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An electron diffraction study of some intermediate plagioclases

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Abstract

The problem of the behavior of the vector **s**, defined by Bown and Gay (1958), in the reciprocal lattice of the intermediate plagioclases is outlined, and the advantages of (1) examining a cogenetic series of plagioclases, and (2) using the technique of selected area electron diffraction are pointed out.

The experimental method is described, and the results obtained are presented for a suite of metamorphic plagioclases of compositions An34, An37, An45, An52, An54, An61, and An69. The computer program written to perform the necessary calculations, and to estimate the errors involved, is described in the Appendix. The results indicate that **s** does not vary continuously across the intermediate plagioclase range, but shows a discontinuity at a composition of ~An50.

Several specimens from different localities are discussed, with reference to (1) comparison with data determined from single crystal X-ray work, (2) the importance of a common history, so that An content is the only variable, and (3) the determination of the compositions coexisting across the Bøggild and Huttenlocher unmixing gaps.

Introduction

One of the most critical areas of the feldspar system is the 'intermediate plagioclase series,' that is, plagioclases within the composition range 25 to 75 percent anorthite which have equilibrated at low to moderate temperatures. These are characterized by their unique diffraction patterns, described, for example, by Chao and Taylor (1940), Gay (1956), and Bown and Gay (1958), and thoroughly reviewed by Smith (1974).

There is considerable evidence that the intermediate plagioclases do not form a continuously varying solid solution series, but exhibit a discontinuity at a composition of approximately 50 percent anorthite (An50), as summarized below.

(1) The cell parameters, and hence the Γ and B functions defined by Smith and Gay (1958) to describe the structural state, all show a discontinuity at approximately An50. In the suite of plagioclases investigated for this study, and described below, such a discontinuity was established from X-ray diffractometer results.

(2) The behavior of plagioclases on ordering from the high temperature $C\bar{1}$ structure to the (e) type superstructure modulating an $I\bar{1}$ lattice appears to be different for specimens with An < 45 from that for more calcic samples, as discussed by McConnell (1972a).

(3) It is probable that the compositional unmixing exhibited by certain labradorites, referred to as the Bøggild intergrowth, after Bøggild (1924), also points to a structural misfit across the unmixing gap, which occurs in the vicinity of An50.

One physical parameter whose behavior between the limiting compositions of the intermediate plagioclase range has not been conclusively established is the reciprocal lattice vector **s** defined by Bown and Gay (1958). The results of Gay (1956), also presented by Bown and Gay (1958), appear to show a continuous variation of **s** across the critical composition of An50. Similar work carried out by Doman, Cinnamon, and Bailey (1956), however, indicated separate linear trends with a discontinuity at An50.

Clearly, further accurate data on **s** would be of value. Also, as the effect of minor element chemistry (especially orthoclase content), deviation from stoichiometry, and exact temperature, pressure, and P_{H_2O} history of a specimen on **s** has not been established, it is of particular interest to examine the variation of **s** within a cogenetic series of plagioclases.

A disadvantage of the single crystal X-ray tech-

TABLE 1. Percentages of Orthoclase, Albite, and Anorthite, the Length s (in Å^{-1}) and Approximate hkl of **s** (with l = 10) for Broken Hill Specimens

Specimen	Or	Ab	An	s	h	k	l
P2	1.2	64.7	33.9±0.6*	0.029 ±0.002**	-3.3	0	10.0
P3	0.7	62.1	37.2±1.5	0.0214±0.0003	-3.3	-1.6	10.0
P4	0.4	55.2	44.5±2.3	0.0175±0.0005	-3.2	-2.4	10.0
P5	1.0	46.6	52.4±0.7	0.0181±0.0009	-2.7	-3.1	10.0
P6	0.4	44.9	54.4±1.4	0.0173±0.0009	-2.6	-3.1	10.0
P7	1.5	37.4	61.1±1.5	0.0117±0.0006	-2.1	-3.8	10.0
P8	0.3	31.1	68.6±1.0	0.010 ±0.002	0.6	-16.8	10.0

