STRUCTURAL CHANGES AT ROOM TEMPERATURE OF HEATED ANORTHOCLASES

DOV BAHAT*

ABSTRACT

Anorthoclases that had gone through structural changes due to heat treatments showed gradual reverse transformations at room temperature. These reverse transformations are attributed to slight displacements of alkali cations in the strained crystals. The present results seem to support Baskin's suggestion (1956) that the monalbite → analbite transformation takes place from nuclei. The persistency of monalbite nuclei at room temperature appears to be a good measure of the original relative disorder states of the anorthoclases.

INTRODUCTION

Anorthoclases from various volcanic cones in Victoria, Australia (Edwards, 1938) were investigated by the *x*-ray powder method: (*a*) before, (*b*) immediately after removal from the furnace, and (*c*) at time intervals after heat treatments at different temperatures. The heat treatments were applied to various portions of the same mineral at temperatures between 500 and 1,050°C, each heat treatment for 24 hours.

The *x*-ray diffraction patterns were obtained on a Philips wide-range goniometer, using Ni filtered copper radiation, and a scanning speed of $\frac{1}{4}°$ of 2θ per minute, with a chart speed of 400 mm/h. Two or three records of each specimen were taken in the range $2\theta = 19.5°–32°$, each time with a fresh dry mount of the same material. The estimated error was $\pm 0.015°$ or less. Each of the feldspars was chemically analyzed in duplicate for potassium, sodium, and calcium. The alkalis were determined by flame photometry, and calcium was determined by a titrimetric method with E.D.T.A. and calcein mixture indicator.

Results for the various anorthoclases studied were qualitatively different for treatments up to 1,000°C, but they were qualitatively the same and quantitatively different for heat treatments at 1,050°C. The feldspars from Mts. Franklin and Anakie are fairly well known to feldspar investigators, and the observed results for these specimens are compared in Table 1 with 2θ calculated data, computed from Carmichael & Mackenzie (1964). In addition, an anorthoclase from Mt. Porndon (not investigated before) which is structurally fairly similar to the feldspar from Mt. Anakie is indexed as well (Table 1).

*Present address: Research and Development Laboratories, Corning Glass Works, Corning, New York.

TABLE 1. ANORTHOCLASES: X-RAY POWDER DATA

		1	1	1	1*	1
			(1,000°C × 24 hours	(900°C × 24 hours after 48 days)	(1,050°C × 24 hours)	(1,050°C × 24 hours after 5 months)
hkl	2θ(calc.)†	2θ(obs.)	2θ(obs.)	2θ(obs.)	2θ (obs.)	2θ(obs.)
$20\bar{1}$	21.742	21.75	21.73	21.74	21.75	21.74
$1\bar{1}1$	22.822	22.81	22.85	22.83	22.81	22.79
		23.09		23.20		
111	23.305	23.30	23.32	23.34	23.29	23.31
$1\bar{3}0$	23.644	23.62	23.67	23.68	23.66	23.62
130	24.083	24.07	24.09	24.07	24.10	24.06
$13\bar{1}$	24.548	24.52	24.61	24.54	24.56	24.53
$2\bar{1}0$	24.861	24.84	24.97	24.85	24.90	25.02
$\bar{1}31$	25.055	25.07	25.17	25.10	25.07	
$1\bar{2}1$	25.567	25.59				
$1\bar{1}2$	25.635		25.69	25.64	25.65	25.62
$22\bar{1}$	25.751					25.77
$\bar{1}12$	26.096	26.09	26.12	26.11	26.12	26.14
040	27.562	27.57	27.61	27.55	27.59	27.54
002	27.857	27.85	27.93	27.90	27.81	27.76
$1\bar{3}1$	29.742	29.72	29.77	29.76	29.74	29.67
140	30.369	30.41				
$04\bar{1}$	30.450	30.48	30.51	30.48	30.48	30.44
$14\bar{1}$	30.618	30.60				
$0\bar{2}2$	30.652		30.66	30.68	30.67	30.64
131	30.867	30.90	30.92	30.90	30.90	30.89
$131-1\bar{3}1$	1.125	1.18	1.15	1.14	1.16	1.22
$1\bar{3}1$ / 131		1/1	1/1	1/1.5	6.5/1	2.5/1

