit cell dimensions given by Waterwiese et al. (1995), values for t can be easily obtained. Goldsmith and Jenkins (1985), however, provided only the differences between two peak positions, \( \Delta \theta(131) \equiv 2\theta(131) - 2\theta(131) \) (CuK\( \alpha_1 \) radiation), that react sensitively to changes in the Al, Si distribution. We calibrate this difference in terms of the parameter (Kroll, 1971, 1973)

\[
\Delta t_r[110][\text{Å}] = t_r[110] - t_r[110] = \frac{1}{2}(a^2 + b^2 + 2ab\cos(\gamma))^{1/2}
\]

\[
-\frac{1}{2}(a^2 + b^2 - 2ab\cos(\gamma))^{1/2},
\]

where \( t_r[110] \) and \( t_r[110] \) denote the translational distances in the [110] and [110] directions of the C-centred lattice. \( \Delta t_r[110] \) is directly related to \( \Delta t_1 \equiv t_1 - t_1 \) as is apparent from the following consideration (Fig. 1). The sequence of tetrahedral sites along [110] is \( T_10 \rightarrow T_20 \rightarrow T_20 \); along [110] it is \( T_1m \rightarrow T_20 \rightarrow T_2m \). Consequently, since the ionic radius of Al is larger than that of Si, the [110] repeat will gain length at the expense of the [110] repeat as Al migrates from \( T_1m, T_20 \) and \( T_2m \) into \( T_10 \) during ordering in the triclinic state. However, finding \( t_10 - t_1m \) for the Goldsmith and Jenkins data does not help much to construct \( t \) vs. \( T \) because to do so we need to know all four individual \( t \) values. Fortunately, there are structure refinements available not only for LA but also for IA (Phillips et al., 1989; Meneghinello et al., 1999; Tribaudino et al., 2018), HA (Prewitt et al., 1976; Winter et al., 1979) and AA (Curetti et al., 2011). From these, we investigate relations between \( t_10 - t_1m \) on the one hand and the four individual \( t \) values on the other hand. Deriving site occupancies from tetrahedral distances, however, inevitably leads to a discussion of the correlations that exist between T–O bond lengths and their specific atomic environments. Therefore, we first pursue this discussion.

## 2 T–O bond length variation

### 2.1 Correlations

The length of an individual T–O bond in a feldspar structure primarily reflects the Al content of the respective tetrahedral site. To some extent, however, the bond length is modified by secondary factors related to the atomic environment of the bond (Fig. 2). The following correlations have been discussed in the literature:

1. **The linkage factor.** Phillips and Ribbe (1973) noted that Si–O → Si bonds are 0.03 Å longer than Si–O → Al bonds.

2. **Bonding to the non-tetrahedral cation (A cation).** T–O distances tend to increase with the number of A cations coordinated to the bridging oxygen atom, this effect being pronounced when the A–O distances are small (Fleet et al., 1966; Brown et al., 1969; Geisinger et al., 1985).

3. **The T–O–T angle.** Shorter T–O bonds tend to be involved in larger T–O–T angles (Phillips et al., 1973; Gibbs et al., 1981; Wenk and Kroll, 1984).

4. **The O–T–O angle.** Geisinger et al. (1985) found that the average of the three O–T–O angles common to a T–O bond is inversely related to its length.

5. **The isotropic displacement factor, \( B_0 \).** Liebau (1985) reported that large atomic displacement factors are associated with small T–O distances and large T–O–T angles.

### 2.2 Modelling correlations

(1, 2) Downs et al. (1996) performed procrystal electron density calculations on low albite by placing spherically averaged wave functions at the known atomic positions (independent atom model). The electron density obtained this way closely approximates the experimental electron density. From a topological analysis, bonded pairs of atoms can be identified. According to Bader (1990), a bond between two atoms is established if a...
saddle point exists in the path between the pair of atoms where the gradient of the electron density is zero and the curvature is positive along the path but negative normal to it. The saddle point defines the bond critical point, \( r_c \).

The concentration of the electron density at \( r_c \), \( \rho(r_c) \), is related to the strength of the bond, typically the larger \( \rho(r_c) \) the shorter the bond (Gibbs et al., 2014). Downs et al. (1996), when considering the environment of the \( \text{O}_{\text{A}2} \) atom in LA, which is bonded to two Si atoms plus one Na atom at a very short distance, noted that the two Si–O bond lengths are the largest in the structure. They asserted this finding to the relatively large electron density in the short Na–O\( \text{A}2 \) bond, “which leaves fewer electrons available for the two Si–O bonds, making them weaker and thus longer”. It therefore appears sensible to relate the length of a T–O bond to the sum of the critical point electron densities \( \rho(r_c) \) that are located in the neighbouring T–O and Na–O bonds (Fig. 2).

Gibbs et al. (2014) investigated experimental and calculated electron density distributions in oxides, silicates and siloxane molecules and established a power law between critical point density \( \rho(r_c) \) and bond length M–O,

\[
\langle \rho(r_c) \rangle = r[1.41/(\text{M–O})]^{4.76},
\]

(3)

where \( r \) is the row number of M in the periodic table, and the angle brackets \( \langle \ldots \rangle \) denote polyhedral averages. The authors demonstrated that \( \rho(r_c) \) numerically agrees with the familiar Pauling bond strength concept, where bond strength \( s = \text{formal valence or coordination number} \).

(3) The third factor that perturbs T–O bond lengths is the T–O–T angle (Fig. 2). Its influence has been the subject of some debate but has been shown to be effective in studies by Gibbs et al. (1981), Wenk and Kroll (1984), Geisinger et al. (1985) and Angel et al. (1990). The T–O–T angle influence is linearised by considering the fractional \( s \)-character, \( f_s(O) \), of the hybrid \( 2s+\lambda-2p \) oxygen orbitals directed toward the two T atoms, where \( \lambda \) is the mixing coefficient, and \( 1/(1+\lambda^2) \) is the fractional \( s \)-character, with \( \lambda^2 = -\sec(T\text{-O}–T) \) (Coulson, 1961; Newton and Gibbs, 1980):

\[
f_s(O) = 1/(1 – \sec(T\text{-O}–T)).
\]

(4) In a similar way, the fractional \( s \)-character of the central T atom, \( f_s(T) \), has been cast by Boisen and Gibbs (1987) into the expression

\[
f_s(T) = 2\cot^2(\theta)_3.
\]

(5)

where \( (\theta)_3 \) is the average of the three O–T–O angles common to a T–O bond (see the scheme in Fig. 2).

(5) The correlation observed by Liebau (1985) between T–O distances and \( B_2 \), competes against the one between T–O distances and T–O–T angles.

