RATE OF Al-Si ORDERING IN SANIDINES FROM AN IGNIMBRITE COOLING UNIT

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ABSTRACT

X-ray diffraction studies of monoclinic alkali feldspars [Orm (Ab+An)r] from a 300-meter-thick ignimbrite indicate that those feldspars in the central portion of the unit are significantly more ordered than those near the margins. The variations in degree of order are indicative of structural states that cover most of the more disordered half of the range between high sanidine and orthoclase. Further Al-Si ordering is believed to have become ineffective at temperatures below approximately 500°C, based upon the lack of significant K-Na unmixing. The length of time required for feldspars to order to their observed state can be estimated by calculation of the time required for the ignimbrite to cool from 800°C, the approximate emplacement temperature, to 500°C; this period was found to be a few hundred to 650 years, depending upon the cooling effects of rain water from above and ground water from below.

INTRODUCTION

The limited information on the rates of ordering of aluminum and silicon between tetrahedral sites of alkali feldspars (K, Na)AlSi3O8 restricts a description of this ordering behavior to the rather imprecise term “sluggish.” Yet knowledge of these rates and their dependence upon the environment of feldspar formation and evolution would be most valuable to the understanding of the thermal histories of many alkali-rich igneous and metamorphic rocks. This paper examines the structural state variations of alkali feldspars in a thick ignimbrite cooling unit where both the initial structural state of the feldspar and the cooling history of the ignimbrite may be estimated within reasonable limits; such limits allow estimation of the rate of ordering of these feldspars. The assumption can be made that the initial structural state of ignimbritic alkali feldspars at the time of emplacement was close to that of the least ordered sanidines found in the ignimbrite sheet; the structural states of alkali feldspars at various liquidus temperatures are not known.

Previous studies of structural state variations of natural alkali feldspars (e.g., Steiger and Hart, 1967; Wright, 1967; Tilling, 1968) have concentrated on attempting to establish from field evidence the tempera-

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atures and thermodynamic orders of the phase transformations, rather than the rate at which ordering took place. Experimental work (e.g., Goldsmith and Laves, 1954; Tomisaka, 1962) has largely been directed toward the same goal as field studies. Recently, Martin (1968, 1969a, b) has succeeded in hydrothermally synthesizing both low-albite and orthoclase; he concludes that the presence of peralkaline hydrothermal fluids has an important catalytic effect on the rate of ordering. Investigations into the cause of the variability of structural states of potassic alkali feldspars in Connecticut pegmatites (Godchaux and Orville, 1970) suggest that a complex of chemical and thermal factors control the ordering process.

For the present study, sanidines from the Oligocene Windous Butte Formation (about 325 meters thick), a compound ignimbrite cooling unit from the Grant Range, east central Nevada, were selected because this calc-alkalic rhyodacitic unit is sufficiently thick to have undergone a lengthy cooling period, and the chemical and mineralogic properties of this ignimbrite have been studied in detail (Scott, 1966, 1971a, b). This particular cooling unit has the characteristic zones described by Smith (1960) which include a chilled, slightly welded basal zone grading upward into a dense black vitrophyre which is overlain by a dense devitrified zone forming most of the interior; the less welded glassy zone found capping uneroded young ignimbrites has been stripped from the Windous Butte Formation. Intratelluric crystals form about $\frac{1}{3}$ of the rock and consist of about 30 percent quartz, 35 percent zoned plagioclase of andesine and oligoclase composition, 25 percent sanidine, 5 percent biotite, and lesser amounts of opaque minerals and hornblende. A small increase in crystal size and abundance occurs within the devitrified portion; this suggests that some pre-eruptive magmatic variations existed but detailed studies (Scott, 1966, 1971a, b) indicate that these are not of the magnitude of the distinct mineralogic and chemical zoning of ignimbrite zoning of ignimbrite units farther south in Nevada (Lipman, et al., 1966).

**METHODS OF STUDY**

A suite of six samples were collected in vertical sequences from the Windous Butte Formation (Lat. 38°39'41"N., Long. 115°21'17"W.); the sample positions from the base of the unit upward are: B13 at 12 m., B14 at 30 m., B15 at 45 m., B17 at 80 m., B18 at 180 m., and B19 at 240 m. The sanidines in these samples were separated from the rest of the crushed rock by magnetic, heavy liquid, and handpicking methods. Small portions of each separate were homogenized at 1050°C for 24 hours and the weight percent of potassium feldspar was determined to be 73±2 percent by the method outlined by Tuttle and Bowen (1968, p. 13). Partial
chemical analyses by atomic absorption spectrophotometry confirm the X-ray determinations of Or content and also indicate that the anorthite content of these specimens is one to two percent CaAl₂Si₂O₈. The X-ray patterns of untreated feldspars from the interior of the cooling unit show a slightly broadened 201 peak; sample B17, located near the center of the unit, has the broadest 201 peak with only incipient splitting (Fig. 1). On the basis of this it can be said that no appreciable exsolution of an albite-rich phase has occurred.

