

## ORDER-DISORDER RELATIONSHIPS OF PLAGIOCLASE IN A PORPHYRITIC BASALT FLOW

JERRY M. HOFFER, *Department of Geology, The University  
of Texas at El Paso.*

### ABSTRACT

The structural state of phenocryst and groundmass plagioclase from a thick prophyritic flow of the Columbia River Basalt ranges from high to intermediate disorder. Two groups have been differentiated: (1) Groundmass plagioclase in a lower structural state than phenocrysts; the groundmass plagioclase is more calcic than  $An_{60}$  and of small size, (2) Groundmass plagioclase in a higher structural state than phenocrysts; groundmass plagioclase generally less calcic than  $An_{50}$  and of large size. In addition, the latter group contains smaller amounts of glass than those of group one. The reversal in structural state relationship between the phenocryst and groundmass plagioclase of (2) is probably due to the sluggishness of the transformation from disorder to order in plagioclase less calcic than  $An_{50}$ .

### INTRODUCTION

The structure of volcanic plagioclases has been reported as ranging from an intermediate disordered state to a highly disordered state (Slemmons, 1962, Smith, J. R. and Yoder, 1956, and Smith, J. V. and Gay, 1958). These results are based on only a small number of samples, however, and no detailed work has been published concerning the determination of the degree of disorder of either phenocryst or groundmass plagioclase from a single volcanic flow or the relationship of the degree of disorder to composition and cooling history.

In this study structural state of groundmass and phenocryst plagioclase was determined and the relationship of the structural state to composition analyzed. The plagioclase samples used for this study were from a thick prophyritic basalt flow of the Columbia River Basalt, the Rock Creek Flow, which crops out in west-central Idaho (Bond, 1963). A complete description of the texture, mineralogy, and sample locations were reported in an earlier paper (Hoffer, 1967).

In a previous study the An content of the groundmass plagioclase was found to vary inversely with size and directly with the amount of associated glass (Hoffer, 1966b). The rate of cooling, after extrusion, determined the composition of the groundmass plagioclase.

### PROCEDURE

Both phenocryst and groundmass plagioclase were separated by crushing, screening, and concentration with a Frantz Isodynamic separator (Hoffer, 1966a). The glass fusion method, modified from Foster (1955), was employed for the determination of composition (mole percent An content) (Hoffer, 1966c). The reliability and accuracy of the modified

glass fusion method is good. The An content of four analyzed plagioclase samples, as determined by the fusion method, was within 0.6 mole percent An of that calculated from the chemical analyses. In addition, An values of duplicate samples gave results within 0.5 mole percent An. Therefore, the accuracy of estimating An content of a plagioclase sample with the glass fusion method is within 1 mole percent An.

The structural state of each plagioclase is reported here in terms of the intermediacy index, I.I. (Slemmons, 1962) and the gamma function (Smith, J. V., and Gay, 1958). The intermediacy index is at present only a qualitative measure of the degree of disorder; the most ordered forms are assigned a value of 100 (I.I. = 100) and the most disordered forms 0 (I.I. = 0). Plagioclases intermediate between completely ordered and disordered forms are assigned values intermediate between 100 and 0. The intermediacy index is not a measure of the degree of ordering because at present the quantitative relation between Al, Si-distribution (whether stable or unstable) and lattice constants are not known (H. U. Bamauer, personal communication). Therefore, the descriptive term intermediacy index is used to denote a relative deviation from the boundary curves of "high" (I.I. = 0) and "low" (I.I. = 100) plagioclase; each equal interval not implying equal degrees of disorder.

The structural state of the plagioclase was analyzed by the X-ray diffractometer method. The difference in  $2\theta$  was determined for two pairs of strong peaks that are sensitive to structural change.  $2\theta(131)-2\theta(1\bar{3}1)$  and  $2\theta(1\bar{3}1)-2\theta(220)$ . From these measurements the  $\Gamma$  function of Smith and Gay was calculated,  $\Gamma = 2\theta(131) + 2\theta(220) - 4\theta(1\bar{3}1)$ . The  $\Gamma$  values of the most-ordered, and least-ordered plagioclases from the literature were then plotted against composition (Smith, J.R., and Yoder, 1956, and Smith, J. V., and Gay, 1958) (see Fig. 1). The intermediacy index was determined for each sample by the use of Figure 1, in which the interval between the most disordered plagioclases (upper curve) and most ordered forms (lower curve) was divided into ten equal intervals from  $An_0$  to  $An_{100}$  (modified from Slemmons, 1962). Slemmons utilized the curve ABCD (Fig. 1) to represent the most ordered forms, but because many "ordered" plagioclases have been reported to fall below this curve (values greater than I.I. = 100), the theoretical lower limit for completely ordered, low temperature plagioclase, line ABD, as suggested by Smith, J. V. and Gay (1958), was used to represent the most-ordered forms (Eisinger, Swinderman, and Slemmons, 1962, and Davis and Slemmons, 1962 and Leavitt and Slemmons, 1962).

