SOME EVIDENCE ON THE VALIDITY OF THE EXSOLUTION MODEL FOR THE FORMATION OF ANTIPERTHITES

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ABSTRACT

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In order for antiperthites to form by an exsolution process, Ca, Na, K, Al, and Si must all be re-arranged throughout the crystal. Alternatively, if an antiperthite forms by "nucleation", the ions need only be re-arranged at the sites of K-feldspar growth. Regardless of the mode of formation, a volume of potassium feldspar must replace a volume of plagioclase.

The validity of the exsolution model was tested by determining potassium solubility in calcium-bearing plagioclase. "Clean" plagioclase was heated both dry and hydrothermally in the presence of K-feldspar. The result was the growth of K-feldspar blebs on the plagioclase with concomitant potassium and sodium gradients increasing, respectively, towards and away from the blebs. Very little potassium was found dispersed within the plagioclase. These results imply that insufficient potassium is held within a host plagioclase to form an antiperthite by exsolution.

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INTRODUCTION

There are two major models for the formation of antiperthites, the exsolution model and the "nucleation" model. The exsolution model, the classic model accepted by most (Barth, 1969), consists of a ternary feldspar unmixing to form potash feldspar intergrowths within a calcium-bearing plagioclase matrix or host during cooling. The alternate model, "nucleation", is based on an outside source of potassium, nucleating on plagioclase surfaces or discontinuities within the plagioclase. The only difference in the two models is the source of potassium.

Both models, of course, require nucleation to initiate the growth of the K-feldspar. Therefore, the nucleation for each model is controlled by high-energy discontinuities within the crystal. The textural pattern produced by either the exsolution or "nucleation" model is, therefore, identical.

Perthites, which consist of albite in a K-feldspar matrix, are easily homogenized at temperatures slightly below the solidus. Thus, the exsolution model for the formation of perthites is supported. If a similar exsolution model for the origin of antiperthites is proposed, one test of the model is to determine if antiperthites can be homogenized under reasonable geologic conditions; this is the purpose of this research.

EXPERIMENTAL PROCEDURES

Three different experimental procedures were used to help alleviate any problems of insufficient or excess energies or error in procedure. First, a "clean" plagioclase and K-feldspar were heated together to just below the solidus at atmospheric pressure and held for 72 hours. A second run of the same components was conducted at high temperature and two Kbars for 48 hours. Finally, a natural antiperthite was run at low temperature and 1.33 Kbars for 92 hours. Any variation in potassium content or potassium gradient due to a change in the experimental environment can thus be noted.

For the 1 atm. and the high water pressure runs, the starting materials were two natural feldspars, Bedford Perthite (a source of K: 90.67% Or, 9.33% Ab) and 1-87-11 plagioclase (10.24% Ca: 48.4% Ab, 49.2% An, 2.4% Or) mixed together in varying proportions. In the moderate water pressure run, the starting material was a natural antiperthite.

ONE ATM.

Both starting materials (Bedford Perthite and 1-87-11 plagioclase) were finely ground to -140 mesh and homogenized by heating to 1050°C for three days to eliminate any pre-existing crystallographic differences involving sodium and potassium. Homogenization was substantiated by both x-ray and microprobe techniques.

The two feldspar components were then mixed in various weight proportions to insure a potassium saturated condition in the plagioclase.

Table 1. Weight Percentages of K-feldspar, 1 ATM., Dry

SAMPLE NUMBER	WT. % K-FELDSPAR	SAMPLE NUMBER	WT. % K-FELDSPAR
1	0.5	6	10.0
2	1.0	7	15.0
3	2.0	8	25.0
4	3.0	9	90.0
5	5.0	10	95.0

Each mixture was then placed in an open boat and heated to 1050±2°C for 72 hours. At the end of 72 hours, the boats were removed to room temperature; cooling time was about 10 minutes. The charges were then mounted for microprobe examination.

HYDROTHERMAL

The experiment was then repeated hydrothermally; first with the same starting materials through the facilities at the University of Toronto and secondly with a natural antiperthite using a similar apparatus at Michigan State University.

As in the high temperature experiment, the starting materials for the high pressure run (Bedford Perthite and 1-87-11 plagioclase) were heated dry to 1050°C for 72 hours to eliminate sodium-potassium and sodium-calcium crystallographic differences. The feldspars were then

mixed in varying proportions as shown in Table 2.

Table 2. Weight Percentages of K-feldspar, 2 kb.

SAMPLE NUMBER	WT. % K-FELDSPAR	BOMB NO.	SYSTEM
1-87-11	0.0	11	closed
3'	2.0	11	closed
3"	2.0	11	closed
4'	3.0	13	open
8"	25.0	13	closed
A'	50.0	13	closed
9"	90.0	13	closed
' = homogenized feldspar " = charges used in 1 ATM. experiment			

The method of loading the charges was that of Fawcett (personal communication, 1970). The sealed charges were then placed in the cold seal pressure vessel (Tuttle, 1949) with spacer rods keeping their position constant.

Pressure was achieved in each bomb through a hydraulic pump and two large-volume water reservoirs maintained at 1000 and 2000 bars. The purpose of the two reservoirs was to minimize both the pumping time and the effects of minor leaks in the pressure system.

Pressure and temperature were checked at eight hour intervals. Pressure showed no measurable fluctuation, reading a constant 2 Kb. pressure. Temperature varied 677.8±1.7°C on bomb no. 13 and 677.0±2.0°C on bomb no. 11.

At the end of 48 hours, the bombs were quenched with cold water and compressed air, reaching room temperature and 1 ATM. pressure in approximately 10 minutes.

The charges were removed, dried for 10 minutes at

110°C and mounted for microprobe analysis.