From X-ray diffraction traces of untreated pure mineral separates of sanidine, the 2θ positions of 28 to 33 peaks per sample which met with the visual and statistical quality outlined by Orville (1967, p. 61) were measured and recorded (scanning speed = 1°/min., Ni-filtered CuKα₁ radiation, Norelco X-ray diffractometer at Florida State University). These data were used to compute the refined unit cell parameters by the least square computer program of Prof. Charles W. Burnham, Harvard University; between 14 and 20 peaks were used in the final refinements. Direct and reciprocal lattice constants, c*/b* ratio, 2θ₀₀₀, 2θ₂₀₄, 2θ₂₀₁, (2θ₀₆₀ − 2θ₀₀₂) and 2Vₓ optical data for the samples are listed in Table 1.

**STRUCTURAL STATES OF ALKALI FELDSPARS**

According to both X-ray and optical data these feldspars are all classed as sanidines, but the relative amount of variation in their structural states depends upon the particular criterion used as the measure of degree of Al-Si order.

The reciprocal lattice constant ratio c*/b* is inversely related to the degree of order (Jones, 1966). The variation in c*/b* found in this study (cf. Table 1) is small, about 20 percent of the range between high sanidine and the sanidine-orthoclase boundary arbitrarily defined by Jones (1966). On the right side of Figure 2 the c*/b* ratios of our sanidines are plotted as a function of stratigraphic position within the cooling unit. (The left side of the figure will be discussed below). As would be expected, sanidines displaying the greatest degree of order occur in the interior of the ignimbrite sheet; sample B15, the most ordered according to this method of evaluation, occurs at the 45 m. level.

A similar trend is obtained when the direct lattice constants, a and b of the sanidines are plotted (Fig. 3) in the diagram of Wright and Stewart (1968): feldspars from the marginal zones of the ignimbrite fall closer to the high sanidine line while those from the interior of the unit are closer to the orthoclase line. If we regard the relative positions of the points representing the projection of feldspars onto a line parallelling the a-axis coordinate of Figure 3 as a measure of the degree of order, then according
Fig. 1. Shapes of 201 peaks in relative stratigraphic position. Note that the 201 peak from sanidines of the most centrally located sample, B17, is the broadest and that the sharpest peaks are those from samples B19 and B13, the uppermost and lowermost samples, respectively.
to the "Wright-Stewart criterion" the most ordered sanidine is sample B17 (from the 80 m. level); it occurs at a position in the figure representing about 40 percent of the distance between high sanidine and orthoclase. The relative degree of order of our sanidines expressed by an arbitrary scale is shown on the right side of Figure 4 as a function of stratigraphic position, as in Figure 2.
Fig. 2. Comparison of the variation of degree of order as indicated by the $c^*/b^*$ ratio on the right side with the time position curve of the 500°C isotherm of the Windous Butte Formation taking into account variable thermal diffusivities and the heat of devitrification on the left. Development of this cooling curve is discussed below in the text. The dashed line of the time-position curve does not include the heat of devitrification factor. The range of error for $c^*/b^*$ values is indicated by the horizontal bars through the values shown as solid circles.

Optical data also confirm the general trend; $2V_x$ values of 0–10° characterize sanidines near the edges of the ignimbrite while those from the inner portions have $2V_x$ values in the 20–40° range (see Tuttle, 1952). However, the generalization of increased order in feldspars from the interior of the cooling unit is not well supported by a plot of $2\theta_{000}$ vs. $2\theta_{204}$ (after Wright, 1968, Fig. 3), and a comparison of the feldspars based on the $(2\theta_{040}-2\theta_{002})$ method suggested by Borg and Smith (1969) shows no trend at all. Because the latter two methods are each functions of the positions of only two X-ray peaks, it is perhaps not surprising to find
Fig. 3. Degree of order indicated by the plot of direct lattice constants $a$ and $b$ (Wright and Stewart, 1968). Open circles represent sanidines from this study, solid circles represent feldspars from the literature. The average range of error for $a$ and $b$ constants for this study is plotted in the lower right corner.