2.3 Regression model

2.3.1 Intra-tetrahedral bond length variations

In our regression analysis, we did not consider the individual T–O distances as the dependent variables but instead used the deviations between individual and mean values, thereby separating intra- and inter-tetrahedral variations:

\[
\text{T–O} – \langle \text{T–O} \rangle = [\text{T–O} – \langle \text{T–O} \rangle] + [\langle \text{T–O} \rangle – \langle \langle \text{T–O} \rangle \rangle].
\]

(6)

This measure helps to avoid effects that do not originate in the local atomic environments of T–O bonds. For example, in fully ordered LA, experimental (Al–O) distances vary from 1.739 to 1.742 Å. (\( \langle \text{T–O} \rangle \)) distances are not constant either, varying from 1.644 to 1.646 Å. Furthermore, when Na-feldspar becomes disordered, the \( \langle \langle \text{T–O} \rangle \rangle \) distances are observed to shrink by 0.002–0.003 Å (Ribbe, 1984).

Our analysis relies on a methodically homogeneous group of six X-ray structure refinements of low-albite crystals available from the literature (Table 1), deliberately omitting neutron structure refinements by Harlow and Brown (1980) and Smith et al. (1986).

We use the notation \( \Delta \text{T–O} \equiv \text{T–O} – \langle \text{T–O} \rangle \), \( \Delta \langle \text{T–O} \rangle \equiv \langle \text{T–O} \rangle – \langle \langle \text{T–O} \rangle \rangle \) and similarly \( \Delta \rho \equiv \rho – \langle \rho \rangle \), \( \Delta \langle \rho \rangle \equiv \langle \rho \rangle – \langle \langle \rho \rangle \rangle \) and so on, where the simple angle brackets mean tetrahedral averages, and the double brackets are grand mean values. \( \rho_{\text{Na}} \) is the sum of the critical point densities in the 0, 1 or 2 Na–O bonds adjacent to the T–O bond under consideration, and similarly \( \rho_T \) is the critical point density in the T–O bond neighbour.

In the first regression run, we have chosen the first term on the right-hand side of Eq. (6), \( \Delta \text{T–O} \equiv \text{T–O} – \langle \text{T–O} \rangle \),
Table 1. Mean tetrahedral distances, \( \langle T-O \rangle [\text{Å}] \), and Al site occupancies, \( t \), of six low albites and one low microcline. \( \langle T-O \rangle_{\text{calc}} = \langle \langle T-O \rangle \rangle + c_3 \left[ t - 0.25 \left( 1 + n_{\text{An}} \right) \right] + c_4 \Delta f_s(O) \) (Eq. 8). \( \langle T-O \rangle_{\text{adj}} \) and \( t \) come from Eq. (9) \( \left( \Sigma t = 1 + n_{\text{An}} \right) \). Site occupancies \( t_{\text{Menegh}} \) from Meneghinello et al. (1999) are listed for comparison.

| Reference/locality          | Site | \( \langle T-O \rangle_{\text{obs}} \) | \( \langle T-O \rangle_{\text{calc}} \) | \( \langle T-O \rangle_{\text{adj}} \) | \( t \) | \( t_{\text{Menegh}} \) |
|-----------------------------|------|-------------------------------|--------------------------------|---------------------------------|-----|-------------------|
| Wainright and Starkey (1968) | T10  | 1.740                         | 1.740                          | 1.738                           | 0.999 |                    |
| Tiburon-LA, Ca., USA        | T1m  | 1.609                         | 1.609                          | 1.613                           | 0.002 |                    |
|                            | T20  | 1.614                         | 1.614                          | 1.613                           | 0.002 |                    |
|                            | T2m  | 1.615                         | 1.615                          | 1.613                           | -0.003 |                   |
| Grand mean \( T-O \)        |      | 1.6444                        |                                | \( \Sigma t \) = 1.000           |      |                   |
| Wenk and Kroll (1984)       | T10  | 1.741                         | 1.741                          | 1.739                           | 0.998 | 0.93              |
| Cazadero-LA, Ca., USA       | T1m  | 1.610                         | 1.610                          | 1.614                           | -0.001 | 0.04              |
|                            | T20  | 1.615                         | 1.615                          | 1.614                           | 0.000 | 0.01              |
|                            | T2m  | 1.617                         | 1.616                          | 1.615                           | 0.004 | 0.02              |
| Grand mean \( T-O \)        |      | 1.6455                        |                                | \( \Sigma t \) = 1.001           |      |                   |
| Armbruster et al. (1990)    | T10  | 1.742                         | 1.742                          | 1.740                           | 1.004 | 0.93              |
| Roc Tournè-LA, France       | T1m  | 1.610                         | 1.610                          | 1.614                           | 0.000 | 0.04              |
|                            | T20  | 1.615                         | 1.615                          | 1.615                           | -0.002 | 0.01              |
|                            | T2m  | 1.616                         | 1.617                          | 1.615                           | -0.002 | 0.02              |
| Grand mean \( T-O \)        |      | 1.6459                        |                                | \( \Sigma t \) = 1.001           |      |                   |
| Downs et al. (1994)         | T10  | 1.738                         | 1.738                          | 1.736                           | 0.978 |                   |
| Crete LA, Greece            | T1m  | 1.611                         | 1.611                          | 1.615                           | 0.010 |                   |
|                            | T20  | 1.616                         | 1.615                          | 1.615                           | 0.010 |                   |
|                            | T2m  | 1.617                         | 1.617                          | 1.615                           | 0.006 |                   |
| Grand mean \( T-O \)        |      | 1.6453                        |                                | \( \Sigma t \) = 1.003           |      |                   |
| Meneghinello et al. (1999)  | T10  | 1.740                         | 1.740                          | 1.738                           | 1.000 | 0.96              |
| Stintino-LA, Italy          | T1m  | 1.609                         | 1.609                          | 1.613                           | 0.002 | 0.03              |
|                            | T20  | 1.614                         | 1.614                          | 1.614                           | 0.006 | 0.00              |
|                            | T2m  | 1.615                         | 1.615                          | 1.613                           | 0.002 | 0.01              |
| Grand mean \( T-O \)        |      | 1.6443                        |                                | \( \Sigma t \) = 1.010           |      |                   |
| Tribaudino et al. (2018)    | T10  | 1.739                         | 1.740                          | 1.737                           | 0.996 |                   |
| Minas Gerais LA, Brazil     | T1m  | 1.609                         | 1.609                          | 1.613                           | 0.000 |                   |
|                            | T20  | 1.614                         | 1.614                          | 1.614                           | 0.006 |                   |
|                            | T2m  | 1.616                         | 1.615                          | 1.614                           | 0.008 |                   |
| Grand mean \( T-O \)        |      | 1.6445                        |                                | \( \Sigma t \) = 1.010           |      |                   |
| Strob (1983)                | T10  | 1.7385                        | 1.7388                         | 1.7386                          | 0.998 |                   |
| Prilep-LM, Yugoslavia       | T1m  | 1.6134                        | 1.6132                         | 1.6144                          | 0.002 |                   |
|                            | T20  | 1.6143                        | 1.6147                         | 1.6138                          | -0.003 |                   |
|                            | T2m  | 1.6151                        | 1.6147                         | 1.6145                          | 0.003 |                   |
| Grand mean \( T-O \)        |      | 1.6453                        |                                | \( \Sigma t \) = 1.001           |      |                   |

