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Charge balance and the stability of alkali feldspars.* By W. S. MACKENZIE, *Department of Geology, University of Manchester, Manchester, England* and J. V. SMITH, *Department of Mineralogy and Petrology, Division of Earth Sciences, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.*

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In a paper on the crystal structures of high- and low-temperature albites, Ferguson, Traill & Taylor (1958) have presented a most interesting theory concerning the balance of electrostatic charges in alkali feldspars which explains very neatly the Al distribution in low albite and the concentration of the Al atoms in the $\text{Si}_1(\text{O})$ tetrahedra of low albites and microclines. However, the consequences of the theory with respect to stability of the potassium feldspars are so diametrically opposed to the observations and conclusions of other workers that it is necessary to question the validity of the theory. Although Ferguson, Traill & Taylor (1958) repeatedly warn their readers that caution is necessary in using the theory of charge balance as a measure of stability and that other factors must not be forgotten, they make no reference to the mineralogical and petrological observations that are at variance with their conclusions. It is to rectify this omission that the present note has been written. We should however like to make it clear that, although we are critical of this one aspect of the paper by Ferguson, Traill & Taylor (1958), we, along with other mineralogists and petrologists, owe a considerable debt to Dr W. H. Taylor and the group of crystallographers who have worked with him on the feldspar structures from the time of the publication of the type structure in 1933 up to the present detailed determination of the structures of high- and low-albites.

The essentials of one of the conclusions of Ferguson, Traill & Taylor (1958) are given by the following skeletal quotation:

'If we again accept balance of charge as a measure of stability, striking conclusions ... can be derived ... (a) microcline, the low-temperature partly ordered potassium feldspar, is *less* stable than sanidine, the high-temperature form ... (b) The structure of a *K* feldspar with a perfect charge-balance, and hence presumably more stable than both sanidine and microcline ... should remain monoclinic $C2/m$... (and) it seems reasonable to conclude that the stable low-temperature form thus predicted may be represented by orthoclase.'

If the authors are discussing relative stability at room temperature, as must be assumed since all their data were obtained under these conditions, the first of their conclusions appears to be a contradiction, for the designation low-temperature vis-a-vis high-temperature surely implies that microcline is more stable than sanidine at room temperature. For a number of reasons we believe that microcline is the stable form at low temperature and high sanidine the form stable at the highest temperatures: the following are the two most important of these reasons: (1) microcline-perthite is the potassium feldspar characteristic of the oldest rocks and of most pegmatites. (2) It has been shown by numerous workers that the effect of heating microcline and orthoclase at elevated temperature, whether under dry or hydrothermal con-

ditions, is to produce a high sanidine (Spencer, 1937; Goldsmith & Laves, 1954; etc.).

The first of these observations provides good evidence that microcline is more stable at low temperature than any other potassium feldspar, including orthoclase: the second proves that sanidine is more stable than microcline and orthoclase at high temperature, and by implication that microcline or orthoclase is more stable than sanidine at low temperatures. No theory regarding the relative stability of the different forms of potassium feldspar can be seriously considered unless it accounts for the effect of temperature on the stability of the various forms. The charge balance theory, in its present form, fails in this respect for it implies no variation of stability with temperature.

To overcome the difficulty of accounting for the very common occurrence of the so-called unstable microcline in microcline-perthites, Ferguson, Traill & Taylor (1958) develop the theory that the presence of sodium during cooling is essential to the formation of a microcline and from this it might be implied that the presence of sodium in the lattice actually favours the formation of a microcline-perthite over an orthoclase-perthite. The opposite conclusion is arrived at from a study of all available information on the chemistry of these feldspars. With regard to the chemical composition of the potassium phase only, specimens consisting of a single orthoclase phase may contain up to 15% of sodium feldspar in solid solution (MacKenzie & Smith, 1955) whereas in the microcline series the few available analyses of maximum microcline and microcline-perthite show not more than 7–8% of sodium feldspar in the potassium phase (MacKenzie, 1954). Goldsmith & Laves (1954*b*) also have noted that some natural potassium feldspars with negligible sodium content exhibit all geometrical gradations from the monoclinic condition to that for maximum microcline. Concerning the bulk composition of perthitic feldspars, Spencer (1937) found that in orthoclase-micropertthites the sodium feldspar content ranged up to 52% whereas in microcline-micropertthites the maximum sodium feldspar content did not exceed 31%. Vogt (1926) and Anderson (1928) also observed a similar limited range of composition for microcline-micropertthites. These observations suggest that the solid solution of sodium feldspar, instead of favouring the formation of microcline, prevents its formation and indeed we believe that a microcline-perthite cannot form until a large proportion of the sodium feldspar, originally present in solid solution in most alkali feldspars, has been exsolved from the potassium phase and the microcline will not acquire maximum deviation from monoclinic symmetry until the sodium feldspar in solid solution is less than 7%.