* *The estimated spread in An content for each specimen.*
** *The standard error in the mean of s for each specimen.*

nique used by previous workers is that the orientation of triclinic crystals is awkward and time-consuming. Transmission electron microscopy (TEM) is a technique which can quickly and easily provide random sections of reciprocal space, using selected area elec-

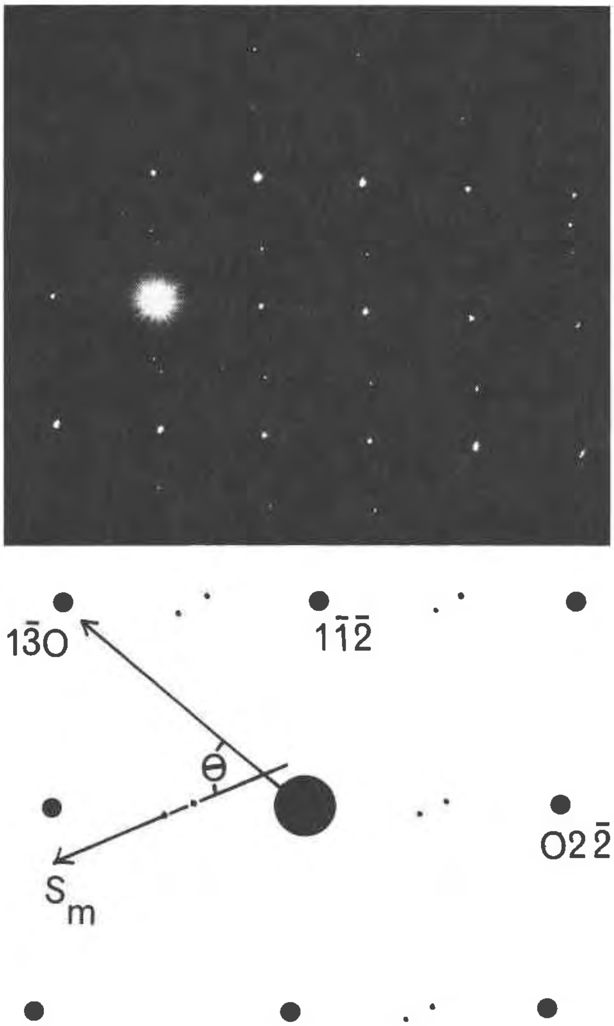

FIG. 1. [311] reciprocal lattice section for P7. The **130** lattice vector, the direction $\mathbf{s}_m$, and the angle θ are illustrated.

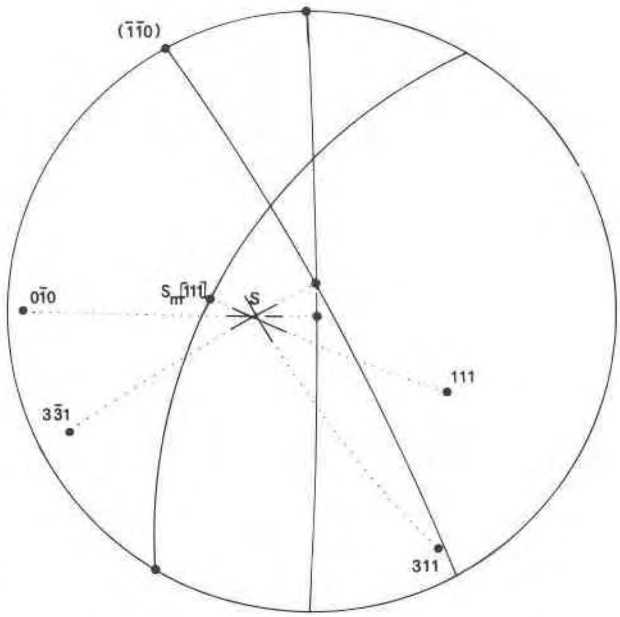

FIG. 2. Analysis of four zones (axes marked without brackets) for P7. For each zone, the trace of the reciprocal lattice section, the vector $\mathbf{s}_m$, and the **hkl** used are plotted, except in the case of [311], where, to avoid confusion, only the **p**-$\mathbf{s}_m$ plane is drawn.

tron diffraction (SAED). A further advantage of TEM is that any chemical inhomogeneity on a fine scale, *e.g.*, exsolution in one of the plagioclase unmixing gaps, is evident.