The texture of the basalt samples in thin section to determine the amount of associated glass and the size of the groundmass plagioclase.

## RESULTS

*Structural state of the groundmass plagioclase.* The structural state of the groundmass plagioclase varies from high-intermediate to high (Fig. 2). Correlations have been found to exist between the structural state and An content of the groundmass plagioclase (see Fig. 3), proportion of associated glass (see Fig. 4), and size of the groundmass plagioclase (see Fig. 5). In general, these correlations indicate that groundmass plagioclases of most disorder are those of lowest An content, associated with only a small proportion of glass, and are of smallest size.

*Structural state of the phenocryst plagioclase.* The structural state of the phenocryst plagioclase ranges from intermediate to high. Correlations between the structural state of the phenocryst plagioclase and glass content ( $r=0.28$ ) and composition ( $r=0.16$ ) are not highly significant.

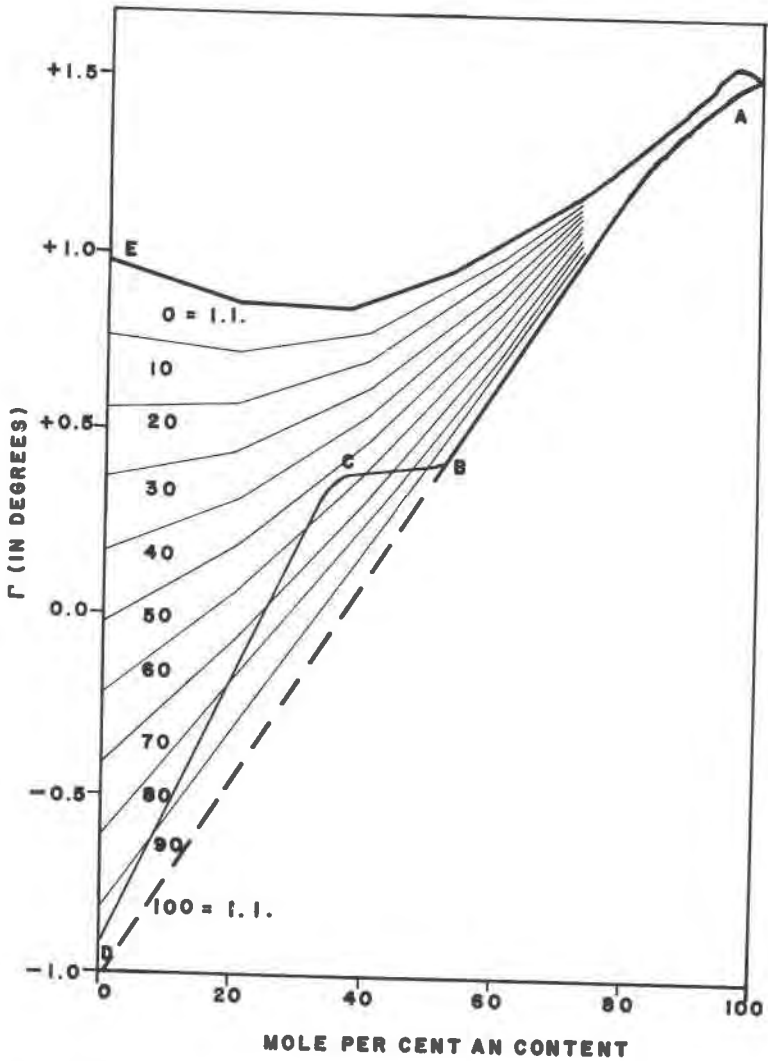


FIG. 1. Variation of the  $\Gamma$  function with composition for the plagioclase series (AE = high structural state, I.I. = 0; ABCD = low structural state based on natural specimens; ABD = theoretical low structural state, I.I. = 100) (modified from Smith and Gay, 1958)