\( \langle T-O \rangle \), as the dependent variable and all five variables discussed above as the independent variables, \( \text{viz.} \Delta \rho_{\text{Na}}, \Delta \rho_T, \Delta f_s(O), \Delta f_s(T), \Delta B_0 \). It was immediately clear that the \( \Delta f_s(T) \) term was insignificant (Student \( t \) value \( = 1.3 \)) as was also found by Angel et al. (1990) in their analysis of An-rich plagioclases. \( \Delta B_0 \) also turned out to be insignificant in the presence of \( \Delta f_s(O) \) (Student \( t \) value \( = 1.8 \)). The correlation coefficient, \( r \), between these two variables is 0.90. Despite the large \( r \) value, substituting \( \Delta B_0 \) for \( \Delta f_s(O) \) deteriorated the fit. \( \Delta B_0 \) was thus not considered any further. Note, however, that Boisen et al. (1990), in their analysis of bond length variations in coesite, the silica polymorphs and the clathrasils, found that both \( \Delta B_0 \) and \( \Delta f_s(O) \) contributed significantly to the regression sum of squares. The three variables left over at this point could be reduced further by combining \( \Delta \rho_{\text{Na}} \) and \( \Delta \rho_T \) into one variable, \( \Delta \rho_{\text{Na,T}} = \Delta \rho_{\text{Na}} + \Delta \rho_T \), as their regression coefficients agreed just within their mutual standard deviations. At this point it is appropriate to briefly discuss our choice of the Na coordination by oxygen atoms on which the determination of \( \Delta \rho_{\text{Na,T}} \) is based. In their topological analysis of procrystal electron densities in LA, Downs et al. (1996) could identify bond critical points only between Na and its five nearest O neighbours. We started with this as-
Figure 3. Distance differences $\Delta T-O [\text{Å}] \equiv T-O - \langle T-O \rangle$ plotted versus individual T-O distances in average low albite, before and after adjustment. Red squares: observed $\Delta T-O$ differences, blue squares: $\Delta T-O$ after adjustment for the $\Delta \rho$ effect (bond critical point electron density), green squares: $\Delta T-O$ after adjustment for both the $\Delta \rho$ and the $\Delta f_s$ effects (fractional s-character of the bridging O atom). For two bonds, T1-O2-O0 and T2-O1-O2, the effects are visualised by arrows. The sizes of the data points comply with the typical error.

The regression results for the equation

$$\Delta T-O \equiv T-O - \langle T-O \rangle = c_1 \Delta \rho_{\text{Na,T}} + c_2 \Delta f_s(O)$$  \hspace{1cm} (7)

are listed in Table 2. The effect that the two factors have on $\Delta T-O$ is illustrated in Fig. 3. In order to avoid overcrowding the diagram by plotting the total number of 6 $\times$ 16 data points, we have taken mean values of all variables of the six low albites to obtain an average low albite. $\Delta T-O_{\text{obs}} = T-O - \langle T-O \rangle$ is seen to vary over a range of 0.05 Å. When the correlation with $\Delta \rho_{\text{Na,T}}$ is accounted for, $\Delta T-O_{\text{adj}} = \Delta T-O_{\text{obs}} - c_1 \Delta \rho_{\text{Na,T}}, r$ the variation drops considerably to only $\pm 0.01$ Å conforming to the large correlation between $\Delta T-O$ and $\Delta \rho_{\text{Na,T}}, r = 0.91$. In contrast, the correlation between $\Delta T-O$ and $\Delta f_s(O)$ is small, $r = -0.14$. However, when considering the correlation between $\Delta T-O_{\text{adj}}$ and $\Delta f_s(O), r$ increases to $-0.92$. Therefore, the scatter left after adjusting $\Delta T-O$ for the $\Delta \rho_{\text{Na,T}}$ factor is further reduced so that the final root mean square deviation is as small as 0.002 Å, a value that corresponds to the esd’s routinely quoted in the literature for T-O distances observed in X-ray and neutron structure refinements. Weighting has been applied in the final run according to the rms values of the six individual LA regressions, which, however, vary little, from 0.0020 Å (Crete LA) to 0.0029 Å (Minas Gerais LA).

### 2.3.2 Inter-tetrahedral variation

The second term on the right-hand side of Eq. (6), $\Delta \langle T-O \rangle = \langle T-O \rangle - \langle \langle T-O \rangle \rangle$, depends primarily on the difference between the tetrahedral Al content and its grand mean value, $\Delta t \equiv t - \langle t \rangle = t - 0.25(1 + n_{\text{An}})$. In principle, the difference between tetrahedral and grand mean $\Delta \rho_{\text{Na,T}}$ values could comprise a second correlation. However, $\Delta t$ and $\Delta \langle \rho_{\text{Na,T}} \rangle$ heavily correlate, $r = 0.97$, so that one of the two variables is redundant, and that is $\Delta \langle \rho_{\text{Na,T}} \rangle$ rather than $\Delta t$, of course. The large correlation is mainly a consequence of the linkage factor inasmuch as the T1O tetrahedron, which is occupied by Al, has short neighbouring Si-O distances hosting large critical point electron densities. In addition, the oxygen atoms of the T1O tetrahedron have small Na-O distances so that in summary $\langle \rho \rangle - \langle \langle \rho \rangle \rangle$ is large and positive for T1O and small and negative for the Si tetrahedra, as is $t - \langle t \rangle$. Discarding $\Delta \langle \rho \rangle$ leaves $\Delta \{f_s(O)\}$ as the next candidate:

$$\Delta \{T-O\} \equiv \langle T-O \rangle - \langle \langle T-O \rangle \rangle = c_3[t - 0.25(1 + n_{\text{An}})]$$

$$+ c_4 \Delta \{f_s(O)\}.$$  \hspace{1cm} (8)

Since we are dealing with fully ordered LA, it was assumed in the regression analysis that $t = t_{\text{1}} = 0 = 1$ for the T10 tetrahedron, and $t = t_{\text{1}} = t_{\text{2}} = t_{\text{2}} = n_{\text{An}}/3$ for the three Si-containing tetrahedra.