Fig. 4. Comparison of the projection of the sanidine positions on the $a$ axis of Figure 3 with the cooling curve of Figure 2.
THERMAL HISTORY OF IGNIMBRITE COOLING UNITS

An estimation of the rate of cooling of a volcanic sheet and, therefore, an estimate of the time required for the feldspars to order to their observed state can be readily calculated using an infinite sheet with a discontinuous upper boundary and a continuous lower boundary as a model. Ingersoll, et al., (1954) and Jaeger (1968) have developed equations and presented data from which we constructed a graphical expression of cooling rates. From Jaeger's cooling-temperature/initial temperature ratio, $T/T_0$, written as a function of the dimensionless position ratio $\xi$ and the dimensionless time number $\tau$, a plot of $T/T_0$ vs. $\tau$ with $\xi$ contours was drawn for the asymmetric cooling conditions of an extrusive sheet and is shown here as Figure 5. The time necessary for any position, $x$, these methods less sensitive to minor changes in structural state than those of Wright and Stewart (1963) and Jones (1966) wherein structural state criteria are based on refined and reciprocal lattice parameters, respectively.
in the unit to cool to a temperature \( T \) from an initial temperature \( T_0 \) is calculated as follows: (1) calculate \( T/T_0 \); (2) determine the position ratio by the relationship \( \xi = x/a \), where \( a = \) one half the thickness of the sheet, \( +x \) values are above the position \( a \), and \( -x \) values are below \( a \); (3) find the intercept between the line representing the \( T/T_0 \) value and the appropriate \( \xi \) contour; (4) the projection of the intercept on the \( \tau \) axis gives the dimensionless time ratio, \( \tau \), for the case in question; (5) the cooling time, \( t \), can be calculated from \( t = \tau a^2/K \) after a suitable thermal diffusivity, \( K \), is chosen for the cooling unit; (use cgs. units).

The initial emplacement temperature of the ignimbrite is estimated to have been about 800°C; the choice of this value is based upon two limiting lines of reasoning: (1) A minimum lower limit is based upon the arguments of Boyd (1961) that take into account the heat loss during emplacement and the minimum welding temperature requirement. (2) A maximum upper limit is based upon the presence of hydrous ferromagnesians (biotite and hornblende) and upon the fact that compositions of coexisting plagioclase and alkali feldspar are more typical of feldspars that crystallized from hydrous melts than dry melts (Scott, 1965); both of these characteristics require a depression of liquidus temperatures because of the presence of water. 800°C is an intermediate value between these limits.

Because common occurrence of perthitic sanidines and orthoclases in nature is clear evidence that K-Na unmixing takes place more readily than Al-Si ordering, and because the bulk composition of the Windous Butte sanidines (Or73) intersects the sanidine—high albite solvus at atmospheric pressure (Thompson and Waldbaum, 1969) at a temperature of approximately 525°C, 500°C is taken by us to be the temperature at which effective ordering ceased as evidenced by the lack of significant exsolution in these feldspars. The time required for this 500°C isotherm to reach various stratigraphic levels in the Windous Butte formation was calculated using Figure 5.

The presence of slightly- to non-welded ash along the top and bottom margins of ignimbrites and of densely welded vitrophyre and devitrified rock in the interior introduces a complication into the calculations because the thermal diffusivity of ash is about 0.003 while that of vitrophyre or devitrified rock is about 0.01 (Ingersoll, et al., 1954, p. 289). Clearly, a realistic cooling model of an ignimbrite must take into account major zonation present in the degree of welding. Such a position vs. time curve for the 500°C isotherm is denoted by the dashed line on the left side of Figure 2. Devitrification to quartz and feldspars is estimated to have produced about 60 calories per gram of glass; when this additional thermal
Effect taken into account as in Jaeger (1961), the solid curve of Figure 2 is constructed. Thus, considering both the variation in thermal diffusivity and heat of crystallization, about 650 years are required for the interior of the unit to cool to 500°C.

**Limits on Ordering Rates of Natural Sanidines**

The calculated curve representing the cooling history of the ignimbrite unit is compared with the relationship between stratigraphic position and degree of Al-Si order of the Windous Butte sanidines, based on the Jones (1966) criterion, in Figure 2 and, based on the Wright-Stewart (1968) criterion, in Figure 4. Although the expected correlation between longer cooling periods and increased degree of order is observable, sanidines possessing the greatest degree of order (indicated by both methods of measurement) occur lower in the cooling unit than the theoretically slowest cooling portion of the ignimbrite. Furthermore, sanidine B19, collected from near the top of the unit, is considerably less ordered than feldspars that existed in an apparently similar thermal environment near the base of the unit. These discrepancies suggest we must question the assumptions that: (1) the cooling curve of Figure 2 and 4 is an accurate model of the cooling history of the ignimbrite, and (2) the degree of order of the feldspars is exclusively a function of cooling rate.