*Relationships of the structural state of phenocryst and groundmass plagioclase.* The groundmass and phenocryst plagioclase can be subdivided into two groups on the basis of structural state. The first group includes those samples in which the groundmass plagioclase has a lower structural state (further deviation from the disordered state) than the correspond-

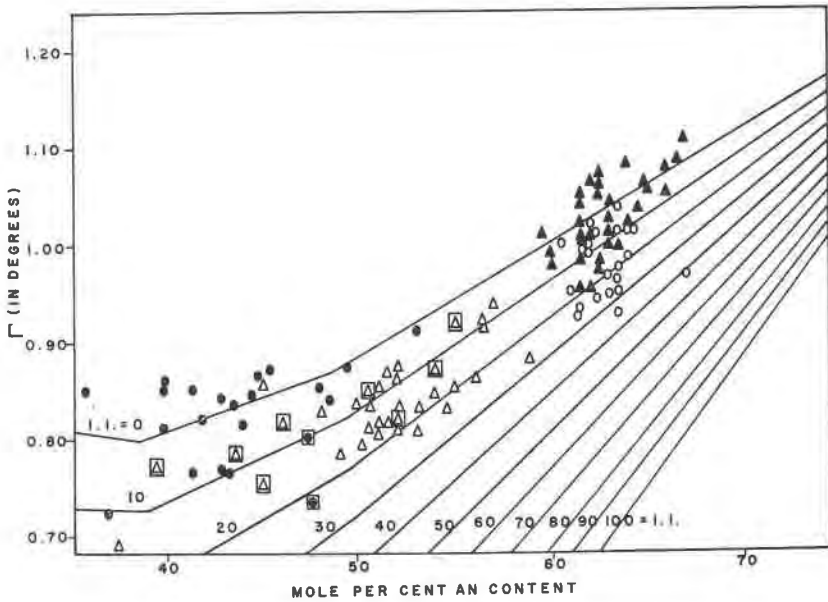


FIG. 2. Relationship of the structural state of the phenocryst and groundmass plagioclase with composition (groundmass plagioclase ( $\Delta$ ) of lower structural state than enclosed phenocrysts ( $\blacktriangle$ ); groundmass plagioclase ( $\bullet$ ) of higher structural state than enclosed phenocrysts ( $\circ$ );  $\square$  or  $\blacksquare$ -phenocryst-groundmass plagioclase differ by three or less units of I.I.). Limits of measurement  $\pm 3$  I.I. units.

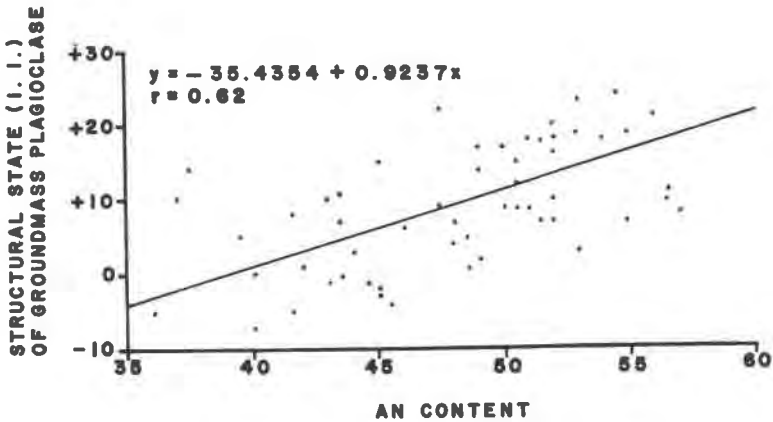


FIG. 3. Variation of structural state of groundmass plagioclase samples with the An content of the groundmass plagioclase, Rock Creek Flow ( $y$ =equation of the line and  $r$  = correlation coefficient).

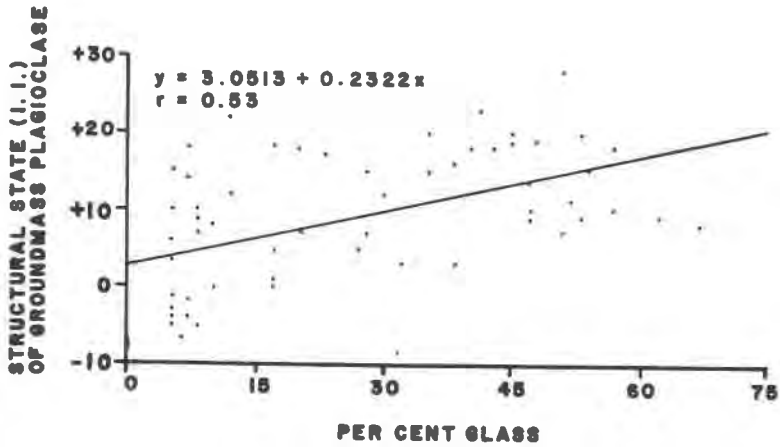


FIG. 4. Variation of the structural state of the groundmass plagioclase samples with per cent glass, Rock Creek Flow ( $y$ =equation of the line and  $r$ =correlation coefficient).