The regression results given in Table 2 demonstrate small standard deviations for the $c_3$ and $c_4$ coefficients and accordingly large Student $t$ values which are much larger than those for the $c_1$ and $c_2$ coefficients, indicating that mean tetrahedral T-O distances can be more precisely fitted than individual distances in low albites. Indeed, the rms value only amounts to $\sqrt{\Sigma ((T-O) - \langle (T-O) \rangle)^2/24} \equiv 0.0003$ Å. The large Student $t$ value of the $c_3$ coefficient when compared to the $c_4$ coefficient demonstrates that – not surprisingly –

| $T-O - \langle T-O \rangle$ | $\langle T-O \rangle$ | $\langle (T-O) \rangle$ |
|---------------------------|-----------------|----------------|
| $c_1 \Delta \rho_{\text{Na,T}} + c_2 \Delta f_s(O)$ | $c_3[t - 0.25(1 + n_{\text{An}})] + c_4 \Delta \{f_s(O)\}$ |
| $\langle T-O \rangle$ | $\langle (T-O) \rangle$ |
| $c_1$ | 0.1312(23) | 0.1312(23) |
| $|\text{Student } t|$ | 56 | 745 |
| $\langle T-O \rangle$ | $\langle (T-O) \rangle$ |
| $c_2$ | $-0.1757(79)$ | $0.1907(51)$ |
| $|\text{Student } t|$ | 22 | 37 |
| $\langle T-O \rangle$ | $\langle (T-O) \rangle$ |
| $r^2$ | 0.97 | 1.00 |
| $\langle T-O \rangle$ | $\langle (T-O) \rangle$ |
| e.s.d. | 0.0022 Å | 0.0003 Å |

Table 2. Results of the regression analyses according to Eqs. (7) and (8). Errors given in parentheses refer to the last decimal places.
Δ(T–O) mainly depends on Δt and to a lesser extent on Δ\(f_s(O)\).

Figure 4 demonstrates the quality of the fit. ⟨T–O⟩ distances calculated from Eq. (8) and observed distances follow straight lines with a slope of 1. No systematic deviation that would point to a deficiency of the model is observed. This could only be achieved after choosing CN(\(Na\)) = 8 rather than 5. From the six LA structures that we are considering, six data points result for each of the four non-equivalent tetrahedra. Ideally, these data points should coincide. They do not because each of the six low albites has its own grand mean T–O distance, an effect that smears the data points over the diagonal. In addition, deviations from complete order have the same effect as can be seen for the Crete LA, which has the smallest \(T_10–O\) distance, indicating slight disorder (also suggested by its lattice parameters).

Equation (8) may be recast into the form of Eq. (1), with the observed bond lengths, ⟨T–O⟩\(_{ob}\), now substituted by the adjusted ones, ⟨T–O⟩\(_{adj}\):

\[
t = 0.25(1 + n_{An}) + \frac{\langle T–O \rangle_{adj} - \langle \langle T–O \rangle \rangle}{c_3} \]

\[
\langle T–O \rangle_{adj} = \langle T–O \rangle_{ob} - c_4 \{ \langle f_s(O) \rangle - \langle \langle f_s(O) \rangle \} \}
\]

(S9)

Table 1 lists the observed and calculated bond lengths (Eq. 8). They deviate from each other by less than 0.001 Å. The adjusted lengths are listed as well. Among these, the respective three \(\langle Si–O \rangle\) distances of each crystal are particularly interesting because they should have the same size after adjustment. The \(T_1m\) tetrahedron, being involved in the largest \(T–O–T\) angle, is always observed to be the smallest of the three Si tetrahedra, while the \(T_2m\) tetrahedron, being involved in the smallest \(T–O–T\) angle, is the largest. After adjustment, the three \(\langle Si–O \rangle\) distances agree within 0.001 Å. The \(t\) column of Table 1 demonstrates the close agreement between calculated and expected LA site occupancies. Results obtained by Meneghinello et al. (1999), \(t_{Menegh}\), are listed for comparison.

3 Al,Si distribution in intermediate to high albite and analbite

A considerable number of structure refinements of Na-feldspars that were heat-treated to produce variable states of disorder are available from the literature. Meneghinello et al. (1999) performed refinements on albites heated at \(T = 1050–1090^\circ C\) for various durations of time. The authors calculated Al site occupancies following the method of Alberti and Gottardi (1988). They could, however, not reproduce full order for LA but obtained \(t_10 < 1\). In addition, the expectation that \(t_{1m} = t_{20} = t_{2m}\) was not met (Table 1). More seriously, the authors found that the Al content of the \(T_1m\) site in HA is larger than that of the \(T_10\) site, which appears implausible. Recently, Tribaudino et al. (2018) investigated peak positions and line widths of Raman spectra taken at several heated low-albite crystals and related the spectral changes to the state of order determined by X-ray structure refinement. The authors applied a macroscopic order parameter originally designed for An-rich plagioclases by Angel et al. (1990). Further refinements of HA come from Prewitt et al. (1976) and Winter et al. (1979). Analbite was prepared by Curet et al. (2011), who heat-treated low albite at \(T > 980^\circ C\) for 2 months and eventually arrived at the equilibrium state of monalbite (metastable analbite after quench). Only one of the available intermediate albites possesses an equilibrated Al,Si distribution. It originates from the suite of reversed experiments at \(P \approx 18\) kbar by Goldsmith and Jenkins (1985). The crystal structure has been refined by Phillips et al. (1989). In Table 3, tetrahedral sizes and Al occupancies of all considered albites are listed.
We found that, in any case, in particular in the HA region, it is \( t_{10} > t_{1m} \), contrasting with Meneghinello et al. (1999). Further, in agreement with Meneghinello et al. (1999), it is always seen that \( t_{2} \approx t_{2m} \); the average of both is denoted below as \( t_{2} \). It is noticeable that in the IA region (\( t_{10} \geq 0.45 \)), \( t_{1m} \) tends to be smaller than \( t_{2} \) rather than the opposite. The reason may be that Al in the first non-equilibrium stages of heating and disordering avoids to some extent the small \( T_{1m} \) tetrahedron in favour of the larger \( T_{2} \) tetrahedra. By contrast, in the equilibrated IA of Phillips et al. (1989) \( t_{1m} > t_{20} = t_{2m} \) as expected.

To characterise the Al-Si distribution in their heated albites, Tribaudino et al. (2018) choose an order parameter that may be rewritten in terms of Eq. (1):

\[
t_{10} - \langle t_{1m} \rangle = t_{10} - \frac{1}{3}(t_{1m} + t_{20} + t_{2m}) = \frac{(T_{10} - O) - \frac{1}{4}((T_{1m} - O) + (T_{20} - O) + (T_{2m} - O))}{K},
\]

where \( K \) denotes the size difference \( \langle Al-O \rangle - \langle Si-O \rangle \). The authors adapted \( K = 0.135 \) Å from Angel et al. (1990), who stated, however, that severe deviations in their calibration of \( K \) occurred for four low albites. In fact, \( K \) appears large compared to the size difference of 0.127(3) Å found from the \( (T-O)_{obs} \) values in Table 1. As a consequence of the large \( K \), the difference \( t_{10} - \langle t_{1m} \rangle \) (termed \( Q_{sd} \) by Tribaudino et al., 2018) tends to be small, especially for more ordered albites. In their unheated albite crystal, for example, \( t_{10} - \langle t_{1m} \rangle = 0.94 \) for \( K = 0.135 \) Å but 0.99 for \( K = 0.127 \) Å. As to be expected from Eq. (10), this difference continuously decreases with increasing disorder.