The hydrothermal run was then repeated using a natural antiperthite. The instrument used was the same with the exception of the large water reservoirs, which were omitted. The charges were maintained at 1.33 Kb±500 p.s.i. and 500.0±2°C for 92 hours. They were then quenched and mounted.

All microprobe work was done on an ARL Model EMXSM Electron Microprobe with a line voltage of 15 Kvolts and a current of .02 Mamps. Both N-S and E-W traverses were done with point counts being taken at critical points along the grain (grain boundaries, to and across K-feldspar blebs, or any anomalies in the calcium, sodium or potassium content found during the scan). In all probe work, care was taken to count sodium first, as it tends to vaporize under the beam.

DATA

Approximately the same results were obtained from the two runs with "clean" materials, the atmospheric pressure run and the 2 Kbar experiment. The run at 1.33 Kbars and low temperature involving a natural antiperthite gave slightly different results, but not contradictory to the previous two experiments. The purpose of these three runs of considerably different conditions was, in fact, two fold: first, to determine whether potassium could be held in solution within a plagioclase

grain under reasonable conditions, and secondly to see if the results were confined to one system, i.e. to one particular energy environment.

The importance of the data lies not in the absolute percentages of potassium or sodium in a given grain, but in the relative amounts, both at bleb sites and that which is being driven through the grain.

RESULTS OF 1 ATM. AND 2 KBAR EXPERIMENTS

One of the most important results of these experiments is the development of K-feldspar blebs (small areas of actual potassium feldspar), primarily on or near grain boundaries, and the corresponding potassium gradients into, and sodium gradients away from, the K-feldspar locations. Plates 1 and 2 are two plagioclase grains after heating to 1050°C at 1 ATM. Plates 3, 4, 5 and 6 are plagioclase grains heated to 677°C at 2 Kbars pressure. On the gradient, potassium increases from a low of 2.2 weight percent K-feldspar to approximately 2.8 weight percent next to the K-feldspar bleb. In one case, grain 8, a second area of high K-feldspar concentration appears to be forming on the opposite grain boundary, with a 4.15 weight percent K-feldspar composition. There is also a concomitant gradient with sodium, however with a negative slope. This same type of potassium concentration along grain boundaries can be seen in the traces of grains 9 and 16, and, to a lesser degree, in

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grain 20. Grain 10 has no high concentrations of K-feldspar but does show potassium and sodium gradients.

The plagioclase grains before heating were "clean", that is, they contained no K-feldspar blebs. Grain 10 apparently had no suitable nucleation site, and, therefore, no K-feldspar bleb formed. The result is a slight gradient in potassium with an inverse sodium gradient. It should be noted that no more than 2.8 weight percent K-feldspar is found in this grain. This also appears to be the maximum amount in other hydrothermal grains when the actual K-feldspar site is discounted.

The plagioclase heated to 1050°C, under atmospheric pressure, contains more K-feldspar (4.8 weight percent) than the hydrothermally treated plagioclase (about 2.8 weight percent). Volume diffusion increases with increasing temperature (Bailey, 1971) and these results apparently reflect the increase in diffusivity of potassium with temperature.

NATURAL ANTIPERTHITES

Several natural antiperthite grains were studied under the E.M.P.; grain 16 is a typical example (see Plate 7). The natural antiperthites were subjected to a lower energy level (500°C, 1.33 Kbars) for a longer period of time (96 hours), and, as is illustrated in the probe trace (Figure 7), there are no observable gradients of either sodium or potassium. It seems

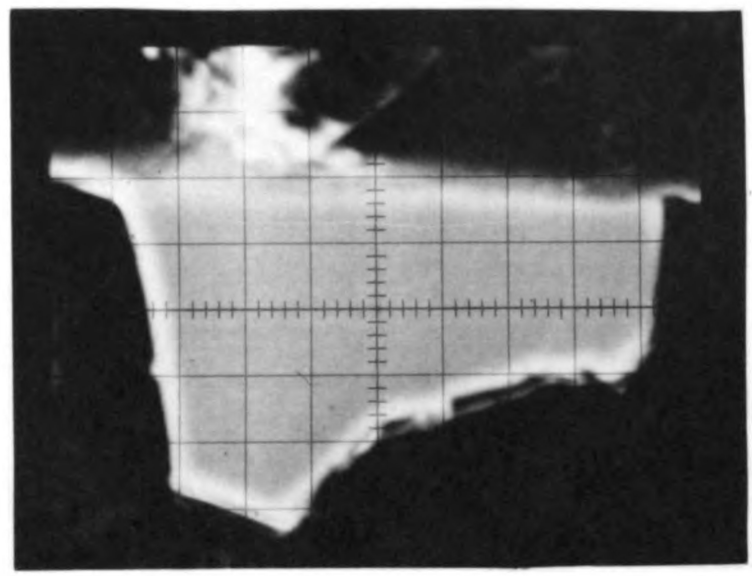


Plate 1. Grain 16 (1 ATM. Dry)
5u/cm.

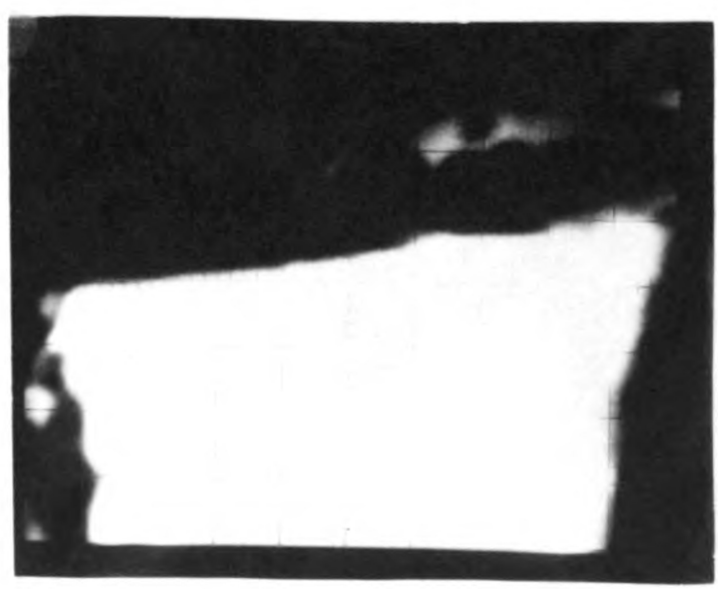


Plate 2. Grain 20 (1 ATM. Dry)
2u/cm.