TABLE 1 (*concluded*)

		2	2	2*	2	3	3*	3
			(900°C × 24 hrs.)	(1,050°C × 24 hrs.)	(1,050°C × 24 hrs. after 5 months)		(1,050°C × 24 hrs.)	(1,050°C × 24 hrs. after 5 months)
hkl	2θ(calc.)†	2θ(obs.)	2θ(obs.)	2θ(obs.)	2θ(obs.)	2θ(obs.)	2θ(obs.)	(2θ(obs.)
$20\bar{1}$	21.797	21.80	21.80	21.79	21.85	21.79	21.78	21.79
$1\bar{1}1$	22.812	22.81	22.87	22.84	22.84	22.83	22.83	22.84
111	23.412	23.42	23.39	23.41	23.42	23.38	23.45	23.42
								23.57
$1\bar{3}0$	23.631	23.64	23.66	23.64	23.65	23.55	23.63	23.69
130	24.179	24.16	24.17	24.24	24.17	24.15	24.17	24.17
$13\bar{1}$	24.531	25.51	24.58	24.55	24.58	24.53	24.55	24.58
$\bar{1}31$	25.157	25.16		25.20	25.10			
$11\bar{2}$	25.631	25.68	25.64	25.60	25.56	25.65	25.54	25.66
$\bar{1}12$	26.201	26.15	26.19	26.19	26.17	26.22	26.20	26.19
040	27.605	27.61	27.65	27.62	27.63	27.60	27.56	27.62
				27.67			27.65	27.72
				27.76	27.78		27.78	27.79
002	27.912	27.91	27.93	27.93	27.85	27.93	28.17	27.92
220	28.126	28.13						
131	29.660	29.68	29.70	29.68	29.69	29.72	29.69	29.72
$0\bar{4}1$	30.376	30.39		30.37	30.40	30.40	30.42	30.42
140	30.478		30.47					
$0\bar{2}2$	30.587	30.56	30.54	30.54	30.57			
$22\bar{2}$	30.629		30.63	30.61	30.62	30.60	30.63	30.64
131	31.059	31.03	31.03	31.04	31.08	31.00	31.02	31.06
$131-13\bar{1}$	1.399	1.35	1.33	1.36	1.39	1.28	1.33	1.34
$\frac{1\bar{3}1}{131}$		$\frac{1}{1}$	$\frac{1}{1}$	$\frac{11}{1}$	$\frac{3}{1}$	$\frac{1}{1}$	$\frac{15}{1}$	$\frac{3}{1}$

Key to Table 1

*X-ray patterns which are diffuse.

†After Carmichael and Mackenzie (1964, Table III, nos. 4 and 11). Nos. 1, 2, and 3 indicate anorthoclases from Mts. Franklin, Anakie, and Porndon, respectively.

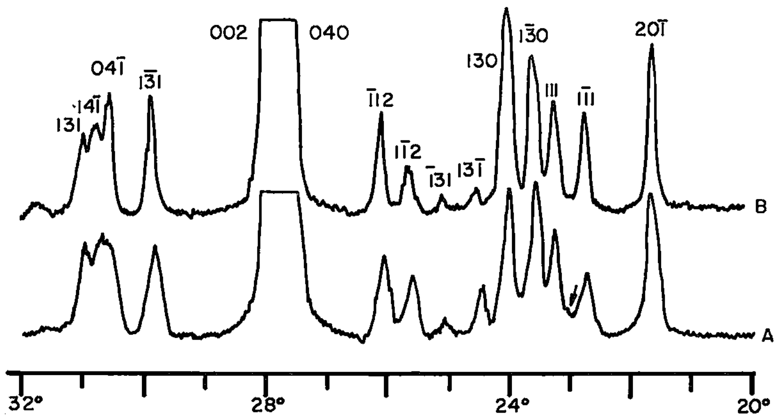

FIG. 1. *X*-ray powder patterns of unheated and heated anorthoclases from Mt. Franklin.
A—Unheated anorthoclase, the same pattern was obtained from the same feldspar 48 days after heat treatment at 900°C for 24 hours. (A small arrow shows an additional reflection due to unmixing.)
B—An anorthoclase immediately after being heated at 900°C for 24 hours.