When site occupancies of Na-rich feldspars are to be derived from uncorrected \( (T-O) \) distances, we suggest that \( K = 0.127(3) \) Å be preferred in Eqs. (1) and (10).

The individual site occupancies listed in Table 3 are plotted versus the difference \( \Delta t_{1} = (t_{10} - t_{1m}) \) in Fig. 5. The relations are linear; that is, it suffices to know \( \Delta t_{1} \) to derive individual \( t \) values. Regression lines originating from \( t_{10} = 1 \) and \( t_{1m} = t_{20} = t_{2m} = 0 \), respectively, have been drawn through the data points, emphasising the refinement results in the HA region for reasons noted above. The resulting equations are simple:

\[
t_{10} = (1 - b_{0}) + b_{0}(t_{10} - t_{1m}) \quad t_{1m} = (1 - b_{0}) - (1 - b_{0})(t_{10} - t_{1m}) \quad (11)
\]
\[
t_{20} = t_{2m} = (b_{0} - 0.5) - (b_{0} - 0.5)(t_{10} - t_{1m})
\]

with \( b_{0} = 0.7288(16) \). Accordingly, the \( t_{10} \) and \( t_{1m} \) lines intersect at \( t_{10} = t_{1m} = 0.271(2) \), where \( t_{20} = t_{2m} = 0.229(2) \); that is, high-Albite transforms to monalbite before it becomes fully disordered as is sometimes misstated in the literature (standard deviations are given in parentheses and refer to the last decimal place(s)).

![Figure 5](https://doi.org/10.5194/ejm-32-427-2020)

**Figure 5.** Al site occupancies \( t_{10}, t_{1m}, t_{20} = t_{2m} \) (Eq. 9) vary linearly with the difference \( (t_{10} - t_{1m}) \). The data are compiled in Tables 1 and 3 (red: Wainwright and Starkey, 1968; Wenk and Kroll, 1984; Armbruster et al., 1990; Downs et al., 1994; Winter et al., 1970; Prewitt et al., 1976; Curetti et al., 2011; black: Phillips et al., 1989; green: Meneghinello et al., 1999; blue: Tribaudino et al., 2018). The sizes of the data points comply with the estimated errors.

### 4 Unit cell dimensions and Al site occupancies

Kroll and Ribbe (1983, 1987) related the length difference \( tr[110] - tr[110] \) to the site occupancy difference \( (t_{10} - t_{1m}) \) (Fig. 1). At the time, structural data of intermediate albites were lacking so that the authors based their calibration on chosen reference values for AA and LA. Introducing the IA and HA refinements of Meneghinello et al. (1999) and Tribaudino et al. (2018) confirms the linear dependence of \( \Delta tr[110] \) on \( (t_{10} - t_{1m}) \) (Fig. 6):

\[
\Delta tr[110][\AA] \equiv tr[110] - tr[110] = a_{0} + a_{1}(t_{10} - t_{1m}), \quad (12)
\]

with \( a_{0} = -0.0341(21) \) Å, \( a_{1} = 0.3092(31) \) Å and esd = 0.006 Å. It is advisable to calibrate the length difference rather than the two individual repeat distances because this largely eliminates the effect of measurement errors in the \( a \) and \( b \) cell dimensions. Combining Eqs. (11) and (12) allows individual site occupancies to be obtained from the length difference \( \Delta tr[110] \):

\[
t_{10} = (1 - b_{0}) + b_{0}(b_{1} + b_{2} \Delta tr[110])
\]
\[
t_{1m} = (1 - b_{0}) - (1 - b_{0})(b_{1} + b_{2} \Delta tr[110])
\]
\[
t_{2} = (b_{0} - 0.5) - (b_{0} - 0.5)(b_{1} + b_{2} \Delta tr[110])
\]

with \( b_{0} = 0.7288(16) \), \( b_{1} = 0.1103(59) \), \( b_{2} = 3.234(32) \) Å\(^{-1} \) and esd(t) = 0.01.
Table 3. Mean tetrahedral distances, \(\langle T-O \rangle\) [Å], and Al site occupancies, \(t\), of 16 intermediate to high albites and 1 analbite. \(\langle T-O \rangle_{adj}\) and \(t\) were obtained from Eq. (9). Values of \(t_{\Delta\mu[110]}\) were derived from the length difference \(\Delta t[110]\) (Eq. 13). \(t\) values have been normalised to \(\Sigma t = 1\). Site occupancies \(t_{\text{Menegh}}\) from Meneghinello et al. (1999) are listed for comparison.

