

Appraisal of the Ferguson method and the linear model using $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$ to estimate tetrahedral Al-contents in alkali feldspar

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ABSTRACT. The new method proposed by Ferguson (1980, 1981) for estimating the *T*-site occupancies in K-rich feldspars from lattice constants is discussed and compared with the linear model using the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$. The latter method appears to be considerably more effective in view of its wider application to alkali feldspars of different compositions and structural states. Ferguson's (1980, 1981) method has been conceived for K-rich feldspars alone and may produce results that tend to be more erroneous the further a K-rich feldspar lies from the two-step ordering paths involved in the formulation of the determinative procedure itself.

IN the last ten years or so, the most widely employed procedure for estimating the Al-contents of the *T*-sites in alkali feldspars from refined lattice constants has been that based on the linear model using the structural indicators $\Delta(bc)$ (Stewart and Ribbe, 1969; Stewart and Wright, 1974; Blasi, 1980), $\Delta(b^*c^*)$ (Smith, 1968, 1974; Blasi, 1980), $\Delta(\alpha\gamma)$ (Blasi, 1978, 1980), and $\Delta(\alpha^*\gamma^*)$ (Smith, 1968, 1974; Stewart and Ribbe, 1969; Stewart and Wright, 1974; Blasi, 1978, 1980).

More recently Ferguson (1980, 1981) has assessed the above procedure and established a new determinative method for estimating Si,Al distribution in K-rich feldspars from appropriate lattice elements.

Since knowledge of the correlation of tetrahedral Al-contents with lattice constants is of great interest in alkali feldspar mineralogy and consequent petrological applications, the present paper will discuss the new method of Ferguson (1980, 1981) by focusing attention on some points that are worth examining thoroughly and will reappraise the soundness of the procedure using the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$.

Outline of Ferguson's (1980, 1981) method

The method of Ferguson (1980, 1981) uses individual lattice constants for estimating $\langle T-O \rangle$ dis-

tances in K-rich feldspars with $N_{Or} \geq \sim 0.85$. These distances are then converted into tetrahedral Al-contents using either the 'modified Jones-Ribbe-Gibbs' or the 'modified Smith-Bailey' relationship, both proposed by Ferguson (1980, 1981) on the basis of data taken from Jones (1968), Ribbe and Gibbs (1969), and Ribbe *et al.* (1974), on the one hand, and from Smith and Bailey (1963) and Smith (1974), on the other. Using an appropriate mathematical procedure, Al-contents can also be directly derived from *b* or *c* or c^*/b^* in monoclinic K-rich feldspars, and from γ or γ^* or $\Delta(131) = 12.5[d(131) - d(\bar{1}\bar{3}1)]$ in triclinic K-rich feldspars.

Discussion

General observations. Ferguson (1980, 1981) proposes the use of individual lattice constants in order to minimize the errors in the derived Al-contents of *T*-sites. This mode of operation may in effect improve the precision of the results but not necessarily their accuracy, which depends on the soundness of the model that interprets the variations in structural states in terms of variations in lattice elements. In fact, in response to variations in the degree of Si,Al ordering, the alkali feldspar framework undergoes distortions that propagate in the lattice in a complicated manner. It is therefore preferable to correlate the effects of such distortions with appropriate combinations of lattice elements as indicated by Stewart and Ribbe (1969), Blasi and Blasi De Pol (1977), and Blasi (1978). The fact that the relationships between *b* and *c*, b^* and c^* , α and γ , α^* and γ^* in the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$ are complicated (Blasi, 1977) is a consequence of the complexities inherent in the problem itself. Despite all this, the combinations of these lattice constants probably tend to minimize errors arising from the complexities of physical effects due to the order-disorder phenomena.

The structural indicators based on individual lattice constants are inevitably also dependent on K,Na substitution. This also applies to structural indicators based on lattice constant ratios, e.g. c^*/b^* , where these are not appropriately combined with other individual lattice constants or other lattice constant ratios. As discussed by Blasi and Blasi De Pol (1977) only a small number of structural indicators based on appropriate combinations of lattice constants can be considered to be at least theoretically independent of K,Na substitution. This seems to be the case with the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$.