ing phenocryst plagioclase (see Fig. 2). In the second group groundmass plagioclase has a higher structural state than the enclosed phenocrysts.

Groundmass plagioclase samples less calcic than  $An_{50}$  are predominantly those of group 2, in which the groundmass plagioclase has a higher structural state than the corresponding phenocrysts; 73 percent of the samples with An content less than 50 percent belong to this group. If the samples in which the structural state of the groundmass and phenocryst plagioclase differ by 3 units or less of I.I. value (circles surrounded by squares) are disregarded, then over 82 percent (19 out of 23) of the groundmass plagioclase samples less calcic than  $An_{50}$  possess a higher structural state value than the enclosed phenocrysts. The mean I.I. value for the groundmass plagioclases of group 2 is +2.

In 96 percent of the samples in which the groundmass plagioclase is more calcic than  $An_{50}$ , however, the groundmass plagioclase has a structural state lower than that of the enclosed phenocrysts (group 1). The mean I.I. value of the groundmass of this group is +13.

The variation of structural state of the groundmass plagioclase in group 1 and 2 is accompanied by variation in the structural state of the phenocryst plagioclases. The plagioclase phenocrysts of group 1 are in a higher structural state (average I.I. value of +2) than the plagioclase phenocrysts of group 2 (average I.I. value of +15) (see Fig. 2).

#### INTERPRETATION OF RESULTS

The variations of structural state of both the groundmass and phenocryst plagioclase can be explained on the basis of the rate of cooling. As

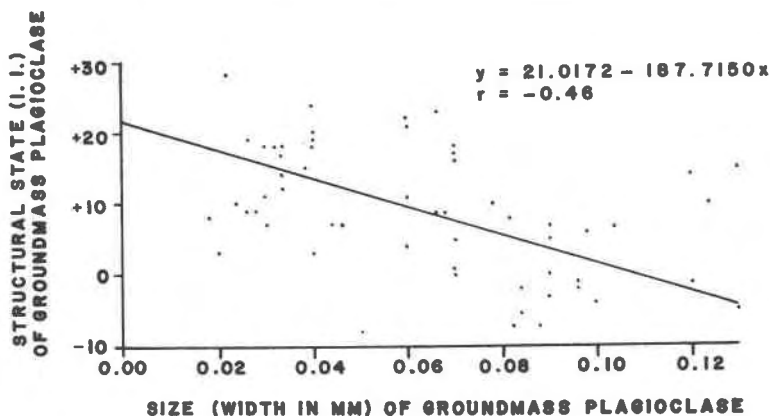


FIG. 5. Variation of structural state of the groundmass plagioclase samples with size (width=smallest dimension) of the groundmass plagioclase ( $y$ =equation of the line and  $r$ =correlation coefficient).

the initial magma cooled at depth, plagioclase phenocrysts, primarily in the high structural state of maximum disorder, crystallized. In areas of rapid cooling the highly disordered initial structural state was preserved in the plagioclase phenocrysts. Under conditions of slow cooling the structure of the plagioclase phenocrysts became more ordered.

The rate of cooling for each sample can be estimated in terms of the size and composition of the groundmass plagioclase and the amount of associated glass (Hoffer, 1966b). For samples crystallizing under conditions of slow cooling, the plagioclase phenocrysts have been found to be in a lower structural state than the plagioclase phenocrysts enclosed in rocks that crystallized more rapidly. Therefore, the samples that indicate a slow rate of cooling and final crystallization at a lower temperature are those in which the plagioclase phenocrysts possess a more ordered state than plagioclase phenocrysts in samples that experienced rapid cooling. The reason for this is that the interval between initial and final crystallization was longer in these samples than in samples with more calcic groundmass plagioclase. For this reason the plagioclase phenocrysts from a rock containing large groundmass plagioclase crystals of low An content and small amounts of associated glass have a lower structural state than plagioclase phenocrysts from a glassy fine-grained rock in which the groundmass plagioclase is of higher An content.