| Reference/locality/treatment | Site   | \(\langle T-O \rangle_{obs}\) | \(\langle T-O \rangle_{adj}\) | \(t\) | \(t_{\Delta\mu[110]}\) | \(t_{\text{Menegh}}\) |
|-----------------------------|--------|-------------------------------|-------------------------------|------|-----------------------|----------------------|
| Curetti et al. (2011)       | T\(_{10}\) | 1.648                        | 1.646                        | 0.27 | 0.27                  |                      |
| Aosta Valley, Italy         | T\(_{1m}\) | 1.643                        | 1.647                        | 0.27 | 0.27                  |                      |
| 32 d, 1000 °C; 28 d, 1060 °C| T\(_{20}\) | 1.643                        | 1.642                        | 0.23 | 0.23                  |                      |
| AA                          | T\(_{2m}\) | 1.642                        | 1.641                        | 0.23 | 0.23                  |                      |
|                             | Grand mean T-O | 1.6439                       |                               |      |                       |                      |
| Prewitt et al. (1976)       | T\(_{10}\) | 1.646                        | 1.645                        | 0.27 | 0.28                  | 0.26                 |
| Synth. HA (700 °C, 5 kbar)  | T\(_{1m}\) | 1.641                        | 1.645                        | 0.27 | 0.27                  | 0.30                 |
| 40 d, 1060 °C               | T\(_{20}\) | 1.641                        | 1.640                        | 0.23 | 0.23                  | 0.22                 |
| HA                          | T\(_{2m}\) | 1.642                        | 1.640                        | 0.23 | 0.23                  | 0.22                 |
|                             | Grand mean T-O | 1.6427                       |                               |      |                       |                      |
| Winter et al. (1979)        | T\(_{10}\) | 1.649                        | 1.647                        | 0.28 | 0.28                  | 0.27                 |
| Tiburon, Ca., USA           | T\(_{1m}\) | 1.641                        | 1.645                        | 0.27 | 0.27                  | 0.30                 |
| 60 d, 1080 °C               | T\(_{20}\) | 1.640                        | 1.640                        | 0.22 | 0.22                  | 0.21                 |
| HA                          | T\(_{2m}\) | 1.642                        | 1.640                        | 0.23 | 0.23                  | 0.22                 |
|                             | Grand mean T-O | 1.6430                       |                               |      |                       |                      |
| Phillips et al. (1989)      | T\(_{10}\) | 1.677                        | 1.676                        | 0.51 | 0.49                  | 0.46                 |
| Clear Creek, Ca., USA       | T\(_{1m}\) | 1.631                        | 1.635                        | 0.18 | 0.19                  | 0.23                 |
| 19 d, 777 °C, 17 kbar       | T\(_{20}\) | 1.632                        | 1.632                        | 0.15 | 0.16                  | 0.15                 |
| IA                          | T\(_{2m}\) | 1.633                        | 1.631                        | 0.15 | 0.16                  | 0.16                 |
|                             | Grand mean T-O | 1.6430                       |                               |      |                       |                      |
| Meneghinello et al. (1999)  | T\(_{10}\) | 1.731                        | 1.729                        | 0.94 | 0.92                  | 0.91                 |
| Stintino, Sardinia, Italy   | T\(_{1m}\) | 1.609                        | 1.613                        | 0.01 | 0.03                  | 0.04                 |
| 3 d, 1050 °C                | T\(_{20}\) | 1.616                        | 1.616                        | 0.03 | 0.02                  | 0.02                 |
| IA                          | T\(_{2m}\) | 1.617                        | 1.615                        | 0.02 | 0.02                  | 0.03                 |
|                             | Grand mean T-O | 1.6436                       |                               |      |                       |                      |
| Meneghinello et al. (1999)  | T\(_{10}\) | 1.719                        | 1.718                        | 0.86 | 0.89                  | 0.84                 |
| Stintino, Sardinia, Italy   | T\(_{1m}\) | 1.612                        | 1.616                        | 0.04 | 0.04                  | 0.07                 |
| 6 d, 1060 °C                | T\(_{20}\) | 1.619                        | 1.618                        | 0.06 | 0.03                  | 0.05                 |
| IA                          | T\(_{2m}\) | 1.618                        | 1.616                        | 0.04 | 0.03                  | 0.04                 |
|                             | Grand mean T-O | 1.6421                       |                               |      |                       |                      |
| Meneghinello et al. (1999)  | T\(_{10}\) | 1.708                        | 1.706                        | 0.77 | 0.79                  | 0.78                 |
| Stintino, Sardinia, Italy   | T\(_{1m}\) | 1.613                        | 1.617                        | 0.06 | 0.08                  | 0.08                 |
| 7 d, 1070 °C                | T\(_{20}\) | 1.621                        | 1.620                        | 0.08 | 0.07                  | 0.06                 |
| IA                          | T\(_{2m}\) | 1.623                        | 1.621                        | 0.09 | 0.07                  | 0.08                 |
|                             | Grand mean T-O | 1.6412                       |                               |      |                       |                      |
| Meneghinello et al. (1999)  | T\(_{10}\) | 1.721                        | 1.719                        | 0.88 | 0.88                  | 0.90                 |
| Stintino, Sardinia, Italy   | T\(_{1m}\) | 1.610                        | 1.615                        | 0.04 | 0.04                  | 0.05                 |
| 7 d, 1080 °C                | T\(_{20}\) | 1.616                        | 1.616                        | 0.05 | 0.04                  | 0.02                 |
| IA                          | T\(_{2m}\) | 1.617                        | 1.615                        | 0.04 | 0.04                  | 0.03                 |
|                             | Grand mean T-O | 1.6411                       |                               |      |                       |                      |
| Meneghinello et al. (1999)  | T\(_{10}\) | 1.705                        | 1.704                        | 0.76 | 0.78                  | 0.78                 |
| Stintino, Sardinia, Italy   | T\(_{1m}\) | 1.615                        | 1.620                        | 0.08 | 0.08                  | 0.10                 |
| 10 d, 1080 °C               | T\(_{20}\) | 1.620                        | 1.620                        | 0.08 | 0.07                  | 0.06                 |
| IA                          | T\(_{2m}\) | 1.621                        | 1.619                        | 0.08 | 0.07                  | 0.06                 |
|                             | Grand mean T-O | 1.6403                       |                               |      |                       |                      |

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Table 3. Continued.

| Reference/locality/treatment | Site | ⟨T–O⟩obs | ⟨T–O⟩adj | t | t_{Δt}[110] | t_{Menegh} |
|-----------------------------|------|----------|----------|---|------------|------------|
| Meneghinello et al. (1999)  | T\textsubscript{1}0 | 1.703 | 1.701 | 0.73 | 0.75 | 0.75 |
| Stintino, Sardinia, Italy   | T\textsubscript{1}m | 1.616 | 1.620 | 0.09 | 0.09 | 0.10 |
| 7 d, 1090 °C                | T\textsubscript{2}0 | 1.622 | 1.621 | 0.10 | 0.08 | 0.08 |
| IA                          | T\textsubscript{2}m | 1.622 | 1.620 | 0.08 | 0.08 | 0.07 |
| Grand mean T–O             |      | 1.6406  |          |    |            |            |
| Meneghinello et al. (1999)  | T\textsubscript{1}0 | 1.664 | 1.662 | 0.44 | 0.43 | 0.43 |
| Stintino, Sardinia, Italy   | T\textsubscript{1}m | 1.631 | 1.635 | 0.22 | 0.21 | 0.25 |
| 12 d, 1090 °C               | T\textsubscript{2}0 | 1.632 | 1.631 | 0.18 | 0.18 | 0.17 |
| HA                          | T\textsubscript{2}m | 1.630 | 1.629 | 0.16 | 0.18 | 0.15 |
| Grand mean T–O             |      | 1.6392  |          |    |            |            |
| Tribaudino et al. (2018)    | T\textsubscript{1}0 | 1.720 | 1.718 | 0.84 | 0.85 |          |
| Minas Gerais, Brazil        | T\textsubscript{1}m | 1.614 | 1.618 | 0.05 | 0.06 |          |
| 11 d, 1076 °C               | T\textsubscript{2}0 | 1.620 | 1.619 | 0.05 | 0.05 |          |
| IA                          | T\textsubscript{2}m | 1.622 | 1.620 | 0.06 | 0.05 |          |
| Grand mean T–O             |      | 1.6439  |          |    |            |            |
| Tribaudino et al., 2018     | T\textsubscript{1}0 | 1.686 | 1.685 | 0.58 | 0.58 |          |
| Minas Gerais, Brazil        | T\textsubscript{1}m | 1.626 | 1.631 | 0.14 | 0.16 |          |
| 20 d, 1076 °C               | T\textsubscript{2}0 | 1.630 | 1.629 | 0.13 | 0.13 |          |
| IA                          | T\textsubscript{2}m | 1.633 | 1.631 | 0.15 | 0.13 |          |
| Grand mean T–O             |      | 1.6438  |          |    |            |            |
| Tribaudino et al., 2018     | T\textsubscript{1}0 | 1.659 | 1.657 | 0.37 | 0.37 |          |
| Minas Gerais, Brazil        | T\textsubscript{1}m | 1.638 | 1.642 | 0.24 | 0.24 |          |
| 25 d, 1076 °C               | T\textsubscript{2}0 | 1.637 | 1.636 | 0.19 | 0.20 |          |
| HA                          | T\textsubscript{2}m | 1.639 | 1.637 | 0.20 | 0.20 |          |
| Grand mean T–O             |      | 1.6437  |          |    |            |            |
| Tribaudino et al., 2018     | T\textsubscript{1}0 | 1.691 | 1.689 | 0.62 | 0.62 |          |
| Minas Gerais, Brazil        | T\textsubscript{1}m | 1.624 | 1.628 | 0.13 | 0.14 |          |
| 28 d, 1076 °C               | T\textsubscript{2}0 | 1.628 | 1.628 | 0.12 | 0.12 |          |
| IA                          | T\textsubscript{2}m | 1.631 | 1.630 | 0.14 | 0.12 |          |
| Grand mean T–O             |      | 1.6437  |          |    |            |            |
| Tribaudino et al., 2018     | T\textsubscript{1}0 | 1.663 | 1.662 | 0.40 | 0.38 |          |
| Minas Gerais, Brazil        | T\textsubscript{1}m | 1.635 | 1.639 | 0.21 | 0.23 |          |
| 32 d, 1076 °C               | T\textsubscript{2}0 | 1.636 | 1.635 | 0.19 | 0.19 |          |
| HA                          | T\textsubscript{2}m | 1.639 | 1.638 | 0.20 | 0.19 |          |
| Grand mean T–O             |      | 1.6435  |          |    |            |            |
| Tribaudino et al., 2018     | T\textsubscript{1}0 | 1.649 | 1.648 | 0.29 | 0.30 |          |
| Minas Gerais, Brazil        | T\textsubscript{1}m | 1.642 | 1.646 | 0.27 | 0.26 |          |
| 40 d, 1076 °C               | T\textsubscript{2}0 | 1.641 | 1.640 | 0.22 | 0.22 |          |
| HA                          | T\textsubscript{2}m | 1.641 | 1.639 | 0.22 | 0.22 |          |
| Grand mean T–O             |      | 1.6431  |          |    |            |            |