The monoclinic case. The method proposed by Ferguson (1980, 1981) for estimating Al-contents of T-sites in monoclinic K-rich feldspars is in principle rather attractive in view of the simplicity of the relevant problem. In this case the determination of the structural state of a given alkali feldspar requires knowledge of two Al-contents alone, i.e. $t1$ and $t2$, which can be virtually reduced to only one when considering that $2t1 + 2t2 = 1$. However, as previously observed, the method of Ferguson (1980, 1981) only partially takes into account the lattice distortions produced by variations in the degree of Si,Al ordering. In fact, it is based on variations in a single lattice direction, that of b or c . The alternative use of ratio c^*/b^* seems to obviate this defect, but, as where b or c are used, it is somewhat influenced by K,Na substitution.

The triclinic case. Major conceptual complications arise in determining Al-contents of T-sites in triclinic K-rich feldspars. In this case, the determination of structural state requires four Al-contents to be known, i.e. $t1o$, $t1m$, $t2o$, and $t2m$, which can virtually only be reduced to two when it is considered that $t2o \sim t2m = t2$ and $t1o + t1m + 2t2 = 1$. The use of γ or γ^* or $\Delta(131)$ here involves similar defects to those already observed when using b or c or c^*/b^* for monoclinic K-rich feldspars.

However, the major weakness of Ferguson's (1980, 1981) method in the triclinic case lies in the fact that it determines tetrahedral Al-contents referred to a single ordering path which is directed toward a highly ordered microcline starting from an orthoclase having a structural state similar to that of specimen Spencer C of Colville and Ribbe (1968). Such an ordering path is clearly followed by a large number of K-rich feldspars and in particular by the suite of specimens studied by Dal Negro *et al.* (1978). However, it does not necessarily represent the sole ordering path for triclinic K-rich feldspars.

In order to understand this situation better, it may be useful to consider as a working example the disordered microcline 273 of Blasi *et al.* (1981),

which follows an ordering path that is tangibly different from that considered by Ferguson (1980, 1981). This is shown by the data presented in Table I and plotted in fig. 1. In particular, the values of $t1o + t1m$ and $t1o - t1m$ derived from $\langle T-O \rangle$ distances are very close to those obtained from the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$ and clearly different from those calculated with Ferguson's (1980, 1981) method. The latter constrains the representative points for the disordered microcline 273 to lie on the two dashed lines in fig. 1, which represent the two ordering paths calculated from γ with the 'modified Jones-Ribbe-Gibbs' and 'modified Smith-Bailey' relationships. Incidentally, the data obtained from γ^* for the disordered microcline 273 are not given in Table I

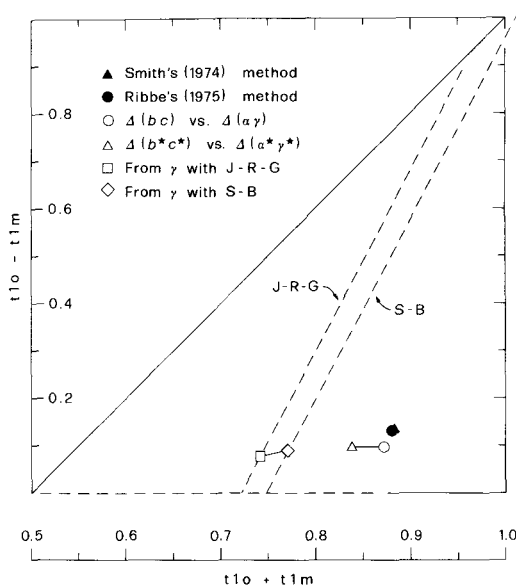


FIG. 1. Relation between sum and difference of Al-contents in $T1o$ and $T1m$ sites, i.e. $t1o + t1m$ and $t1o - t1m$, for disordered microcline 273 (Blasi *et al.*, 1981) as deduced (a) from $\langle T-O \rangle$ distances following the methods of Smith (1974) and Ribbe (1975), (b) from $\Delta(bc)$ and $\Delta(\alpha\gamma)$ or $\Delta(b^*c^*)$ and $\Delta(\alpha^*\gamma^*)$ following the calculation procedure devised by Blasi (1977), (c) from γ with both the 'modified Jones-Ribbe-Gibbs' (briefly J-R-G) and the 'modified Smith-Bailey' (briefly S-B) relationships involved in the method developed by Ferguson (1980, 1981).