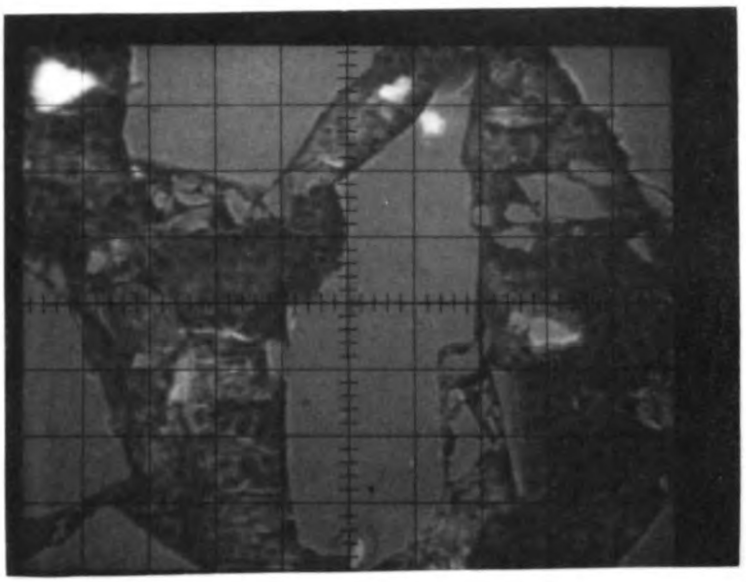


Plate 3. Grain 6 (Hydrothermal, 2 Kb.) 6.6u/cm.

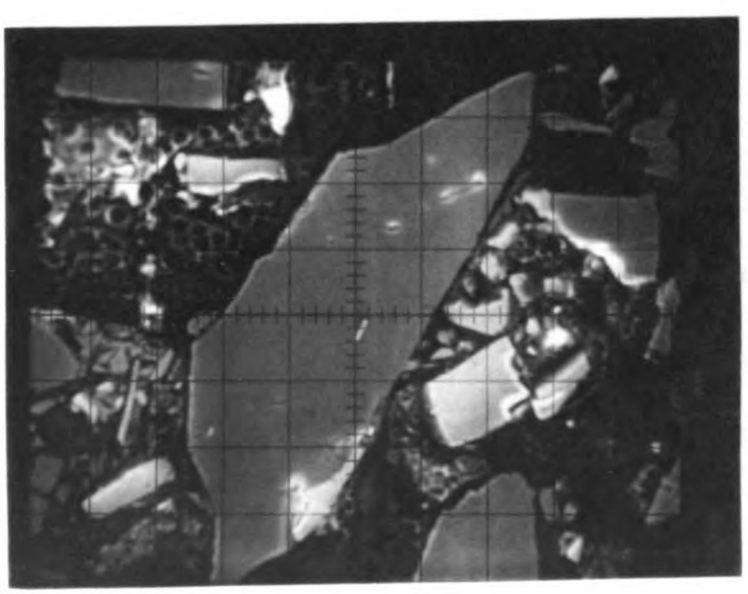


Plate 4. Grain 8 (Hydrothermal, 2 Kb.) 8.2u/cm.

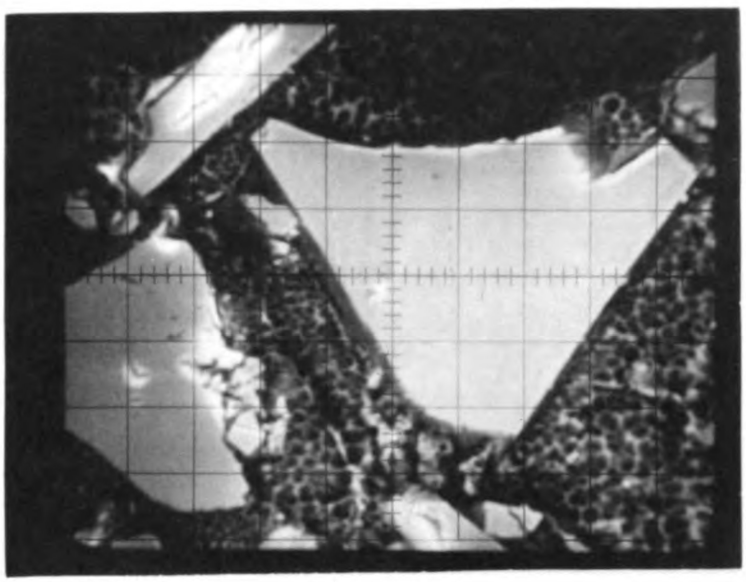


Plate 5. Grain 9 (Hydrothermal, 2 Kb.) 6.0u/cm.