RESULTS

When the feldspar from Mt. Franklin was heated at 525°C for 24 hours, no change from the original *x*-ray pattern occurred. When treatment at 575°C was applied, there was already a significant change. There was a pronounced sharpening of the (1$\bar{1}$1), (111), (1$\bar{3}$0), and (130) reflections. This sharpening was slightly increased at higher temperatures, and at 900°C the sharpening (and intensifying) of the reflections was completed and a small reflection at $2\theta = 23.09°$ disappeared. The same sample that had been heated at 900°C was re-examined after 8, 30, and 48 days, and the *x*-ray patterns obtained indicated a gradual return to the original pattern of the unheated feldspar (Fig. 1). Return was completed within 48 days. The same heat treatment was applied to the feldspar from Mt. Anakie. *X*-ray patterns indicated that apart from slight sharpening of the reflections, this feldspar was not significantly affected by heat treatments even at 1,000°C for 24 hours.

After being exposed to a heat treatment at 1,050°C for 24 hours, all the anorthoclases showed characteristically the following properties: (a) very low intensity and a wide broadening of most reflections, (b) very high intensity of the reflection (1$\bar{3}$1) and a low intensity of reflection (131), but reflections generally stayed in the original locations without a significant change in spacing. When the same samples were examined again by *x*-rays 5 months after the heat treatment, the patterns obtained were

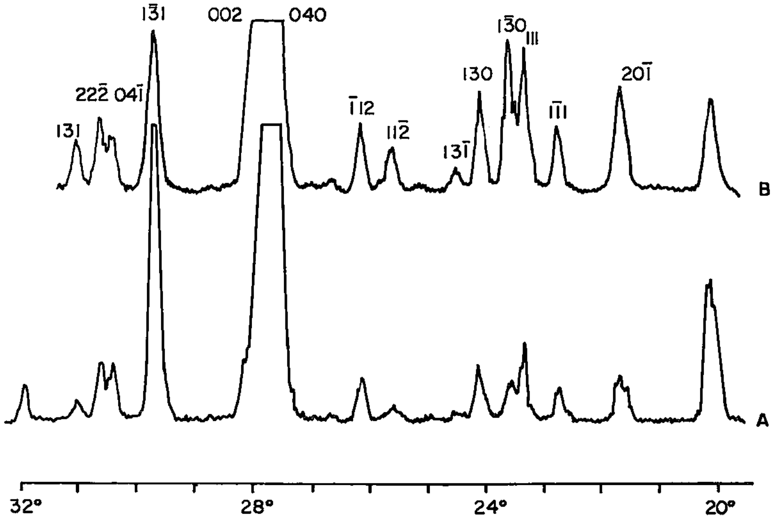

FIG. 2. X-ray powder patterns of heated anorthoclase from Mt. Porndon at 1,050°C for 24 hours.
A—An anorthoclase immediately after the heat treatment.
B—The above feldspar 5 months after the heat treatment. This pattern is similar to the pattern of the unheated sample with the exception that in the latter reflections (131) and ($1\bar{3}1$) have similar intensities. The first reflection on the right side of the figure is due to a (101) reflection of an internal standard $KBrO_3$ (2θ = 20.205).

different. They were characterized by the tendency to acquire their original structure before the heat treatment. These structural changes were especially emphasized in the feldspar from Mt. Porndon (Fig. 2).

Discussion

By observing the reflections of the feldspar from Mt. Franklin, one can see a small extra reflection in the x-ray pattern of the original sample ($2\theta = 23.09°$) and in the x-ray pattern of the sample when examined 48 days after the heat treatment. This reflection does not appear in the x-ray pattern taken immediately after the heat treatment. Since this reflection does not appear in the calculated data, it is obvious that it indicates a secondary unmixed phase. It is concluded that an unmixing of this feldspar occurs during 48 days after the heat treatment at room temperature. Observations on structural changes of feldspars at room temperature at time intervals after heat treatments in the laboratory are not common. Such an observation was made by Brown (1960). He noticed very slow structural changes in albite at room temperature.