Following the same reasoning, the groundmass plagioclase of largest size, lowest An content, and associated with the least amount of glass would be expected to have the lowest structural state. However, in the majority of the samples containing groundmass plagioclase more sodic

than  $An_{50}$ , the structural state of the groundmass plagioclase is higher than that of the enclosed phenocrysts (see Fig. 2). The explanation for this situation may be that the transformation from complete disorder to order (or partial order) becomes more sluggish as the An content decreases. Support for this hypothesis is found in the work of Smith and Gay (1958), who have suggested on the basis of experimental work that the low natural plagioclase from  $An_0$  to  $An_{50}$  do not represent maximum ordering and are actually partially disordered and preserved in a metastable state. As evidence of this, they cite observations of diffuse subsidiary reflections from crystal X-ray photographs for plutonic plagioclases in the range  $An_{20}$  to  $An_{41}$ , which indicate some degree of disorder for samples of so-called complete order. They state that the lower limit of the ordered plagioclase would, therefore, fall below the values reported for the ordered natural plagioclase crystals. This theoretical lower limit is represented by a dashed line ABD of Fig. 1. Line ABD for the completely ordered plagioclase is derived by extrapolation of line AB to  $An_0$ . At  $An_0$  the values from the line ACD fall within the range of experimental error of the values obtained for natural low-temperature albite. In addition, Smith and Gay suggest that equilibrium is not easily attainable even under plutonic conditions so as to allow the completely ordered structure to form. This is based on the argument that if equilibrium were easily attainable, the ordered structure would form even under hypabyssal and volcanic conditions. This is why no natural specimens have been found to exist in a state of complete order in the range  $An_0$  to  $An_{50}$ .

It is significant to note that the postulated metastable field starts at  $An_{50}$ , the region in which the groundmass plagioclase samples from the Rock Creek flow show higher structural state than the enclosed phenocrysts (see Fig. 2). Above  $An_{50}$ , the reverse is true, the plagioclase phenocrysts have higher structural state than the associated groundmass plagioclase. Therefore, it is suggested that below  $An_{50}$  the transformation from disorder to order (or partial order) is more sluggish than above  $An_{50}$ . This would explain how a phenocryst (composition of  $An_{60}$  to  $An_{73}$ ), formed at high temperature and under conditions of slow cooling, could reach a more ordered structural state than did the surrounding groundmass plagioclase crystals which formed at a lower temperature and under conditions of slow cooling. This would also explain the fact that groundmass plagioclase crystals more calcic than  $An_{50}$  are in a lower structural state than that of the groundmass plagioclase of composition less than  $An_{50}$ .

The reversal of structural state relationship between the groundmass and phenocryst plagioclases at approximately  $An_{50}$  (composition of the groundmass plagioclase) could also be due partly to the fact that in a

coarse-grained rock with little glass more time was available for the disorder-order change in the phenocryst plagioclase structure. In finer grained and more glassy rocks the initial high-temperature state of disorder was preserved in the plagioclase phenocrysts, but a less, disordered state was preserved in the groundmass plagioclase crystals.

#### SUMMARY AND CONCLUSIONS

The structural state of the phenocryst plagioclase in the Rock Creek flow is intermediate to high, whereas that of the groundmass plagioclase is high-intermediate to high. The structural state of the groundmass plagioclase is related to the An content, size of the groundmass plagioclase crystals, and the amount of associated glass. The structural state of the phenocryst plagioclase, however, shows no significant relationship to the composition of the phenocrysts and the amount of associated glass.

The groundmass plagioclase can be divided into two groups. Samples with groundmass plagioclase of group 1 generally contain large amounts of glass, groundmass plagioclase of high An content and small size, and, therefore, represent an environment of rapid cooling. Samples containing groundmass plagioclase of group 2 are those that have a small amount of associated glass and groundmass plagioclase of large size and low An content, representing conditions of slower cooling.

In general, the plagioclase phenocrysts of group 2 possess a lower structural state than the plagioclase phenocrysts of group 1. This is as expected, but, the structural state of the groundmass plagioclase of the first group is lower than that of the groundmass plagioclase of the second group. It is suggested that the transformation from disorder to order is more sluggish for groundmass plagioclase of composition less than An<sub>50</sub> than for groundmass plagioclase more calcic than An<sub>50</sub>.

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