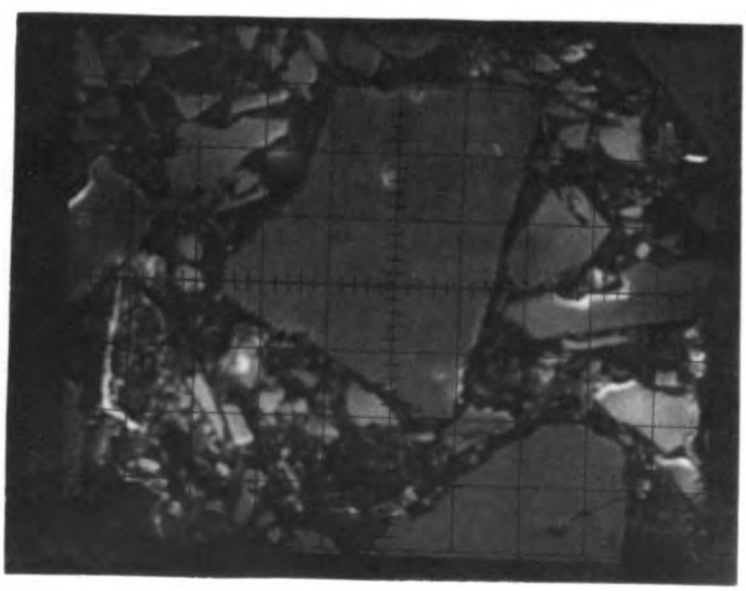


Plate 6. Grain 10 (Hydrothermal, 2 Kb.) 6.0u/cm.

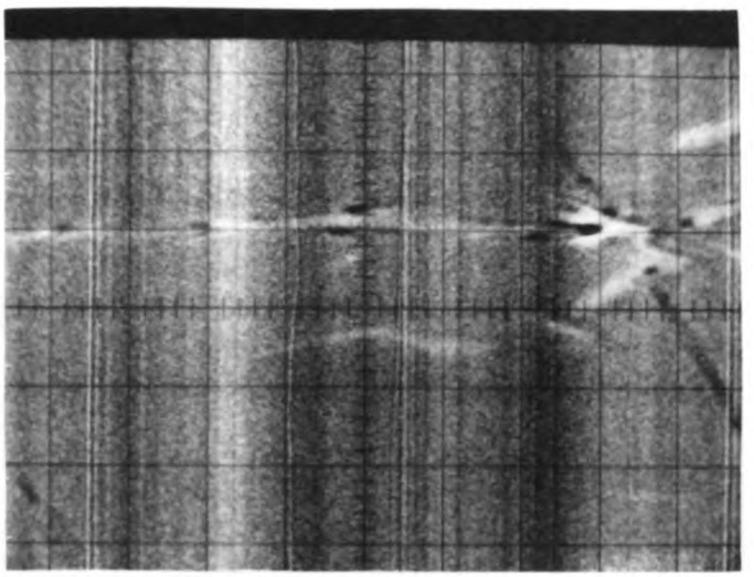


Plate 7. Grain 15 (Natural anti-perthite, hydrothermal, 1.33 Kb.) 2u/cm. Electron Photograph.