Baskin (1956) discussed the significance of the appearance of smeared

x-rayed reflections indicating the development of a mosaic structure in heated albite. This phenomenon was attributed to a partial transformation of analbite (high albite with triclinic symmetry) to a monalbite (high albite with monoclinic symmetry). Upon completion of the transformation the x-ray reflections became sharp again, the mosaic structure disappeared. By observations made on the intensities of the x-ray reflections of the feldspar which had been heated, Baskin reached the conclusion that a crystal does not go through the displacive transformation from analbite to monalbite as a unit, but rather from a number of nuclei.

In analogy to Baskin's observations, it is considered that the anorthoclases, when heated up to 1,000°C, perform two rapid displacive transformations at the appropriate temperatures (Mackenzie 1952, and Laves 1952) when heated and when cooled down. After being heated up to 1,050°C, however, the displacive transformation with the decrease of temperature is not complete. This is indicated by the smeared reflections and by the difference in the intensities of the reflections shown by the Victoria anorthoclases. It can take five months or more for the transformation to the original structure to complete at room temperature. At 1,050°C apparently the displacive transformation is not governed by the anorthoclase structure, but it is rather strongly affected by monalbite nuclei.

Studies on triclinic-monoclinic transformations in albite that were carried out by Grundy *et al.* (1967) and Hall & Quareni (1967) indicate that some albites may become monoclinic before melting and some may not. Grundy *et al.* (1967) found that by synthesizing albite at temperatures close to the melting point or by prolonged heating of natural or synthetic albites at temperatures close to the melting point, a high Al/Si disordering may be acquired and a triclinic-monoclinic transformation may be achieved before melting. Brown (1960, 1967) found that monoclinic albite is capable of existing at room temperature, if the crystal contains a large proportion of potassium in it. Soldatos (1965) described a natural monoclinic cryptoperthitic sodium feldspar modification in a potassium feldspar (sanidine) host. It is, therefore, conceivable that in the anorthoclases that have been exposed to 1,050°C, a certain amount of Na feldspar nuclei could maintain monoclinic symmetry at room temperature for several months. The fact that there are almost no variations in triclinicity [(131)-($1\bar{3}1$)] but only changes in reflection intensities seems to support Baskin's suggestion that the structural transformation takes place from nuclei. Not all parts of the crystal have the same readiness for transformation, but as soon as the transformation occurs, it is instantaneous. Therefore, no gradual changes in triclinicity are observed. This is to be distinguished from the diffusive transformation which occurs between microcline and sanidine. The latter transformation has a slow rate with lattice angles showing intermediate states between those of the maximum triclinic microcline and those of the monoclinic sanidine.

It was mentioned above that structural changes at room temperature were quantitatively different for the various Victoria anorthoclases. The persistency of the monalbite nuclei in the feldspar from Mt. Porndon immediately after the heat treatment at 1,050°C appears to be higher than in the other anorthoclases. The suggested explanation for this is the following: The anorthoclases are generally disordered feldspars, but they are disordered to different extents. It is possible that the anorthoclase from Mt. Porndon is more disordered than the others and as such it has a more effective analbite $\rightarrow$ monalbite transformation at 1,050°C, and therefore, immediately after the heat treatment, more monalbite was quenched. Probably, by a long heat treatment of the anorthoclases the disordered state would be equalled and consequently the effectiveness of the analbite $\rightarrow$ monalbite transformation would be the same. In the natural anorthoclases the effectiveness of the analbite $\rightarrow$ monalbite transformation (due to a short heat treatment) seems to be a good measure for their relative order/disorder states. Accordingly, the anorthoclase from Mt. Porndon is more disordered than the anorthoclase from Mt. Anakie, and the latter feldspar is more disordered than the feldspar from Mt. Franklin, as the intensity ratios of the $1\bar{3}1/131$ reflections immediately after the heat treatment at 1,050°C for 24 hours are 15/1, 11/1, and 6.5/1 respectively (Table 1). From the experiment performed by Hall & Quareni (1967) on Brown's (1960) feldspar, it is inferred that the presence of potassium in the crystal was not responsible only for the existence of the monoclinic albite at room temperature, but it was also the required condition for the transformation of triclinic albite to monoclinic albite in the first place. Also, in relation to the new definition of high albite proposed by Grundy *et al.* (1967), it may be added that at the presence of a certain minimum amount of potassium (which is not yet known) a transformation of triclinic albite to monoclinic albite before melting, may take place even if the triclinic albite is not completely disordered. The chemical data on the Victoria anorthoclases (Table 2) indicate, however, that there is no direct correlation between the intensity ratios of the $1\bar{3}1/131$ reflections (immediately after the heat treatment at 1,050°C for 24 hours, Table 1), which are believed to indicate various order/disorder states, and the potassium proportion in the anorthoclases. The decrease of triclinicity [(131)-($1\bar{3}1$)] on the other hand is reasonably well correlated with the increase of orthoclase content of the anorthoclases (Table 2), as could be expected (Carmichael & Mackenzie, 1964).