The dashed lines represent the ordering paths for K-rich feldspars with $N_{or} \geq \sim 0.85$ calculated from γ following Ferguson's (1980, 1981) method with J-R-G and S-B relationships. In the monoclinic field, the lines for J-R-G and S-B relationships apparently overlap, but single data points do not coincide except for $t1o + t1m = 2t1 = 0.5$.

Table I. Comparison of Al-contents of *T*-sites determined by different procedures for disordered microcline 273

Al-contents of <i>T</i> -sites	From $\langle T-O \rangle$ distances using		From refined lattice constants using			
	Smith's method (1974)†‡	Ribbe's method (1975)†‡	$\Delta(bc)$ and $\Delta(\alpha\gamma)$ §	$\Delta(b^*c^*)$ and $\Delta(\alpha^*\gamma^*)$ §	γ with J-R-G†‡	γ with S-B†‡
t1o	0.507(14)	0.506(13)	0.484(2)	0.467(2)	0.410(2)	0.430(2)
t1m	0.375(16)	0.375(13)	0.388(3)	0.371(3)	0.331(1)	0.340(1)
t2o	0.055(16)					
t2m	0.055(16)	0.060(8)	0.064(2)	0.081(2)	0.1244(2)	0.1050(3)
t1o+t1m	0.882(21)	0.881(15)	0.872(4)	0.838(4)	0.740(1)	0.770(1)
t1o-t1m	0.132(21)	0.131(21)	0.096(3)	0.096(3)	0.079(2)	0.090(3)

Mean *T*-O distances from structure refinement:†‡

$\langle T1o-O \rangle = 1.677(2)$, $\langle T1m-O \rangle = 1.660(2)$, $\langle T2o-O \rangle = 1.619(2)$, $\langle T2m-O \rangle = 1.619(2)$ Å.

Direct and reciprocal lattice constants:§

$a = 8.5833(4)$, $b = 12.9753(11)$, $c = 7.2081(4)$ Å, $\alpha = 90.098(6)$, $\beta = 116.022(4)$, $\gamma = 89.776(7)^\circ$, $V = 721.39(6)$ Å³;
 $\alpha^* = 0.129649(6)$, $b^* = 0.077070(6)$, $c^* = 0.154383(7)$ Å⁻¹, $\alpha^* = 90.001(5)$, $\beta^* = 63.978(4)$, $\gamma^* = 90.202(6)^\circ$.

Estimated standard errors (1σ) are given in parentheses and refer to the last decimal place.

† Principal quantities taken from Blasi *et al.* (1981).

‡ Principal quantities and estimated standard errors taken from Blasi *et al.* (1981).

§ Principal quantities calculated following the method of Ferguson (1980, 1981).

¶ σ 's calculated according to the Law of Propagation of Errors (see Blasi, 1977) assuming that (a) covariance terms can be neglected, (b) coefficients in the equations used to calculate Al-contents can be treated as constants, and (c) individual *T*-O distances can be considered as uncorrelated.

and fig. 1 since they are practically equal to those obtained from γ . This is due to the fact that the method of Ferguson (1980, 1981) assumes a linear relationship between γ^* and γ .

Finally, it is important to point out that in addition to the conversion of individual lattice constants to $\langle T-O \rangle$ distances, the method of Ferguson (1980, 1981) also involves the conversion of $\langle T-O \rangle$ distances to Al-contents. In the specific case of the disordered microclines the first conversion can give rise to the largest errors in determining the structural state. The second conversion also entails a complicated and delicate process (Ribbe *et al.*, 1974; Smith, 1974), which largely depends on the values that one assumes for the Al-O and Si-O distances as well as for their difference.