In this context, a method has now been devised to obtain **s** from several such sections with a degree of accuracy which appears satisfactory both from the statistical estimate of the errors involved and from the consistency of the results obtained. A cogenetic series of plagioclases has been thus examined, with the results described below.

Experimental method

The samples used in this study were a suite of plagioclases separated from the metamorphosed gabbros of the amphibolite-granulite facies of Broken Hill, New South Wales. These rocks are fully described by Binns (1962). The plagioclase compositions were determined by electron-probe microanalysis, at least twenty different spot analyses being made of each separated feldspar, thus giving a reliable value for the average compositions, and an estimate of the spread of composition in each sample. The results are included in Table 1.

The specimens were prepared for TEM by pipetting a suspension of finely crushed grains in alcohol on to a carbon-coated copper grid, and evaporating the

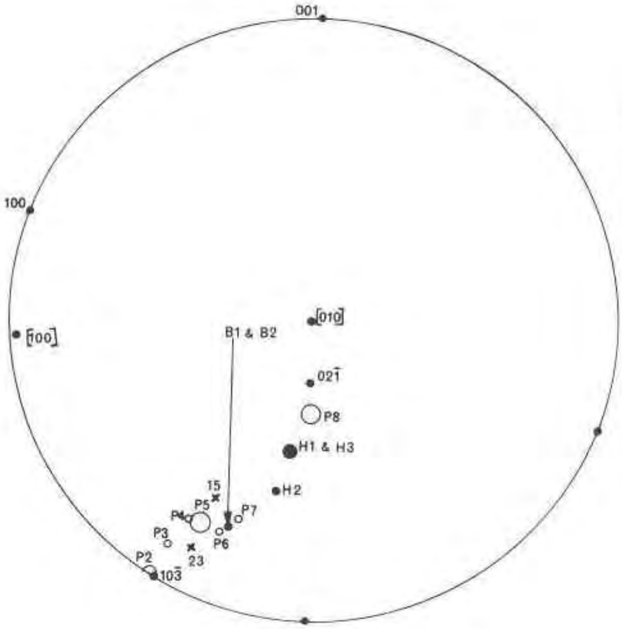

FIG. 3. [010] projection of $\hat{s}$. Open circles: result for Broken Hill specimens (the radius = the angular error); full circles: results for unmixed specimens, or poles of planes and directions of axes, as marked; crosses: results for Skaergaard specimens. The data of Bown and Gay (1958) are spread about the great circle joining (10$\bar{3}$) and (02$\bar{1}$) approximately.

alcohol. They were examined on a AEI EM6G electron microscope, and many SAED patterns of each specimen were taken.

All the plagioclases showed (a) and (e) reflections, while those of composition An > 50 showed (f) satellites also. The (e) reflections were diffuse for the more sodic specimens, and both (e) and (f) reflections were

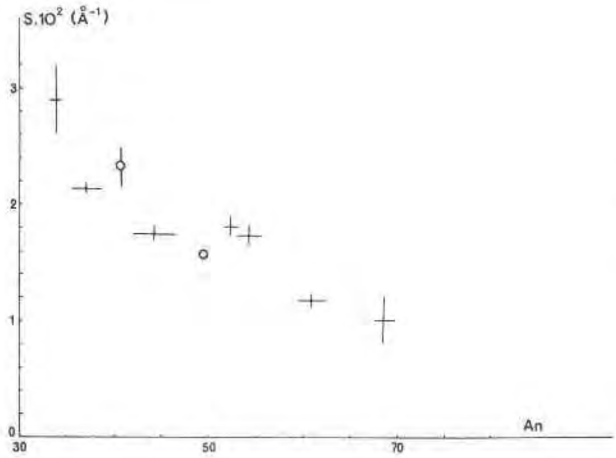

FIG. 4. Plot of s versus composition (in % An); circles: Skaergaard specimens.