5 Calibration of tr[110] – tr[\overline{1}10] versus Δθ(131)

In order to transfer the values of Δθ(131) = 2θ(131) − 2θ(131) (CuKα1) of Goldsmith and Jenkins (1985) into individual site occupancies via Eq. (13), we need to calibrate Δθ(131) in terms of Δtr[110]. The largest number of suitable data covering nearly the full range between AA and LA can be found with Martin (1970). We added data by Grundy and Brown (1969), Kroll et al. (1980), Phillips et al. (1989), Waterwiese et al. (1995), and Tribaudino et al. (2018) and attached the reference values of AA and LA of Kroll and Ribbe (1983). The resulting diagram is shown in Fig. 7. The variation in data is nearly linear and can be fitted by the expression

$$\Delta tr[110] [\text{Å}] = 0.741(54) - 0.465(70) \Delta \theta(131) + 0.043(20) \Delta \theta(131)^3 - 0.0058(23) \Delta \theta(131)^5.$$

(14)
The effect of pressure on the state of order

When confining pressure is applied to albite that is initially in a disordered state (IA or HA), its Al, Si distribution will change towards order. This was attributed by Orville (1967) and Goldsmith and Jenkins (1985) to the entropy and volume changes of LA to HA in terms of the Clausius–Clapeyron equation

\[ \frac{dT}{dP} (\text{LA} \rightarrow \text{HA}) = \frac{\Delta V}{\Delta S}. \]  

The authors emphasise that “the calculations were made although the transition takes place over a temperature range whereas the Clausius–Clapeyron equation is normally applied to univariant reactions with coexisting phases”. Goldsmith and Jenkins (1985) suggested \( \frac{dT}{dP} = 2.9 \text{ K kbar}^{-1} \) from data of Holland (1980). This means, for example, when an internally equilibrated IA is subjected to a pressure of 10 kbar, then in order to counteract the ordering tendency it would be necessary to increase the temperature by some 30 K to preserve the original state of order. Downs et al. (1994) investigated the structural changes in LA with pressure and suggested a mechanism for the pressure-dependent ordering. They found that the mean \( \theta - O_{C} - T \) angle in alkali feldspars tends to stiffen with increasing Al, Si disorder so that, conversely, a disordered albite would yield to pressure by ordering.

In order to estimate the pressure effect, we follow an approach different from the Clausius–Clapeyron equation. It relies on the direct comparison of equilibrated structural states attained at low pressures (LPs) and high pressures (HPs). For this comparison, however, only LP samples equilibrated at \( T \geq 750 \text{°C} \) are suitable because for kinetic reasons it is unlikely that equilibrium is achieved below that temperature (Goldsmith and Jenkins, 1985). Figure 8 combines HP data of Goldsmith and Jenkins (1985) and Waterwiese et al. (1995) and LP data of Grundy and Brown (1969) and Kroll et al. (1980). A third-order polynomial has been drawn through the LP data, and the differences between the temperatures of the HP experiments and the temperatures found on the LP curve for the same \( \Delta \theta(131) \) values have been related to the corresponding pressure differences, resulting in \( \langle \Delta T / \Delta P \rangle = 4.2(2) \text{ K kbar}^{-1} \). The scatter of the HP data is to some degree due to the different pressures of the experiments (15–21 kbar). A curve has been drawn for \( P = 18 \text{ kbar} \), at which most of the Goldsmith and Jenkins experiments have been performed. The value of \( 4.2(2) \text{ K kbar}^{-1} \) is not necessarily applicable, however, down to the temperatures where ordered low albite is stable.

Waterwiese et al. (1995) have taken care of this problem by applying a thermodynamic approach. Using Landau theory, Salje et al. (1985) have treated the thermodynamic behaviour of Na-feldspar in terms of two coupled order parameters, \( Q \) and \( Q_{out} \), related to the displacive lattice distortion and to the state of Al, Si order, respectively. Both order parameters are unity for LA at 0 K, but at equilibrium conditions they decrease with increasing temperature, eventually reaching zero at the HA–MA transition. Salje et al. (1985) calculated thermodynamic state properties \( \Delta Y = Y(\text{albite}) - Y(\text{MA}) \) as a function of temperature \( Y \) denotes internal energy \( U \) or entropy \( S \) for equilibrated albites. Taking the differences \( Y_{t}(T) = \Delta Y(T) - \Delta Y(T_{0}) \) \( (T_{0} = 298.15 \text{ K}) \), Waterwiese et al. (1995) obtained state properties owing to the transition from LA towards MA. In addition, they devised a method to describe \( Y_{t}(T) \) so that the Gibbs energy \( G_{t}(P, T) \) is fully determined. As stated above, when albite, being in internal equilibrium at pressure \( P_{1} \) and temperature \( T_{1} \), is subjected to pressure \( P_{2} > P_{1} \), then in order to avoid ordering, the temperature has to be raised, \( T_{2} > T_{1} \), so that \( G(P_{1}, T_{1}) = G(P_{2}, T_{2}) \). Since \( U_{t}(T) \), \( S_{t}(T) \) and \( V_{t}(T) \) are
known, it is possible to find from

\[ U_0(T_1) - T_1 S_0(T_1) + P_1 V_0(T_1) = U_0(T_2) - T_2 S_0(T_2) + P_2 V_0(T_2) \]  

