

A high-temperature X-ray study of the equilibrium forms of albite

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SUMMARY. Complete lattice parameters have been determined at a series of temperatures up to 950 °C using a furnace on a powder diffractometer for six synthetic supposed equilibrium albites, a non-equilibrium albite, two natural albites, and a heat-treated natural albite. The supposed equilibrium albites were prepared hydrothermally by MacKenzie (1957) for long periods of time and reached or nearly reached a state of no further change at their temperatures of synthesis between 500 and 1000 °C. A crystal of natural albite and three crystals of heat-treated natural albite were studied by high-temperature, single-crystal methods on a Buerger precession camera up to 1000 °C for comparison.

The lattice angles for each albite decrease smoothly with increasing temperature; the *a*-axis and the volume increase smoothly with increasing temperature. The rates of change increase with increasing temperature. The *c* and in some cases the *b*-axes appear to decrease initially in the range 25–300 °C and then subsequently increase. The thermal dilatation is highly anisotropic—the change in *a* is about twice that in *b* and about six times that in *c* over the whole range 25–850 °C. The effect of a temperature rise on the lattice parameters of the albites is very similar to the effect of the substitution of potassium on the room-temperature parameters.

Plots of α^* against γ^* for each albite at a sequence of temperatures up to 950 °C fall on nearly straight parallel lines, all albites becoming less oblique (triclinic) with increasing temperature. Of the equilibrium albites, only the one synthesized at 1000 °C becomes monoclinic below the melting point. The ratio d_{010}/d_{001} or c^*/b^* is a measure of order in the albites and does not vary with temperature. The similar behaviours of this ratio and of other lattice parameters as a function of the temperature of synthesis confirms the two-step ordering process in albite.

THIS work was undertaken to obtain complete lattice parameters and thermal expansion data at a series of temperatures up to 950 °C on low-albite and six synthetic intermediate and high albites. We were fortunate to be able to study a selection of the albites synthesized by MacKenzie (1957). The albites chosen for study were those that had been held for the longest times at constant temperature and pressure and had reached or nearly reached a steady state as judged by their diffraction patterns at room temperature (MacKenzie, 1957, fig. 3; compare Eberhard, 1967)—they are thus presumably close to the equilibrium forms, and it is for this reason that their study is of such interest. Two natural albites, some heated natural albites, and a non-equilibrium² synthetic albite were studied for comparison.

A similar high-temperature X-ray study of a natural low-albite and of a synthetic nearly-high albite by Stewart and von Limbach (1967), which was published after

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² An equilibrium albite is one that has reached a steady state with time under given conditions of formation. A non-equilibrium albite is one that has not reached a steady state under the conditions of formation. It is possible that the equilibrium forms are also the stable forms at their conditions of formation. The corollary that the non-equilibrium forms are metastable under all conditions is not necessarily true. All forms except low-albite are metastable at room temperature.

our experimental work was completed, is available for comparison. Evidence is now available to show that high-albite becomes monoclinic above a temperature of about 930 °C (Grundy, Brown, and MacKenzie, 1967). The lattice angles of microcline and a series of plagioclases have been measured at temperatures up to 1200 °C (Grundy and Brown, 1967).

Experimental

A high-temperature diffraction furnace was constructed based on one designed by Skinner, Stewart, and Morgenstern (1962). In order to avoid contamination of the sample by the specimen plate (Stewart and von Limbach, 1967) a nickel specimen plate was used. The disadvantage of using nickel is that the upper practical temperature limit to which the furnace could be used was 950 °C due to the oxidation of the nickel above this temperature. Two Pt/Pt-13 % Rh thermocouples were sited symmetrically one on each side of the specimen plate. The temperature of the specimen plate was calibrated up to 1000 °C using recrystallized magnesium oxide, for which the change in cell edge with temperature is accurately known (Campbell, 1962). The accuracy in the middle of the temperature range was checked by determining the inversion temperature of cryolite, which was found to be 565 °C compared with the better value of 563 °C found by Keith and Tuttle (1952). The accuracy of the temperature determination in the furnace is thought to be within ± 10 °C. The precision is better. The feldspar powder was smeared on the specimen plate with acetone.