TABLE 2. ANORTHOCLASES: CHEMICAL ANALYSES

	1	2	3
CaO	1.44	1.87	1.12
Na_2O	8.35	8.29	8.85
K_2O	3.75	3.23	3.33
Feldspar Components (wt.%)			
An	7.10	9.28	5.52
Ab	70.65	70.15	74.88
Or	22.16	19.09	19.68
$131-1\bar{3}1$	1.18	1.35	1.28

Nos. 1, 2, and 3 indicate anorthoclases from Mts. Franklin, Anakie, and Porndon, respectively. Triclinicity is reproduced from Table 1 on natural unheated anorthoclases.

Because of lack of enough energy, it is unlikely that the structural changes at room temperature described above are due to Al/Si ordering. It is, however, conceivable that due to a structural strain in the crystal a slight displacement of the alkali cations (mostly or solely sodium) would occur even at room temperature and cause a structural change.

ACKNOWLEDGMENTS

This study has been carried out in the department of Geology and Mineralogy, University of Melbourne, under the tenure of the Taft Interchange Scholarship and the Williams Scholarship, which are gratefully acknowledged.

The writer is most grateful to Dr. R. J. W. McLaughlin for helpful discussions and assistance.

REFERENCES

BASKIN, Y. (1956): Observations on heat treated authigenic microcline and albite crystals. *J. Geol.*, **64**, 219–228.

BROWN, W. L. (1960): Lattice changes in heat-treated plagioclase: The existence of monalbite at room temperature. *Z. Krist.*, **113**, 297–329.

——— (1967): A reinterpretation of monalbite. *Min. Mag.*, **36**, 80–82.

CARMICHAEL, I. S. E. & MACKENZIE, W. S. (1964): The lattice parameters of high temperature triclinic sodic feldspars. *Min. Mag.*, **33**, 949–962.

EDWARDS, A. B. (1938): The tertiary volcanic rocks of central Victoria. *Quart. Journ. Geol. Soc.*, **116**, 243–320.

GRUNDY, H. D., BROWN, W. L., & MACKENZIE, W. S. (1967): On the existence of monoclinic $NaAlSi_3O_8$ at elevated temperatures. *Min. Mag.*, **36**, 83–88.

HALL, K. M. & QUARENI, S. (1967): A note on monalbite. *Min. Mag.*, **36**, 78–79.

LAVES, F. (1952): Phase relations of the alkali feldspars. II. The stable and pseudostable phase relations in the alkali feldspar system. *J. Geol.*, **60**, 549–574.

MACKENZIE, W. S. (1952): The effect of temperature on the symmetry of high temperature soda-rich feldspars. *Amer. J. Sci.*, *Bowen Volume*, 319–342.

SOLDATOS, K. (1965): Ueber eine monokline kryptoperthitische Natronfeldspat-Modifikation. *Z. Krist.*, **121**, 317–320.

Manuscript submitted February 21, 1968, emended April 16, 1968