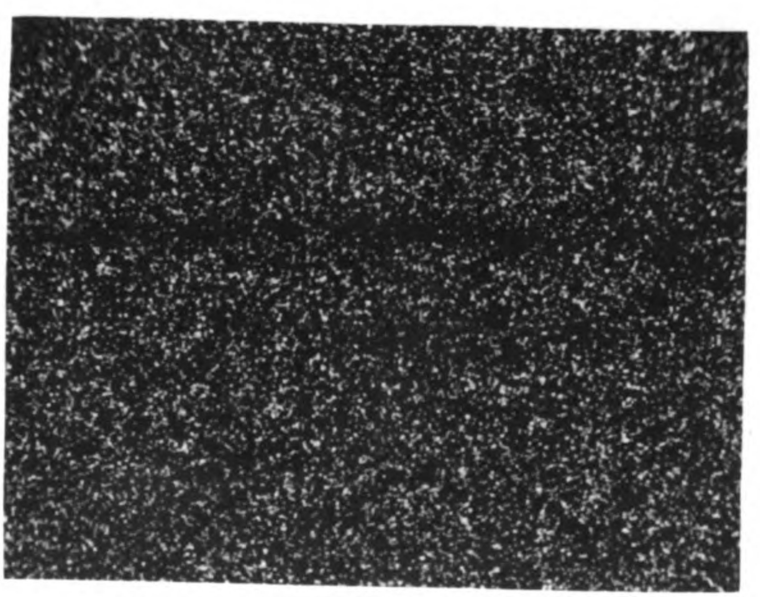


Plate 8. Grain 15 Na-photograph

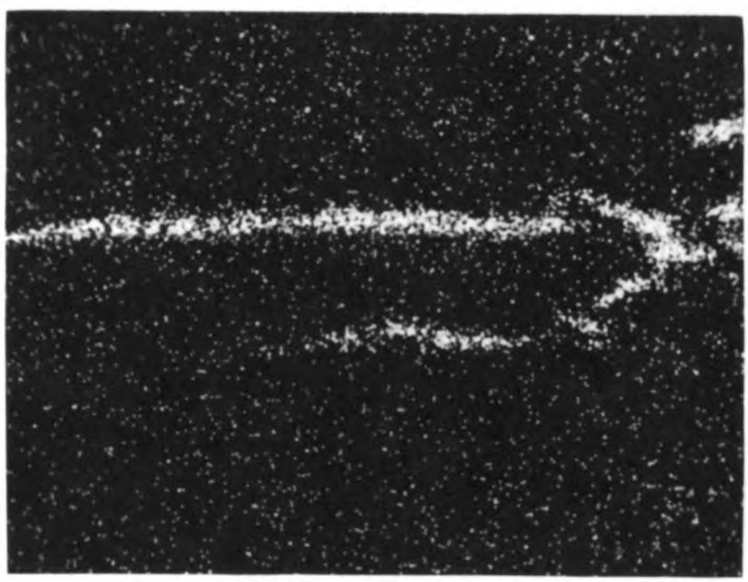


Plate 9. Grain 15 K-photograph

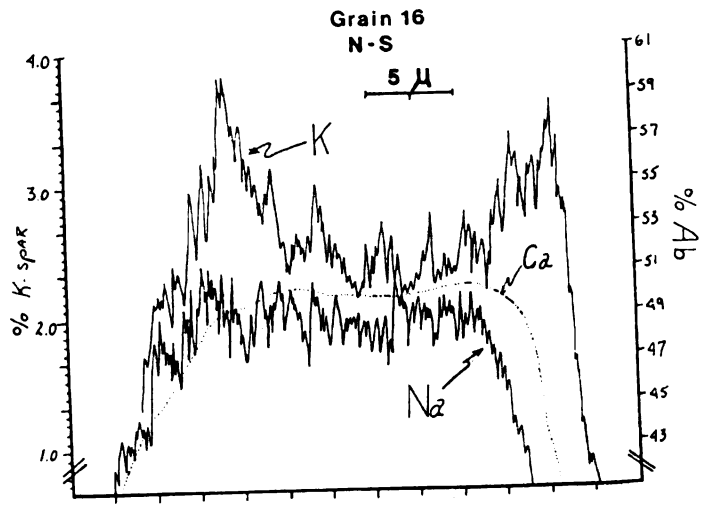


Figure 1. N-S probe trace of grain 16.

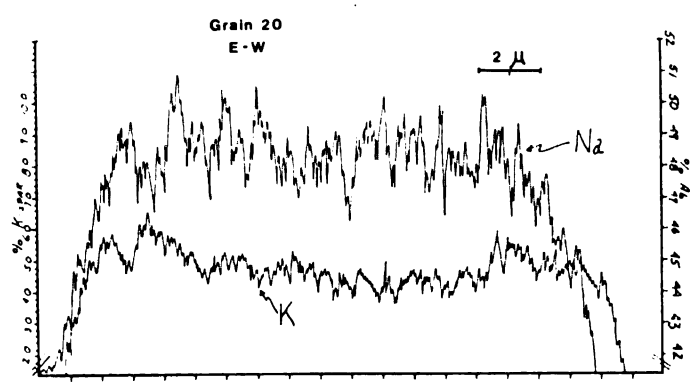


Figure 2. E-W probe trace of grain 20.

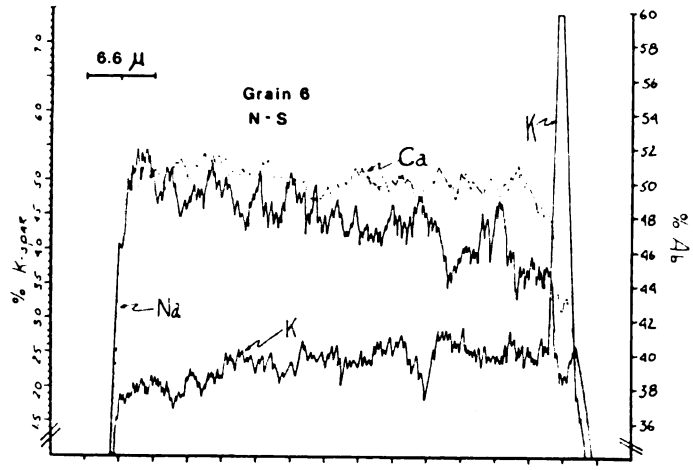


Figure 3. N-S probe trace of grain 6.

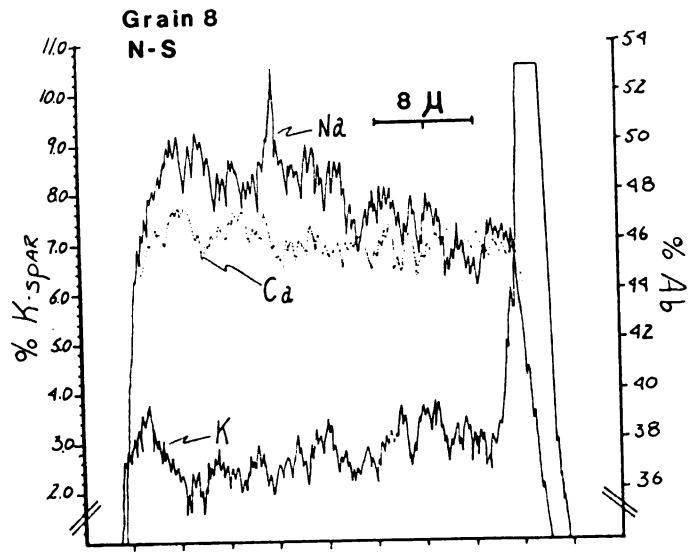


Figure 4. N-S probe trace of grain 8.