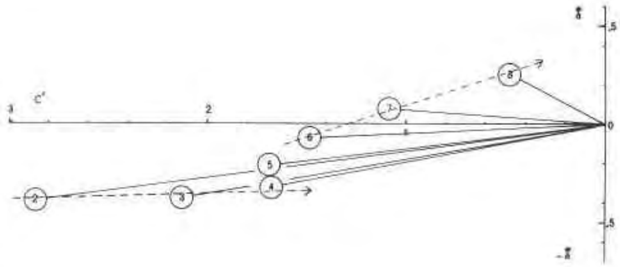

FIG. 5(a) Section of reciprocal lattice model, projected down [010]. c' is the direction normal to [010] and to a^*. The projection of **s** for each specimen is labelled. Units are $\text{Å}^{-1}.10^{-3}$. Arrows give direction of increasing An.

sharp for the more calcic. The reciprocal lattice sections which were of low enough order to be indexed unequivocally, and which showed clear (e) and/or (f) pairs, were indexed using a computer program written by Booth, Gittos, and Wilkes (1974).

In each section, the angle between the projection of $\mathbf{s}(\mathbf{s}_m)$ and a known reciprocal lattice vector **hkl** was measured, as illustrated in Figure 1. The separation $2s_m$ was also measured for at least four different pairs of (e) or (f) reflections in each section indexed, and an average value of s_m calculated.

For a given reciprocal lattice section, **s** lies in the plane containing the zone axis **p** and $\mathbf{s}_m$. The intersection of these planes for several different sections of the same specimens gives **s**.

For each specimen, at least four different reciprocal lattice sections were measured, and plotted stereographically. As an example, the results for P7 are shown in Figure 2. The $\mathbf{s}_m$-**p** planes were found to intersect in a small polygon (indicating a reliable result) whose centroid ≡ $\hat{\mathbf{s}}$, the unit vector representing the direction of **s**, for P7.

In a given reciprocal lattice section, s, the magnitude of **s**, is given by

$$s = s_m / \cos \phi$$

where ϕ is the angle between $\mathbf{s}_m$ and **s**. This

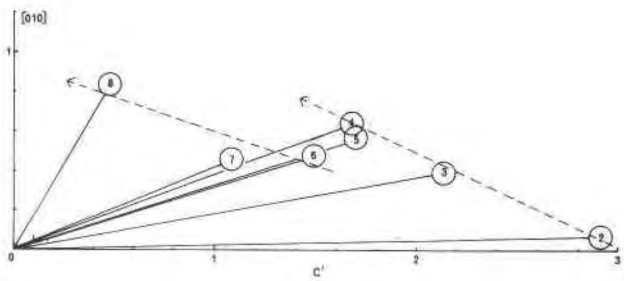

FIG. 5(b) Second orthogonal section, projected down a^*.

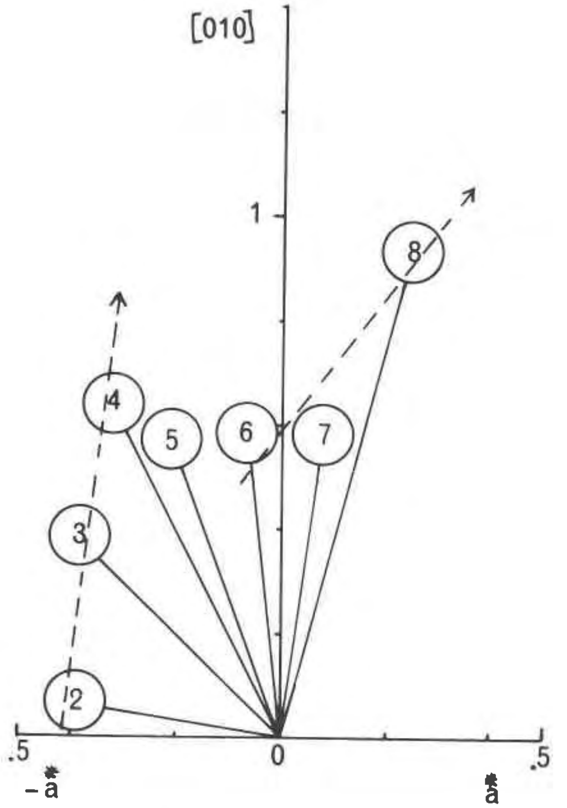

FIG. 5(c) Third orthogonal section, projected down c'.