The furnace was used on a Philips goniometer and the specimen scanned between 18 and 52° at a rate of $\frac{1}{2}$ ° 2 θ per minute using Ni-filtered Cu radiation. Only one traverse across this range was made at each temperature to avoid irreversible changes occurring due to prolonged heating. Because of the number of samples run, our precision is lower than that of Stewart and von Limbach (1967), who made three traverses at each temperature. The settings of the goniometer were: receiving slit 0.02 mm, scatter and divergence slits 1°. A Geiger counter was used and the ratemeter set so that full-scale deflection was never less than 400 counts/second. The time constant was 4 seconds. The diffraction charts were measured with a vernier-rule reading to within 0.002° 2 θ . The angular values were corrected for systematic errors using the 111 and 200 reflections from the nickel specimen plate, standardized against MgO during the calibration of the furnace.

The diffraction patterns were indexed making use of line positions calculated from lattice constants for low- and high-albite determined from precession photographs at a series of temperatures (Grundy and Brown, 1967) and of line intensities calculated from the room-temperature atomic co-ordinates (Ferguson, Traill, and Taylor, 1958). With these data it was possible to index the patterns and to assess the suitability of each peak for the calculation of the cell parameters. In the vicinity of 900 °C interpretation of the diffraction patterns of the highest albites became difficult due to partial merging of their diffraction peaks (see below). Errors due to the difficulty in locating the exact centres of diffraction peaks were reduced by a careful selection of the peaks measured. It is thought that the 2 θ values of the measured reflections are precise to within ± 0.02 ° 2 θ . The lattice parameters were calculated from these 2 θ values using a least-squares method. The difference between the observed and calculated values for the peaks used was usually ± 0.01 ° or less. The precision in the parameters is about ± 0.05 ° for the angles and ± 0.006 Å for the axes.

Complete lattice parameters were determined at room-temperature both before and after (sometimes in the middle of) the high-temperature study. No systematic changes occurred in these parameters due to the short-time heating in the diffractometer furnace, with the possible exception of low-albite (F 101) after heating to 950 °C, though in this case the pattern recorded after heat-treatment was poor.

The materials used are shown in table I. F 9/6, F 9/13, and F 9/32 were prepared by long-term heating in an electric furnace of natural albite from an Alpine vein, Schyn-Schlucht, Switzerland. A new analysis of F 9 gave $\text{Ab}_{99.4}\text{Or}_{0.5}\text{An}_{0.1}$ (compare Brown, 1960, S404). F 101 has the composition $\text{Ab}_{98.2}\text{Or}_{1.8}\text{An}_{0.0}$ (Kracek and Neuvonen, 1952) and was the same material as used by them. 901 was synthesized from a glass by D. L. Hamilton. The remaining synthetic albites are those made by W. S. MacKenzie (1957) and are the supposed equilibrium forms at 500, 600, 700, 750, 800, 850, 900, and 1000 °C. All the materials used in the preparation of these synthetic and heat-treated feldspars were sealed in gold or platinum capsules to avoid external contamination (Brown, 1967).

Results

In table I are set out the lattice parameters for Amelia albite and for the supposed equilibrium forms of albite synthesized by MacKenzie. For specimens 222 and 227, only room-temperature data are given. Results for the non-equilibrium synthetic albite 901 are also given in table I. Lattice parameters for the nearly pure albite F 9 both without and with previous long heat-treatment are given in tables I and II. Specimens F 9/6 and F 9/13 were examined by the precession method only, whereas specimens F 9 and F 9/32 were examined by both single-crystal and powder methods.