(16)

the temperature \( T_1 \) at which the albite at \( P_1 \) has the same state of order as it has at \( (P_2, T_2) \). \( T_2 \) must be larger than \( T_1 \) because \( V_0 \) is positive. We have used Eq. (16) to adjust the experimental temperatures of Goldsmith and Jenkins (1985) and Waterwiese et al. (1995) to \( P = 1 \) bar. In the range of \( 600 \, ^\circ C < T < 1000 \, ^\circ C \), the calibration according to Fig. 8 practically coincides with the adjustment after the Waterwiese method, the largest deviation being just \( 4 \, ^\circ C \). Below \( 600 \, ^\circ C \), the deviation becomes larger because \( \Delta T/\Delta P \) is not a constant but steadily decreases to reach zero at \( 25 \, ^\circ C \).

7 The Al,Si distribution at equilibrium with temperature and pressure

We are now prepared to convert the \( \Delta 2\theta(131) \) indicator of order reported by Goldsmith and Jenkins (1985) into individual site occupancies valid at ambient or any other pressure using Eqs. (13), (14) and (16). We have added the HP runs of Waterwiese et al. (1995) in which (nearly) internal equilibrium has been achieved as well as the LP runs of Grundy and Brown (1969) and Kroll et al. (1980) at \( T \geq 750 \, ^\circ C \). Figure 9 displays the variation with temperature of the thermodynamic order parameter \( Q_{od} = (t_1 0 - t_1 m)/(t_1 0 + t_1 m) \) (Salje 1985). The data points refer to the pressure \( P = 1 \) bar. In addition, the Goldsmith and Jenkins data in the IA region are also plotted for \( P = 18 \) kbar, omitting the data in the LA and HA regions to avoid confusion. The three regions can be characterised by linear changes connected by smooth transitions. Goldsmith and Jenkins (1985) note that, at a pressure of 18 kbar, LA begins to disorder at \( \approx 660 \, ^\circ C \), while IA turns into HA at \( \approx 790 \, ^\circ C \). At 1 bar these temperatures would be lower by about \( 70 \, ^\circ C \), i.e. 590 and 720 \, ^\circ C \, after application of the Waterwiese adjustment method. The disordering from LA to HA thus proceeds in a continuous manner and extends over only \( 80 \, ^\circ C \), from 620 to 700 \, ^\circ C \, when we consider only the temperature range in which most of the disordering occurs. Note that the analogous microcline to sanidine transition in K-feldspar, where the influence of the displacive order parameter \( \bar{Q} \) is missing, is discontinuous (Carpenter and Salje, 1994).

The HA regime extends over a temperature range that is more than twice as large as the IA regime. Whereas in the IA region Al,Si order and disorder are the dominant structural processes, displacive structural shearing dominates in the HA region; that is, in the IA regime, the \( Q_{od} \) order parameter dominates over the \( Q \) parameter, while the opposite is true for the HA regime. The changes in \( Q \) and \( Q_{od} \) are reflected in the variation in the lattice angles \( \alpha \) and \( \gamma \). During disordering in the IA regime, Al leaves the \( T_1 0 \) sites in the [110] diagonal in favour of the \( T_1 m \) sites in the [110] diagonal (Fig. 1), thereby widening the lattice angle \( \gamma \) towards \( 90^\circ \). On the other hand, during heating in the HA regime, it is mainly the lattice angle \( \alpha \) that changes towards \( 90^\circ \) in response to the decrease in structural shearing.

From Fig. 9 we can judge the effect that increasing pressure has on the state of order. The effect is relatively small for
where $t_2$ at $T$ (HA $\rightarrow$ MA). Above that temperature, monalbite is the stable state up to the melting point (1118°C). In that region, the disordering process is non-convergent as it is in sanidine. Even if $t_1 = t_2$ could be reached before melting, no phase transition needs to be related. Rather, at this point, a crossover could occur from a regime where $t_1 > t_2$ to a regime with $t_1 < t_2$. The thermodynamic condition for a crossover is discussed by Kroll et al. (2006) for the case of olivine MgFe[SiO$_4$]. A more general treatment is given by Christy (1995).

### 8.2 The pressure correction

The transition from LA to HA at 1 bar occurs over practically the same temperature range as it does at $\approx 18$ kbar, the two pairs of straight lines being nearly parallel (Fig. 9). Brown and Parsons (1989) compared the results of available non-reversed hydrothermal experiments and suggested a curve that has a gentler slope than indicated by the Goldsmith and Jenkins data. It has already been mentioned that the value for $(\Delta T/\Delta P) = 4.2$ K kbar$^{-1}$ derived for the range $T > 750$°C may not be valid towards temperatures at which LA is fully ordered. For the Waterwiese method, $\Delta T/\Delta P$ reaches zero at $T = 25$°C. The approach towards zero becomes pronounced only below ca. 500°C. The gentle slope of the Brown and Parsons curve would indicate that this effect sets in at higher temperatures. The method of Waterwiese et al. (1985) relies on the $\Delta U$ and $\Delta S$ data of Salje et al. (1985), which, however, result in a course of $Q_{od}(T)$ that clearly deviates from the one set by the Goldsmith and Jenkins data, whether corrected or not (Fig. 9). This causes an element of uncertainty that cannot be resolved at present.

### 8.3 State of order in feldspars other than albite

There is only one feldspar other than low albite whose state of order we can be confident of; that is low microcline (LM). Anorthite, which is also usually taken to be fully ordered, is problematic, as shown by Angel et al. (1990), who found that the Val Pasmeda crystal had $Q_{od} = 0.92$. For LM, we have chosen the careful refinement by Strob (1983; Table 1). The sequence of sizes of the Si-centred tetrahedra is the same as in LA, $(T_{1m}–O) < (T_{20}–O) < (T_{2m}–O)$, though the differences are less pronounced. From Eq. (8), assuming full order, we obtain calculated (T–O) distances that deviate from the observed ones only in the fourth decimal place. Furthermore, the three (Si–O) distances, which after removing the T–O–T angle influence (Eq. 9) should agree, do so with deviations in the fourth decimal place. Finally, the AI site occupancies comply with the assumption of full order. It thus appears that the analysis presented above can be applied to the full range of alkali feldspar compositions.
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