As the difference between the values of Al-O and Si-O distances, Smith (1974, p. 70) has chosen a value of 0.133 Å and Ribbe (1975, p. R-22, 1979, p. 406) a value of 0.130 Å. Ferguson (1980, 1981) has adopted a value of 0.136 Å for the 'modified Smith-Bailey' relationship and of 0.155 Å for the 'modified Jones-Ribbe-Gibbs' relationship. The latter is the conversion relationship strongly preferred by Ferguson (1980, 1981). However, a value of 0.155 Å seems to be exceedingly high mainly when compared with the value of 0.128 Å inferred from neutron diffraction data obtained by Harlow and Brown (1980) for an Amelia low albite. As a result, the 'modified Jones-Ribbe-Gibbs' relationship

gives the largest discrepancies in tetrahedral Al-contents in disordered microcline 273 as compared with the corresponding data derived from the methods of Smith (1974) and Ribbe (1975) using $\langle T-O \rangle$ distances directly determined by structure refinement (Table I and fig. 1).

Conclusions

The method of Ferguson (1980, 1981) gives an estimate of the Al-contents of the *T*-sites that can be valid only for K-rich feldspars having $N_{Or} \geq \sim 0.85$ and placed on the two-step ordering paths indicated by dashed lines in fig. 1. These two conditions are highly restrictive and severely limit the extent to which the method can be applied to alkali feldspar mineralogy.

The values of tetrahedral Al-contents obtainable with this method tend to be more erroneous the further a K-rich feldspar lies from the two-step ordering paths indicated by the dashed lines in fig. 1. This has clearly been demonstrated with the data presented for the disordered microcline 273 studied by Blasi *et al.* (1981).

The linear model using the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$ depends essentially (a) on the soundness of the values chosen for the lattice constants of the alkali feldspar end-members, (b) on the assumption of linear contouring in the quadrilaterals of the alkali feldspar end-members in the bc , b^*c^* , $\alpha\gamma$, $\alpha^*\gamma^*$ diagrams,

(c) on the assumption of $t2o = t2m = t2$ for every alkali feldspar structure, (d) on the assumption of complete order and complete disorder in alkali feldspar end-members of low and high structural states, respectively.

These assumptions are proved by the data presented and extensively discussed by Stewart and Ribbe (1969), Smith (1974), Stewart and Wright (1974), and Ribbe (1975). Further support is given by the more recent findings of Hovis and Peckins (1978) and Harlow and Brown (1980) which confirm linear contouring on the bc or b^*c^* diagram and a virtually complete order in low albite, respectively.

In any case, it should be considered that the linear model using the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$ represents an approach to a complicated physical reality, which leaves problems open to future research. Recently Blasi (1980) has shown that structural indicators $\Delta(bc)$ and $\Delta(b^*c^*)$ furnish slightly different values in response to non-linear mutual variations in lattice constants with Si,Al ordering. No real superiority of $\Delta(bc)$ or $\Delta(b^*c^*)$ seems to be at present clearly demonstrable (Blasi, 1980). Indeed, in some circumstances the use of the mean value for the two structural indicators would seem to be effective. In spite of these difficulties, Blasi *et al.* (1981, figs. 3 and 4) showed that the structural indicators $\Delta(bc)$, $\Delta(b^*c^*)$, $\Delta(\alpha\gamma)$, $\Delta(\alpha^*\gamma^*)$ in K-rich feldspars used in structure refinement provide values of Al-contents closely comparable with those derived from $\langle T-O \rangle$ distances by means of the methods of Smith (1974) and Ribbe (1975).

The most interesting feature of the method considered is that, besides giving an estimate of structural state, it enables all the possible ordering paths between the one- and two-step ideal trends to be revealed. In addition, since this method is, by its construction, independent of K,Na substitutions, it can be used to estimate tetrahedral Al-contents in alkali feldspars of different compositions. This represents a great advantage over the method developed by Ferguson (1980, 1981). In this way it is in fact possible to compare the structural states of K- and Na-rich feldspars co-existing in the same rocks as well as those of K- and Na-rich phases coexisting in perthitic intergrowths, as in the multiphase microperthite from which the disordered microcline 273 studied by Blasi *et al.* (1981) has been separated.

All these aspects render this method particularly valid, and it can advantageously be used for better comprehension of alkali feldspar mineralogy and relevant petrological problems.

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