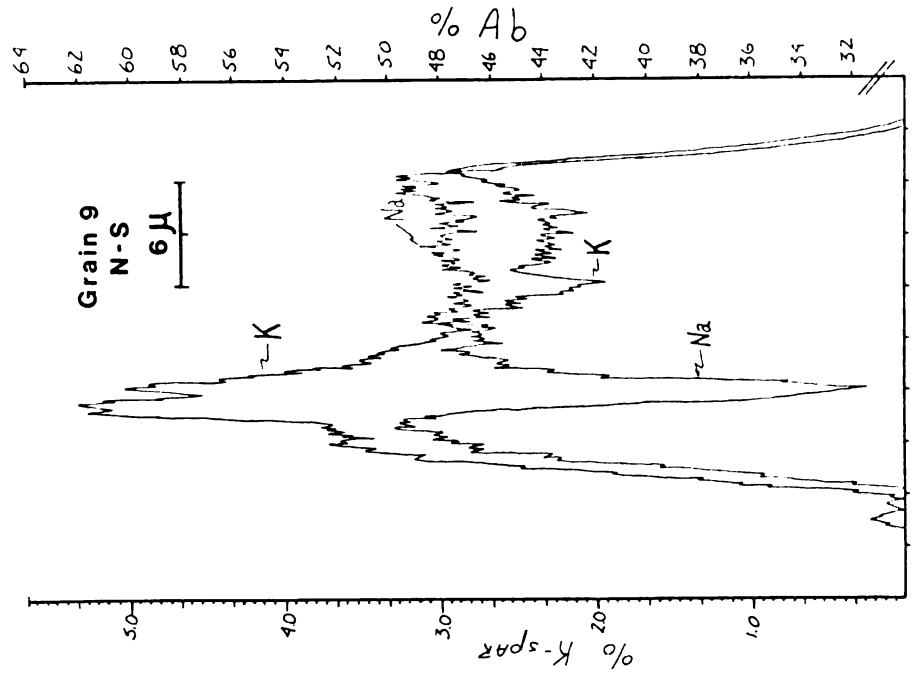


Figure 5. N-S probe trace of grain 9.

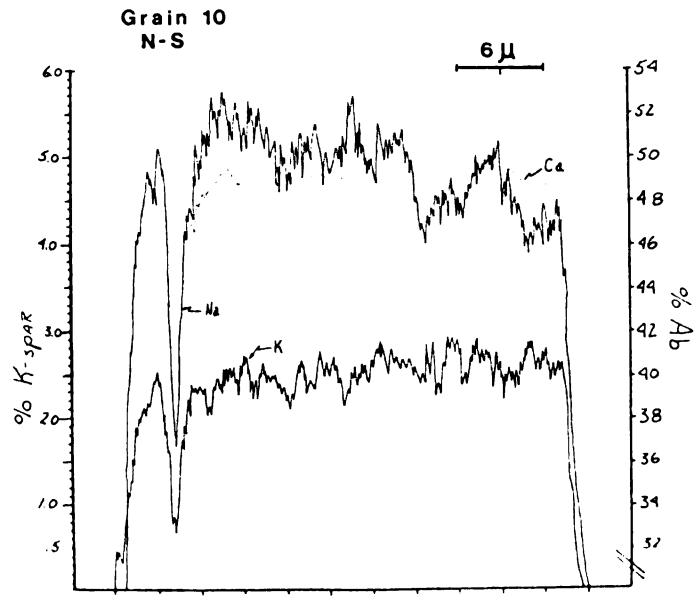


Figure 6. N-S probe trace of grain 10.

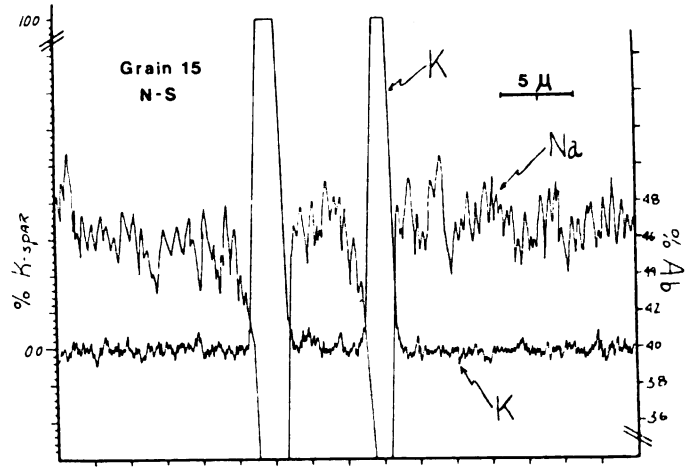
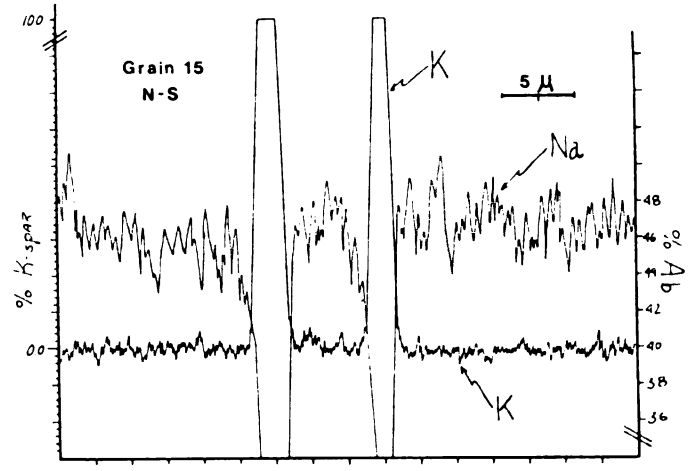


Figure 7. N-S probe trace of grain 15.



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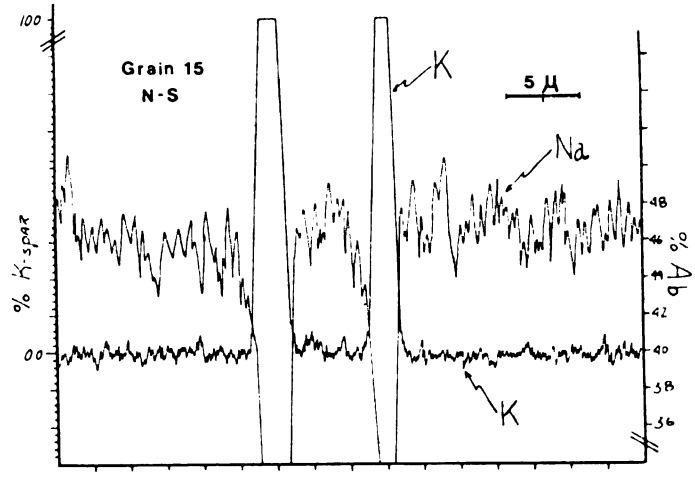

Figure 7. N-S probe trace of grain 15.

evident that, for any migration of sodium or potassium to occur, there must be a high energy environment. Even then, the actual weight percent held in "solution" appears to be very low.