Room-temperature results. The lattice parameters obtained for low-albite (Amelia albite, table I, F 101) compare reasonably well with those for other low-albites (see table I in Stewart and von Limbach, 1967, and in Bambauer, Eberhard, and Viswanathan, 1967). The slightly higher values for the axial parameters and the volume may indicate that this sample of Amelia albite contains slightly more Or in solid solution than normal (compare Deer, Howie, and Zussman, 1963, vol. 4, table 13). The nearly pure albite F 9 has a smaller volume and axial parameters more in accord with values in the literature; judging from the lattice angles, it would appear to be slightly disordered. The lattice parameters obtained for high-albites also agree reasonably well with those in the literature (Orville, 1967; Stewart and von Limbach, 1967, table 4). Lattice parameters for two intermediate albites have been determined by Wright and Stewart (1968).

Compared to the results of other workers, our axial dimensions appear to be biased to slightly greater values, whereas those of Stewart and co-workers are biased to slightly smaller values. These differences may be due to one of two major causes. The first is some form of instrument misalignment such that the angular positions of the diffraction peaks are all displaced to slightly smaller or larger angles, hence giving slightly larger or smaller axial parameters. The second possibility is that all our synthetic samples contain potassium, hence giving slightly larger cell parameters due to the presence of Or in solid solution. The fact that the axial dimensions and volume for F 9 and F 9/32 are lower than those for the other albites in table I may possibly suggest that these latter all contain Or in solid solution, of the order of several percent. As it is considered that no compositional changes occurred inside the diffractometer furnace (such as were found by Stewart and von Limbach, 1967, p. 396), the potassium, if present, must have been in the samples as synthesized by MacKenzie and by Hamilton (F 901). On the other hand, the axial dimensions of a series of plagioclases (Grundy

and Brown, in preparation) also appear to be slightly biased to greater values compared to those of Smith (1956) or Bambauer, Eberhard, and Viswanathan (1967).¹

High-temperature results. The effect of a short-term rise in the temperature of a crystal is to change instantaneously and reversibly its lattice parameters. The object of the study was to determine these changes in albite. In order to avoid irreversible changes the period of heating in the furnace was reduced to a minimum. For all of the albites studied no difficulty was found in measuring and indexing the patterns, with the exception of the high-albites at temperatures above about 900 °C where the lines of the type hkl and $h\bar{k}l$ start to merge. This section will be restricted to cases where no ambiguity exists.

The reciprocal lattice angles increase smoothly with temperature, α^* increasing the most, γ^* slightly less, and β^* only very slightly. The variation in α^* and γ^* with temperature is shown in fig. 1. The direct lattice angles decrease smoothly with temperature, α decreasing (fig. 2) by about the same amount as α^* increases; β and γ decrease only slightly. The rates of change in general increase with successive increments of temperature; this is clearly seen in those angles that change the most.

The effect of a large increase in temperature is to increase all the dimensions of the lattice. This is not the case with a smaller increase in temperature, some of the dimensions appearing to decrease before subsequently increasing. In all the albites studied, the a -axis increases smoothly with temperature (fig. 3*a*). This is not the case with the c -axis, which decreases or does not change at all in the natural and synthetic albites examined in the temperature range 25 °C to about 300–400 °C (fig. 3*c*); thereafter it increases.² For other important directions approximately in the plane (010), namely the directions perpendicular to the faces (001) and ($\bar{2}01$), the thermal expansions are positive throughout the entire temperature range. The X-ray data obtained in this study also suggest that the b -axis of low-albite either decreases initially (F 101) or remains unchanged (F 9) in the temperature range 25 °C to about 300 °C (fig. 3*b*). Thereafter it increases.³ The b -axis of the intermediate albites appears to increase continuously with temperature. The situation in high-albite is less clear though there is a suggestion that the b -axis of high-albite decreases slightly or remains constant between 25 °C and about 150 °C. The percentage changes in the axial lengths and volume with temperature of the albites are given in table III, for the ranges 25–300, 300–850, and 25–850 °C. It is clear that the expansion of the albites is strongly anisotropic, especially at low temperatures, where the changes are negative for the c -axis and in some cases for the b -axis.