Ferguson, Traill & Taylor (1958) state that 'this argument provides at least a partial explanation for the contrast between the abundance of intermediate microclines and the rarity of albites intermediate in structure between low albite and high albite. We believe that a much more likely explanation is provided by the evidence

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from petrological and phase equilibrium studies which indicate that microcline forms at a lower temperature than low albite (Tuttle & Bowen, 1950; Goldsmith & Laves, 1954b): the lower temperature should result in a more restricted ionic movement and a slowing down of the ordering of the Al and Si atoms permitting a higher temperature structure to persist more easily at low temperature.

In a more general sense we feel that the use of charge balance as a measure of stability must be treated with reservation and indeed Ferguson, Traill & Taylor (1958) have given excellent reasons for this, the chief among these being the partly and perhaps largely covalent character of bonds in silicates. Just two examples of structures in which there is no good balance of charges will be mentioned. In the pyroxene structure the oxygen atom which is linked to the two silicon atoms of the chain, and therefore theoretically inactive, is also bonded to a Ca, Mg, Fe atom (Warren & Bragg, 1928). A second example is melilite in which calcium is surrounded by eight oxygen atoms, four at 2.45 Å and four at 2.70 Å: only by ignoring the shorter contacts can a local balance of charge be achieved (Smith, 1953). We feel that although Pauling's second rule is of fundamental importance and frequently obeyed in detail, other considerations may be of comparable or greater importance and may lead to deviations.

There is a fundamental point concerning the calculation of charge balance for disordered structures which should be mentioned here. If the charges are effective only over short distances comparable to a single unit-cell edge, the charge balance must be worked out for each type of unit cell and an average taken for the different types. If the charge effectively acts over long distances, say several cell edges, it is permissible to take a single average using the mean atomic content at the lattice points for just one unit cell. Ferguson, Traill & Taylor have used the second method of calculation and hence have implicitly assumed that charge operates over long distances. We feel that where stability is concerned it would probably be more correct to use the first type of calculation since atoms act as partial electrostatic screens and charge can only operate over short distances, subject to the general electrostatic neutrality of the whole crystal.

Using the first type of calculation the following results are obtained. In high sanidine there are four types of

unit cells occurring with equal frequency. Assuming that the coordination of the K ion is the same for each type, the charge distributions are those given in Table 1. columns (a), (b), (c), and (d). The orthoclase structure proposed by Ferguson, Traill & Taylor (1958) has the same four types of unit cell but the proportions are different viz. 36%, 36%, 14% and 14%. Assuming that the Al is in the Si₁(O) position and that the coordination of the K ion is the same as in intermediate microcline, the charge balance of maximum microcline is that given in column (e) of Table 1.

The local charge balances are considerably poorer than the 'space' charge balances calculated by Ferguson, Traill & Taylor (1958). The deviations from local charge balance for high sanidine and orthoclase are both 1.2 and are much larger than that for maximum microcline, 0.5. Thus if local balance of charge is used as a criterion of stability, orthoclase and high sanidine should be of equal stability at room temperature and both of them less stable than maximum microcline. This conclusion is quite different from that reached by Ferguson, Traill & Taylor (1958) and illustrates the importance of taking into consideration the effective range of the electrostatic forces in calculating the charge balance of disordered structures.

The factors which control the stability of potassium feldspars will be discussed in detail by one of us (J. V. S.) in a later publication. In addition to charge balance, the effect of strain between unit cells of different Al, Si arrangements and the effect on the entropy of the number of ways of placing Al and Si atoms in ordered and disordered arrays will be considered. The conclusion will be that charge balance is of less importance than strain and 'disorder entropy' in controlling the stability of the potassium feldspars. On the other hand charge balance is thought to play an important role in deciding which tetrahedron contains the Al atoms in maximum microcline. In consequence, while we cannot agree with the dominant role assigned by Ferguson, Traill & Taylor (1958) to charge balance in determining thermodynamic stability, we think that charge balance is of importance in determining the details of the crystal structure of the feldspars.

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Table 1. Charge balances in potassium feldspars

	(a)	(b)	(c)	(d)	(e)
	7.5	8.5	8.2	8.0	8.1
	8.5	7.5	8.0	8.2	7.8
	8.1	7.9	7.4	8.4	8.0
	7.9	8.1	8.4	7.4	8.2
Total unbalance	1.2	1.2	1.2	1.2	0.5

Columns (a), (b), (c), (d) refer to the four types of unit cell in high sanidine and orthoclase: column (e) to the unit cell of a maximum microcline with perfect order. The figures give the total of the valencies attached to the four oxygen atoms of a tetrahedron. The total unbalance is the sum of the deviations from 8.