INTERPRETATION OF DATA

These experiments were designed to test the validity of the exsolution model. If the exsolution model were viable it would be expected that, under conditions near the solidus (in the high temperature experiment, some grain boundaries were fused), some evidence of solid solution between K-feldspar and plagioclase would be present. This is not the case and the present author considers that the exsolution model for antiperthite formation is not valid.

A surprising result of these experiments was that antiperthitic plagioclase was produced; there are potassium feldspar concentrations on high energy surfaces (grain boundaries, crystal defects, etc.). Even though there was sufficient energy within the system to mobilize potassium and sodium, as evidenced by their respective compositional gradients, very little potassium was found dispersed in the plagioclase matrix.

If the exsolution model were viable, the potassium diffusing into the plagioclase to form the K-feldspar bleb should have homogenized in large proportions within the host. Under hydrothermal conditions, 2.8 weight

percent K-feldspar is the maximum held within plagioclase. Grain 6 is a good example of this. The potassium can be seen to increase from approximately 2.2 weight percent K-feldspar on the far edge to approximately 2.8 weight percent next to the bleb. In conjunction with this, grains 8, 9 and 10 support the hypothesis of low potassium solubility. In some cases (grains 8 and 9 for example) it appears that there is a concentration of potassium into domains. This is interpreted as being a nucleation phenomena since they are always associated with grain boundaries. In both of these examples there is a local enrichment of potassium up to 4.0 weight percent K-feldspar. Grain 10, on the other hand, shows no concentration of potassium. Apparently there was no suitable nucleation site available, and no K-feldspar bleb formed, merely gradients of sodium and potassium.

This data is not inconsistant with a solute-vacancy complex model, a model which has been well supported by experimental evidence in ceramic systems (Westbrook, 1967). This model, in summary, is that at high temperatures, there will be a supersaturation of vacancies and a certain fraction of these are theoretically and experimentally associated with a vacancy-impurity complex (Westbrook, 1967). These vacancies and the associated vacancy-impurity complex will decay during the quench toward high energy surfaces. Thus, as the crystal tends to relieve itself of the vacancies, there will be a net flow of vacancies

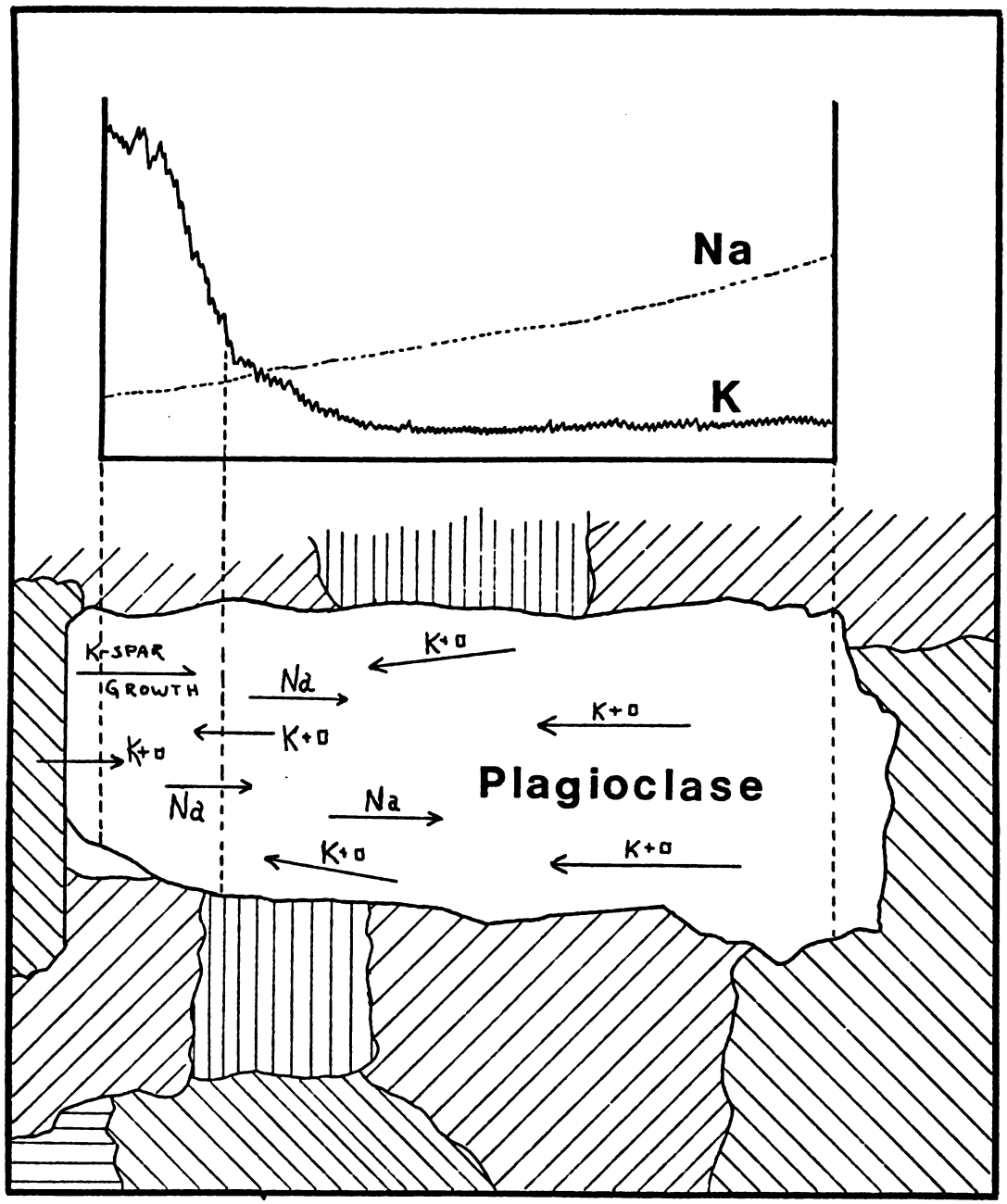

Figure 8. Model for the concentration of solute-vacancy complexed potassium and the growth of K-feldspar blebs.