The coefficient of thermal expansion of the volume of all the albites is about the same (table III) and agrees very well with previous values of Kozu and Ueda (1933),

¹ This problem is at present under investigation. In any case the relative values should not be affected.

² This initial decrease in the dimensions of the c -axis for both low and high-albite is also found in the X-ray results of Stewart and von Limbach (1967, tables 2 and 5 and fig. 6). A negative coefficient of dilation was previously found in the case of adularia by Fizeau (1868, pp. 1079–81).

³ The data obtained by Stewart and von Limbach, though not showing any decrease, indicate a change in slope from a very low rate to a greater rate of increase at about 300 °C. Fizeau (1868) and Saucier and Saplevitch (1962) found small negative coefficients in the direction of the b -axis for adularia.

TABLE I. *Lattice parameters from powder-diffraction data (lengths in Ångstroms, angles in degrees, molecular volume (V) in cm³, and temperature in degrees centigrade)*

T	d_{010}	d_{001}	α^*	γ^*	a	b	c	α	β	γ	V
<i>F 101. Natural albite, Amelia Co., Virginia</i>											
25*	12·758	6·395	86·38	90·45	8·149	12·793	7·165	94·27	116·59	87·69	100·25
25†	12·769	6·393	86·43	90·45	8·147	12·804	7·163	94·21	116·59	87·72	100·29
25‡	12·768	6·392	86·40	90·35	8·165	12·803	7·165	94·20	116·63	87·81	100·48
140	12·760	6·397	86·55	90·53	8·167	12·794	7·159	94·12	116·47	87·69	100·52
300	12·765	6·402	86·65	90·60	8·179	12·797	7·155	94·03	116·34	87·68	100·76
450	12·790	6·413	86·77	90·73	8·186	12·822	7·167	93·97	116·33	87·59	101·22
600	12·808	6·424	86·92	90·87	8·208	12·839	7·173	93·86	116·25	87·52	101·79
750	12·799	6·425	87·20	91·00	8·234	12·826	7·169	93·61	116·19	87·51	102·03
850	12·826	6·429	87·42	91·00	8·252	12·850	7·177	93·37	116·27	87·61	102·51
950	12·838	6·436	87·58	91·23	8·252	12·862	7·171	93·29	116·06	87·45	102·71
<i>F 9. Natural albite, Schyn-Schlucht, Grisons, Switzerland</i>											
25*	12·764	6·385	86·27	90·18	8·134	12·800	7·153	94·26	116·56	87·93	99·97
25†	12·767	6·380	86·22	90·13	8·142	12·803	7·149	94·29	116·57	87·96	100·04
160	12·768	6·386	86·37	90·25	8·147	12·802	7·150	94·18	116·49	87·91	100·18
290	12·772	6·393	86·53	90·35	8·168	12·804	7·154	94·04	116·46	87·89	100·55
410	12·779	6·398	86·65	90·47	8·174	12·810	7·154	93·97	116·40	87·82	100·75
570	12·794	6·409	86·83	90·50	8·194	12·822	7·163	93·78	116·34	87·88	101·28
750	12·824	6·419	87·15	90·72	8·219	12·849	7·164	93·53	116·21	87·80	101·95
850	12·830	6·421	87·30	90·73	8·244	12·853	7·168	93·37	116·27	87·85	102·31
<i>F 9/32. Natural albite, heated 32 days at 1060 °C</i>											
25*	12·829	6·349	85·98	88·07	8·169	12·860	7·109	93·52	116·45	90·16	100·38
