

## Charge Balance and the Stability of Alkali Felspars: A Discussion

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The analysis of the structures of low albite and high albite led to the suggestion that local balance of charge might be an important factor in determining the stability of the K-felspars as appeared to be the case for the Na-felspars.

Difficulties in accepting this hypothesis, raised by MacKenzie & Smith (1959), are discussed both in relation to the meaning of the hypothesis and in its application to petrological data.

### 1. Introduction

MacKenzie & Smith (1959) have recently commented on certain sections of our recent paper on low-temperature and high-temperature albites (Ferguson, Traill & Taylor, 1958). They very kindly sent us copies of their paper before publication, and we can therefore follow up without delay their valuable contribution to the discussion of the role of local balance of charge in determining the structural details and the relative stability of the alkali felspars.

Some of the difficulties encountered by MacKenzie & Smith can be removed by a fuller statement than was given in our previous paper. Others call for a more detailed discussion of mineralogical and petrological observations; this will be presented in another publication by one of us (R. B. F.), and the treatment of these topics in this paper will therefore be as brief as possible. In addition to questions about the alkali felspars raised by MacKenzie & Smith, the role of charge balance in relation to other felspar structures is mentioned. For convenience, particular aspects of the balance of charge hypothesis are considered first (§ 2) and the application of the hypothesis to mineralogical and petrological data afterwards (§ 3); there is, of necessity, some overlap.

### 2. Balance of charge and structure

(i) MacKenzie & Smith remark that our experimental measurements were made at room temperature and conclude that 'the charge balance theory, in its present form, ... implies no variation of stability with temperature'; they also point out that after heating to a sufficiently high temperature either microcline or orthoclase is converted into sanidine, leading to the conclusion that 'sanidine is more stable

than microcline and orthoclase at high temperature', and vice versa at low temperature. On these grounds they reject the charge balance hypothesis as a criterion of stability.

In our opinion these difficulties are not real. They probably arise from a too-brief development of the charge-balance hypothesis in our previous paper; they disappear if it is realised that the result of our treatment is displayed as a number representing the differences in the electrostatic potential energies of particular structures assumed to be ionic in character, and takes no account of the kinetic energy of thermal vibration involved in the process of transformation caused by a change of temperature, nor of the rate of transformation. Our statements about the relative stabilities of the alkali felspars should be expanded somewhat as follows:

The high-temperature structures (high albite and sanidine) achieve only a relatively poor local balance of charge (represented in our treatment by  $\Sigma|\Delta|=0.3$ , 0.2 approx.) because the tendency towards such a balance is more than offset, at the high temperature, by the effects of thermal vibration. The fact that our determination of the structures of these materials was made at room temperature does not influence the argument since they are assumed to retain at room temperature an atomic distribution with the same degree of order as corresponds to equilibrium at high temperature, i.e. the conditions of occurrence in the rock have been such as to quench, and so preserve, the high-temperature structure.

By contrast, a low-temperature material would be expected to achieve a better balance of charge. For the pure Na-felspar low albite this is the case, represented by  $\Sigma|\Delta|=0.1$ . For pure K-felspar we predict optimum charge balance ( $\Sigma|\Delta|=0$ ) for a partially-ordered monoclinic structure which we have called

ideal orthoclase, and we have suggested that this may in fact correspond to an actual orthoclase (Spencer's specimen *C*) the structure of which is being re-examined and refined.

The poor charge balance ( $\Sigma|\Delta|=0.3$ ) for the low-temperature microcline studied by Bailey & Taylor (1955) we attribute to the presence of Na in the high-temperature material from which it was formed: we suppose that its presence prevented the Si, Al distribution from assuming the form best suited to a pure or nearly pure K-felspar before (with falling temperature) this distribution was 'frozen in'. Migration of the K, Na ions remains rapid at much lower temperatures, thus permitting perthitization and resulting in the eventual formation of the pure (or nearly pure) K-felspar with an Si, Al distribution unsuited to the large cation.

It is hardly necessary to add that a direct experimental check is at present impossible, since no laboratory process is known which produces felspar structures of low-temperature type.

(ii) In calculating balance of charge for any structure in which a site is randomly or partly-randomly occupied our method was to proceed in terms of an 'average atom'—e.g.  $\text{Al}_4\text{Si}_4$  at the centre of each tetrahedron in sanidine or high albite. MacKenzie & Smith direct attention to the difficulty of visualising, on an atomic scale, the reality which lies behind this procedure, and show that it corresponds to the assumption that the electrostatic forces are relatively long-range in character. They then treat the case of sanidine by assuming four types of unit cell, with Al concentrated in one or other of the four types of tetrahedral site; in this way they obtain a different numerical value for the degree of unbalance in the electrostatic forces now assumed to be short-range in type.

In our opinion the question raised here does call for discussion. We agree that our method is empirical, and makes no attempt to decide what precisely is the physical reality behind the 'average atom' procedure: the method leads to consistent results when applied to low albite and high albite and (the argument runs) may be expected to work equally well when applied to low and high K-felspars.

The arithmetic which leads MacKenzie & Smith to their Table I seems to us to be at least as much open to criticism as ours. In the first place, it could be argued on general grounds that the electrostatic forces are in fact fairly long-range in character—e.g. this assumption lies behind many discussions of refractive indices in terms of structure. Secondly, their method takes into account the atomic detail of *one* factor but does not treat other effects which must be associated with their model. Also, it becomes difficult to envisage a realistic application of their procedure to any but the simplest—i.e. the most extreme—case of randomness as in sanidine.