relationship results from the 'spiking' of reciprocal lattice points in the direction normal to a thin crystal, and is accurate so long as care is taken to keep the thin crystal normal to the beam. An average of s was obtained for each specimen, with a small spread of values about the mean.

A computer program was written to perform the same operations by methods of vector algebra, and to estimate the errors associated with the mean values of $\hat{s}$ and s, thus allowing the treatment of several sections to become a simple routine. The algebra and statistics used are given in the Appendix.

The results obtained for $\hat{s}$ and s are produced in Table 1, and plotted in Figures 3 and 4 respectively.

Results

The results of Table 1 are best represented as a model of reciprocal space, so that the variation of $\hat{s}$ and s can be seen simultaneously. Three orthogonal sections of the model are illustrated in Figure 5a, b, and c. Clearly there is not a continuous variation, but some discontinuity appears between P4 and P6.

From Figures 3 and 4, both $\hat{s}$ and s follow the general trend established by Bown and Gay (1958), but a discontinuity at ~An50 is apparent.

The parameter δ_c, used by Gay (1956) and Doman *et al* (1965), was also calculated, as

$$\delta_c = 180\,(1 - s'c)$$

where s' is the component of s parallel to [001]. The results are plotted in Figure 6, along with the linear trends drawn by Doman *et al* (1965) and by Gay (1956) as the best fit to their scatter of δ_c values. The Broken Hill results parallel the two trend lines of Doman *et al* (1965) but lie consistently on the side of higher δ_c.

Discussion

While the results for the Broken Hill plagioclases pointed to a discontinuity in **s**, the number of data points was small in comparison with the previous X-ray data. The estimated errors in the mean value of s were lower than the comparable errors quoted by Gay (1956) for most specimens. To check the significance of differences in accuracy, two of the specimens investigated by Gay (1956) were re-examined. These were specimens 23 and 15, quoted as An41 from the Skaergaard Ferrogabbro, and An50 from the Skaergaard Middle Gabbro, respectively.

The results obtained were in close agreement with the results of Gay (1956). They are plotted along with the Broken Hill results on Figures 3 and 4. Specimen 15 fits well on the anorthitic extreme of the more sodic plagioclases, but specimen 23 does not conform

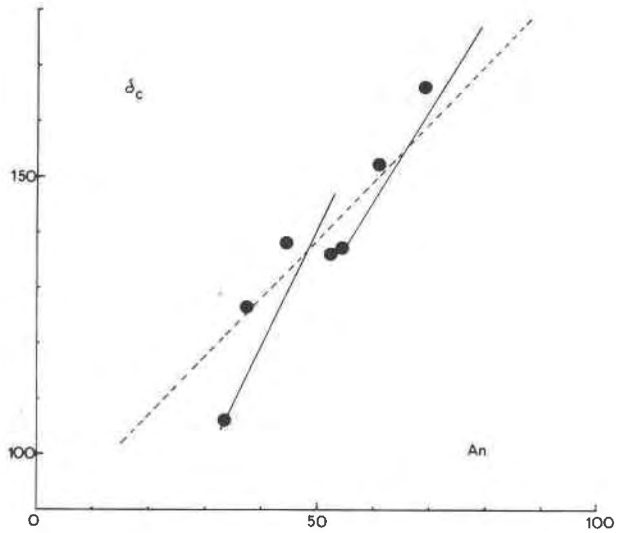

FIG. 6. Plot of δ_c in degrees versus composition in percent An. Solid line: data of Doman *et al* (1965); broken line: data of Gay (1956); circles: Broken Hill specimens.