150	12·838	6·367	86·18	88·13	8·177	12·867	7·119	93·34	116·32	90·19	100·82
300	12·864	6·367	86·45	88·48	8·180	12·889	7·122	93·21	116·39	89·93	101·03
450	12·864	6·374	86·78	88·67	8·192	12·885	7·115	92·93	116·20	89·90	101·26
600	12·893	6·387	87·20	89·00	8·202	12·909	7·129	92·63	116·23	89·73	101·77
750	12·910	6·396	87·93	89·32	8·225	12·918	7·126	91·97	116·09	89·75	102·27
850	12·925	6·405	88·50	89·65	8·238	12·929	7·142	91·50	116·22	89·65	102·68
950	12·958	6·388	89·95	90·03	8·265	12·958	7·108	90·07	116·02	89·94	102·96
<i>219. Synthetic albite, crystallized for 2680 hours at 500 °C and 14 000 lb/in.²</i>											
25*	12·779	6·389	86·28	89·60	8·160	12·810	7·152	93·95	116·48	88·60	100·48
25†	12·777	6·392	86·22	89·62	8·162	12·809	7·162	94·04	116·57	88·54	100·55
140	12·795	6·392	86·30	89·73	8·180	12·827	7·154	94·00	116·44	88·46	100·90
300	12·804	6·391	86·62	89·83	8·179	12·830	7·145	93·69	116·36	88·51	100·91
450	12·816	6·404	86·80	89·98	8·196	12·841	7·153	93·56	116·28	88·44	101·39
600	12·842	6·408	86·90	90·05	8·210	12·866	7·157	93·48	116·28	88·41	101·83
750	12·857	6·425	87·17	90·27	8·245	12·878	7·168	93·29	116·18	88·31	102·62
850	12·854	6·422	87·42	90·32	8·244	12·872	7·164	93·03	116·19	88·38	102·52
<i>220. Synthetic albite, crystallized for 1761 hours at 600 °C and 14 000 lb/in.²</i>											
25*	12·817	6·372	86·05	88·72	8·170	12·848	7·137	93·77	116·51	89·46	100·65
25†	12·812	6·365	86·17	88·68	8·167	12·842	7·132	93·63	116·56	89·55	100·46
140	12·824	6·372	86·25	88·83	8·166	12·852	7·130	93·61	116·41	89·44	100·65
300	12·833	6·376	86·63	89·08	8·182	12·856	7·132	93·30	116·43	89·35	100·93
450	12·858	6·386	86·80	89·13	8·196	12·879	7·138	93·14	116·34	89·38	101·45
600	12·863	6·391	87·05	89·35	8·209	12·881	7·144	92·97	116·39	89·26	101·71
750	12·881	6·402	87·38	89·53	8·242	12·895	7·146	92·69	116·26	89·23	102·40
850	12·895	6·404	87·80	89·72	8·250	12·905	7·141	92·31	116·18	89·23	102·60
<i>230. Synthetic albite, crystallized for 1200 hours at 700 °C and 14 000 lb/in.²</i>											
25*	12·824	6·368	86·02	88·53	8·170	12·855	7·129	93·72	116·45	89·65	100·64
25†	12·821	6·368	86·10	88·62	8·161	12·851	7·126	93·67	116·40	89·61	100·51
140	12·836	6·366	86·17	88·70	8·176	12·866	7·125	93·64	116·42	89·55	100·78
300	12·853	6·373	86·47	88·93	8·189	12·878	7·128	93·42	116·39	89·44	101·15
450	12·871	6·390	86·77	89·05	8·205	12·892	7·137	93·14	116·27	89·46	101·72
600	12·878	6·393	87·08	89·20	8·219	12·895	7·137	92·86	116·24	89·45	101·97
750	12·902	6·402	87·50	89·43	8·246	12·915	7·141	92·51	116·18	89·40	102·61
850	12·904	6·407	87·78	89·57	8·250	12·914	7·145	92·26	116·17	89·39	102·73

* Before; † during; and ‡ after the high-temperature measurements.

TABLE I (cont.)