In addition, any proposed detailed discussion which

claims to be physically realistic may have to take account of recent developments (Megaw, 1958) in relation to the possible role of stacking faults in producing random or partly-random structures in the felspars. Too little experimental evidence is available at present for a decision on the significance of these new ideas for our present problem, and for this as well as for the other reasons given above we consider it best to retain our 'average atom' method, fully aware of the difficulties which arise if an attempt is made to confer physical precision on the model which it represents.

(iii) In the discussion so far, it is assumed that it is legitimate to treat the alkali felspars as ionic structures and to associate local balance of charge with structural stability. MacKenzie & Smith doubt the validity of these assumptions, quoting in support of their views the pyroxenes and melilite as examples of structures which do not satisfy the balance of charge requirement. We have already made it abundantly clear in our original paper that the discussion in terms of balance of charge cannot necessarily be justified in principle. As mentioned above, having shown that it produces a consistent model when applied to the albites, we simply show what conclusions follow from its application to the other alkali felspars, microcline and sanidine, for which accurate structures are known. The picture thus obtained is, in our opinion, very reasonable from the mineralogical point of view. MacKenzie & Smith also refer to the difficulty of reconciling our model with the likelihood that the bonds internal to  $\text{SiO}_4$  (and probably  $\text{AlO}_4$ ) tetrahedra are at least partly covalent in character. We too have already stressed this in our earlier paper. In this connection we may remark that the analysis of celsian  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (Newnham & Megaw, 1958) has revealed a considerable degree of ordering tending to a distribution in which every  $\text{SiO}_4$  shares all corners with  $\text{AlO}_4$  and vice versa. Preliminary findings for anorthite  $\text{CaAl}_2\text{Si}_2\text{O}_8$  indicate a similar trend. The relative importance of local balance of charge and of the Al-avoidance rule (Loewenstein, 1954) to which the celsian and anorthite structures tend to conform, may depend upon *either* the size of the cation (K, Ba, Na, Ca) *or* the relative numbers of  $\text{AlO}_4$  and  $\text{SiO}_4$  groups. Any attempted interpretation of the Al-avoidance rule in terms of covalent or ionic forces should probably await a fuller discussion of the importance of these two factors.

(iv) In our earlier paper we suggested that the relative abundance of intermediate microclines, by contrast with the rarity of albite intermediate in structure between low and high forms, might arise from the influence exerted by the Na ions in the K, Na felspar from which the microcline forms. MacKenzie & Smith now make the interesting suggestion that this is, instead, a consequence of the lower temperature of formation of the microclines which 'freezes in' a configuration still far from perfectly ordered. We

think discussion of this point should await confirmation of the finer details of the low albite structure (from the three-dimensional refinement now in progress), and also information on the difference between the structure of a maximum microcline and that of the only microcline so far analysed—the intermediate material Spencer's specimen *U*. For our tentative suggestion—supported only by indirect evidence—about the role of Na in microcline formation is in part a development from the suggestion made by Bailey & Taylor (1955) that a maximum microcline may correspond to a further concentration of Al in that tetrahedron which is already Al-rich in the intermediate structure.

### 3. Mineralogical and petrological evidence

In the preceding Section we have been concerned primarily to remove misunderstandings and to discuss the physical significance of our charge-balance hypothesis. It is (so far as we know) the only attempt yet made to provide any explanation on a structural basis (as distinct from a classification) of the facts about the alkali feldspars, and in requiring the influence of temperature-changes to be included it is more general in character than any treatment depending on composition-variations alone. A full discussion of the application of our hypothesis to important petrological and mineralogical observations is to be published elsewhere by one of us (R. B. F.); here we restrict ourselves to a very brief consideration of certain specific topics mentioned by MacKenzie & Smith, and regarded by them as adverse to our hypothesis.

(i) MacKenzie & Smith deduce that 'microcline is more stable at low temperature than any other potassium feldspar, including orthoclase' from the fact that 'microcline perthite is the potassium feldspar characteristic of the oldest rocks and most pegmatites'. This very general statement fails to direct attention to the additional (and very relevant) facts that granitic rocks and pegmatites commonly contain abundant Na-feldspar, and that although microcline is the most abundant K-feldspar in old plutonic rocks, orthoclase is also sometimes found under these conditions. Our hypothesis accounts for the relative abundance of the microclines, and also suggests an

explanation for such orthoclase occurrences when only a small amount of Na-feldspar is present.

(ii) MacKenzie & Smith consider that the presence of Na is *unfavourable* to microcline formation, since (a) the overall Na-content of some orthoclase-microperthites is higher (50%) than for microcline microperthites (30%), and (b) an orthoclase may contain in solid solution a higher proportion of Na feldspar (15%) than has been observed in a microcline or in the K-rich component of a microcline perthite (7%).

These facts do not contradict what we have said in our earlier paper. The discussion of the K-Na feldspars, in terms of our hypothesis, involves the separation of the cooling range into two regions; in the upper, the Si, Al distribution (and so the geometry of the crystal structure) may vary in accordance with the K-Na ratio and with the cooling rate; in the lower, migration of K and Na ions may continue although no further change in the Si, Al distribution can take place. At least two possible mechanisms can be suggested which account for the known facts about the relationships of microcline, orthoclase and sanidine: we favour one of these, which is treated fully elsewhere (R. B. F., forthcoming publication).

We should hesitate to claim more than that these treatments demonstrate the possibility of devising reasonable models to fit the facts about the alkali feldspars. Moreover, too little is known about perthite formation for detailed discussion of the interactions between the K-rich and Na-rich components, though even early work (e.g. Chao & Taylor, 1940) may hint at the factors involved. Finally, reference may again be made to the possible bearing on the problem of recent ideas about stacking faults in feldspar structures (Megaw, 1958).

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