TABLE 2. Localities and Compositions of Unmixed Specimens Mentioned in the Text

Specimen	Locality	Or	Ab	An
B1	Labrador	3.0	42.6	53.4 *
B2	Labrador	2.2	43.7	54.1 **
H1	Broken Hill	0.2	23.0	76.8 **
H2	Stillwater	0.6	22.9	75.9 *
H3	Bushveldt	1.4	22.7	74.7 *

* *Chemical analyses by J. H. Scoon.*
** *Electron probe analyses.*

to the Broken Hill pattern, even taking into account inaccuracies in the compositional determination (subsequent electron probe analysis indicated a composition of ~An45: Gay, personal communication). This result emphasizes the importance of comparing the members of a cogenetic series only.

McConnell (1972b) has pointed out that the variation of **s** is of use in establishing the compositions coexisting across the unmixing gaps in the low plagioclases. The trend established for the Broken Hill series is particularly relevant to labradorites showing Bøggild exsolution, as these are all from metamorphic terrains (see Nissen, 1967). Two unmixed labradorites, specimens B1 and B2, and three bytownites showing Huttenlocher exsolution (see Nissen, 1968), specimens H1, H2 and H3, were examined. Their localities and bulk compositions are given in Table 2. Values of $\hat{\mathbf{s}}$ were established for each, and are included in Figure 3, where they fit well with the Broken Hill trend. Further work on these results is proceeding, as the method is a potentially powerful one.

Conclusion

The simple SAED method outlined above gives consistent results for **s**. These show that, for a cogenetic series of plagioclases, some discontinuity appears in **s** at a composition of approximately 50 percent anorthite, as predicted from the behavior of other plagioclase parameters.

Appendix: Basis of computer program

$\mathbf{p}_i$, the ith zone axis, and $\mathbf{h}_i$, the ith **hkl**, are transformed to orthonormal axes, using the matrix method described by Bond (1946), and normalized. θ, the angle between $\mathbf{h}_i$ and $\mathbf{s}_{mi}$ is known. Then $\mathbf{h}'_i$, the unit vector in the zone $\mathbf{p}_i$ inclined at 90° to $\mathbf{h}_i$, is

$$\mathbf{h}'_i = \mathbf{p}_i \times \mathbf{h}_i$$

and

$$\mathbf{s}_{mi} = \mathbf{h}_i \cos\theta + \mathbf{h}'_i \sin\theta$$

Defining $\mathbf{g}_i$

$$\mathbf{g}_i = \mathbf{p}_i \times \mathbf{s}_{mi}$$

we can calculate the intersection of the ith and jth $\mathbf{p}$-$\mathbf{s}_m$ planes

$$\mathbf{s}_{ij} = \mathbf{g}_i \times \mathbf{g}_j$$

Each $\mathbf{s}_{ij}$ is multiplied by an implicit weighting factor w_{ij}, where w_{ij} is the sine of the angle between the intersecting planes, placing the highest weight on those which are most nearly perpendicular. Then

$$\hat{\mathbf{s}} = \Sigma \mathbf{s}_{ij}, \text{ normalized,}$$

the sum over ${}^n_2C$ intersections, where n is the number of reciprocal lattice planes considered. We can also calculate ψ, the angular error in $\hat{\mathbf{s}}$, after normalizing $\mathbf{s}_{ij}$, as

$$\cos\psi_{ij} = \mathbf{s}_{ij} \cdot \hat{\mathbf{s}}$$

$$\psi = \Sigma \psi_{ij} w_{ij} / \{{}^n_2C(w_{ij} - 1)\}$$

To calculate s, we have n results for s_i

$$s_i = s_{mi}/\cos\phi_i$$

and we can calculate the mean

$$s = \Sigma s_i / n$$

No weighting was used, as for both (e) reflections of a pair to appear clearly in the section, $\phi < 30°$. The error in the mean value of s was estimated as

$$\sigma = \Sigma\sqrt{(s^2 - s_i^2)}/\sqrt{\{(n-2)n\}}$$

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