and impurities toward thses surfaces. This process will favor a dissociation of the vacancy-solute complex near the grain boundary, thus producing a build-up of free solute atoms near these high energy surfaces.

As this model applies to the antiperthite system, the potassium is the solute in complex with the vacancies. Due to the existing solid solution of the alkali feldspars, the K-feldspar would act as an unlimited sink for sodium. Contrary to this, plagioclase would be a limited sink for potassium. The result is a free movement of sodium into the K-feldspar and a concomitant restricted diffusion of potassium into the plagioclase. Decay of potassium-vacancy complexes could occur on any high energy surface (grain boundaries, either in contact or as free surfaces, twin planes, crystal defects, etc.) with the growth of potassium feldspar proceeding outwards. Indeed, a large number of such surfaces may actually be a driving force for the concentration of potassium within the plagioclase. As stated above, plagioclase is greatly restricted to the amount of potassium, and the data indicate that the limit is approximately three weight percent K-feldspar.

Regardless of the exactness of this model, it is clear that the K-feldspar forms along high energy surfaces if such surfaces are available, and that the host plagioclase is incapable of holding sufficient quantities of potassium in "solution" to form exsolution antiperthites.

DISCUSSION

Both models for the formation of an antiperthite, the exsolution model and the "nucleation" model, involve the replacement of a volume of plagioclase feldspar by a volume of potassium feldspar.

Because of the two feldspar solid solutions, there is little problem with the mobility and replacement of Na and K or Na and Ca. Thus it is logical to assume that these ions will be randomly distributed throughout the original feldspar in a high-temperature disordered state. Because of this random distribution, the feldspar may be considered homogeneous.

With the exsolution model, three simultaneous diffusions must take place: (1) diffusion of potassium from matrix to potential bleb site, (2) diffusion of calcium and sodium away from bleb site, (3) re-proportionment of aluminum and silicon to the proper ratios, both inside and outside the bleb. The first two, the diffusion of potassium and the diffusion of sodium and calcium are of no major consequence, involving little crystal structure distortion. The re-proportionment of aluminum and silicon presents a greater problem, since the Al-O and Si-O bonds are the strongest found in feldspar. In either model these tetrahedral bonds are broken; in the exsolution model, the readjustment takes place throughout the plagioclase grain with many Al-Si-O bonds being broken, whereas, in the "nucleation" model the only

disruption is at the K-feldspar location.

As stated by Vogel (1970), "regardless of the origin of the potash feldspar, the growth of the potash feldspar within the plagioclase grain involves the replacement of a volume of plagioclase by a volume of potash feldspar".

Several researchers (Vogel, Smith and Goodspeed, 1968; Griffin, 1969; Vogel, 1970) have cited evidence that this replacement is not a result of exsolution and its thermodynamic explanation, but rather "nucleation" energies and kinetics.

Griffin (1969) referred to the occurrence of zoning (halos and rims) around the antiperthitic blebs as support of the "nucleation" theory. These zones would not be present if the blebs formed by exsolution, but rather, would become homogenized as exsolution took place. A study by Vogel, et. al. (1968) suggested a twofold hypothesis: "1. The exsolution of microcline from plagioclase is permitted by the structure of plagioclase between An_{33} to An_{50}." or "2. The development of antiperthite is dependent upon the feldspar phase that crystallized first." Although the present study involved plagioclase within the An_{33-50} range, the author believes the microprobe results clearly support the latter hypothesis.

Several researchers (Sen, 1959) distinguish between exsolution antiperthites and "replacement antiperthites". However, as stated, earlier, regardless of the means of formation of the antiperthite, a volume of plagioclase

must be replaced by a volume of K-feldspar. Secondly, the only real distinction between the two antiperthites of Sen appears to be size. If there exists an excess of potassium migrating through the host plagioclase, it will grow on previously nucleated blebs, rather than forming new smaller blebs. The only factors that govern the size of the antiperthite formed are, therefore, the pressure-temperature environment, time, and the amount of potassium available for diffusion. It does not appear feasible to assume that larger amounts of potassium will be held in solid solution to exsolve into a coarse grained antiperthite at higher temperatures as conditions in the present study were just below the solidus at two considerably different pressures.

SUMMARY

If the exsolution model is valid, then, at temperatures near the solidus, a homogeneous potassium-rich plagioclase should be produced. This model was tested under both dry and hydrothermal conditions; the maximum amount of K-feldspar dissolved was less than 5 weight percent. Whether or not this small amount of potassium is actually in solid solution is a matter of conjecture. It may be that the potassium is being driven through the plagioclase along sub-micron defects, or in the case of the high temperature run, driven through the crystal lattice by volume diffusion (Bailey, 1971).

The formation of potassium and sodium diffusion gradients as well as K-feldspar blebs within the plagioclase during these experiments supports a "nucleation" model for the formation of antiperthites. This data is consistent with Westbrook's (1967) solute-vacancy complex model for the diffusion of sodium and potassium and the formation of antiperthites.

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