No attempt was made in the above calculation of the cooling curve to evaluate the effect of environmental factors such as rain water or ground water on the cooling rate. Although the Great Basin is rather arid at present, Axelrod (1956) indicates that climatic conditions were considerably wetter in Nevada during the Tertiary. Given a temperate climate with a meter of rainfall per year, the entire Windous Butte Formation could have cooled to 100°C in less than 200 years provided that perfect penetration and a homogenous distribution of rain water prevailed. However, it is much more realistic to assume that only a portion of the rain water penetrated into the porous upper zones and that the zone of rain water penetration would be limited by the vaporization isotherm underlain by a sharp thermal gradient. Such a downward-migrating cooling front would greatly decrease the cooling time for the upper portion of the unit and displace the slowest-cooling portion to a position lower in the unit. This may explain why the stratigraphically highest sanidine is the least ordered and the most ordered sanidines occur lower in the unit than would be predicted from the calculated cooling curve of Figures 2 and 4. Penetration of rain water into the porous and permeable upper zones of an ignimbrite should be considerably more...
effective than into the relatively impermeable crust of Kilauea Iki where Ault, et al. (1961) found rain water cooling to affect only the upper meter in a five month period.

Heat transfer by ground water migration can be a profound factor in the cooling of an extrusive sheet (Christiansen and Lipman, 1966). In a few Grant Range localities, evidence of heat transfer by ground water migration has been observed at the base of the ignimbrite sheets where underlying water-lain tuffs have been fused to a depth of one meter. Because fusion of glass shards in rhyolitic tuffs requires a temperature in excess of 550°C (Aramaki and Akimoto, 1957; Boyd, 1961) and since the contact temperature does not exceed one half the emplacement temperature (Jaeger, 1968), heat transfer by convection or migration of superheated vapors (in addition to simple conductive heat transfer) must have occurred; otherwise an impossibly high emplacement temperature in excess of 1100°C would be required to produce the observed fusion. Fusion of sediments beneath the Windous Butte Formation has not occurred, however, and the influence of ground water circulation upon the cooling history is impossible to evaluate. McBirney (1968) suggests that fiamme in ignimbrites may be created by depression of the melting point of the glass by introduction of vaporized ground water; although such an origin for the black vitrophyre of the Windous Butte Formation is possible, it is unlikely because of the uniform thickness of the vitrophyre over variable underlying terrains. Also no quantitative estimate of the amount of water vapor involved or the cooling effect can be made. Nonetheless, such convective heat transfer may have played a significant role.

With recognition of the imprecisely known magnitude of the cooling effect of rain water and ground water, the best estimate of the time required for the sanidines of the Windous Butte Formation to order to their present state is between a maximum of 650 years and a minimum of perhaps a few hundred years.

These time limits on ordering do not include the effects of any chemical and physical aspects (beyond the purely thermal aspect) of the environment of cooling ignimbrites, but such effects are believed to be negligible. A possible pressure effect (as noted by Martin, 1968, 1969a) can be discounted because the pressure differential is too small, less than 20 to 30 bars, even in thick ignimbrites. Studies of Martin (1968, 1969a) have shown a substantial increase in the rate of ordering in the presence of a vapor phase with a high alkali ion/hydrogen ion ratio but electron microprobe analyses of margins and interiors of sanidine crystals from thick ignimbrites (Scott, unpublished results) show the same composition which suggests that reaction between alkali feldspars and coexisting
vapor has not taken place. However, we cannot eliminate the possibility that the vapor phase catalyzed the ordering process without exchanging alkalis with the feldspar; until independent evidence for such an effect can be found, we will assume that time and temperature are the only major variables affecting the degree of order in this environment.

It is not possible to extrapolate our results and compare them to those of McConnell and McKie's (1960) and Parsons' (1968) studies of ordering in albite-rich alkali feldspars, not only because of the uncertain effects of feldspar composition on rate of ordering, but also—and more importantly—because of differences in research aim between our work and theirs. They were concerned with the attainment, or rate of attainment, of the equilibrium degree of Al-Si order at various temperatures, whereas we have dealt only with the time required to attain a given degree of order with no consideration of whether or not the observed state represents the equilibrium Al-Si distribution for 500°C (which, as noted above, we believe to be the minimum temperature of effective ordering).

Although the rate of ordering devised here may well be generally applicable to feldspars in ignimbrites, it would be unwise to assume that it can be extrapolated to other petrogenetic environments. Extension of this study to a wider ordering range and different environments should include investigation of the structural states of alkali feldspars in thermal aureoles of shallow plutons which have intruded sanidine-bearing air-fall tuff.

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