T	d_{010}	d_{001}	α^*	γ^*	a	b	c	α	β	γ	V
<i>222. Synthetic albite, crystallized for 1422 hours at 750 °C and 14 000 lb/in.²</i>											
25*	12·838	6·369	86·05	88·37	8·159	12·868	7·128	93·60	116·40	89·86	100·64
25*	12·838	6·367	86·02	88·37	8·161	12·869	7·123	93·64	116·35	89·85	100·64
<i>225. Synthetic albite, crystallized for 1440 hours at 800 °C and 14 000 lb/in.²</i>											
25*	12·833	6·357	85·98	88·25	8·160	12·865	7·114	93·62	116·38	89·96	100·44
25‡	12·833	6·366	85·95	88·25	8·160	12·865	7·128	93·65	116·45	89·94	100·58
140	12·847	6·365	86·15	88·42	8·174	12·876	7·122	93·51	116·41	89·85	100·82
300	12·858	6·369	86·53	88·57	8·187	12·881	7·120	93·16	116·35	89·88	101·09
450	12·872	6·380	86·77	88·72	8·203	12·892	7·127	92·97	116·29	89·83	101·53
600	12·896	6·384	87·13	88·92	8·218	12·911	7·131	92·66	116·31	89·79	101·94
750	12·914	6·395	87·63	89·22	8·248	12·925	7·136	92·25	116·24	89·71	102·60
850	12·920	6·400	88·08	89·42	8·248	12·928	7·135	91·85	116·16	89·71	102·71
<i>227. Synthetic albite, crystallized for 1440 hours at 850 °C and 14 000 lb/in.²</i>											
25*	12·836	6·352	86·00	88·18	8·160	12·868	7·114	93·56	116·48	90·03	100·38
25*	12·839	6·359	85·92	88·18	8·157	12·871	7·122	93·66	116·48	89·99	100·48
<i>329. Synthetic albite, crystallized for 41 hours at 900 °C and 7000 lb/in.²</i>											
25*	12·839	6·350	85·93	88·05	8·166	12·871	7·111	93·57	116·45	90·15	100·45
25‡	12·843	6·352	85·95	88·02	8·159	12·877	7·113	93·54	116·47	90·20	100·43
140	12·837	6·356	86·20	88·23	8·172	12·865	7·114	93·37	116·43	90·08	100·57
300	12·857	6·356	86·52	88·40	8·186	12·881	7·108	93·10	116·37	90·06	100·87
450	12·874	6·367	86·90	88·62	8·198	12·892	7·115	92·77	116·33	90·01	101·28
600	12·894	6·383	87·22	88·85	8·212	12·909	7·126	92·54	116·26	89·91	101·84
750	12·911	6·398	87·85	89·10	8·228	12·920	7·134	91·95	116·19	89·95	102·35
850	12·923	6·391	88·32	89·25	8·252	12·928	7·129	91·51	116·24	90·01	102·63
900	12·926	6·390	88·57	89·42	8·253	12·930	7·121	91·31	116·16	89·95	102·62
<i>307. Synthetic albite, crystallized for 66 hours at 1000 °C and 2000 lb/in.²</i>											
25*	12·854	6·350	85·90	88·00	8·157	12·888	7·113	93·58	116·48	90·19	100·47
25‡	12·843	6·353	85·92	88·07	8·155	12·876	7·114	93·60	116·45	90·12	100·40
140	12·852	6·358	86·22	88·10	8·172	12·880	7·112	93·28	116·37	90·24	100·72
300	12·868	6·361	86·55	88·33	8·193	12·892	7·115	93·02	116·40	90·15	101·12
450	12·892	6·372	86·88	88·43	8·206	12·911	7·119	92·70	116·31	90·21	101·60
600	12·905	6·383	87·33	88·80	8·215	12·919	7·126	92·38	116·27	90·02	101·95
750	12·921	6·393	87·92	89·10	8·246	12·929	7·132	91·88	116·24	89·98	102·58
850	12·936	6·400	88·78	89·45	8·238	12·939	7·130	91·09	116·11	90·02	102·67
950	12·950	6·411	90·00	90·00	8·261	12·950	7·143	90·00	116·17	90·00	103·21
<i>901. Synthetic albite, crystallized for 3 hours at 610 °C and 14 000 lb/in.²</i>											
25*	12·860	6·356	85·92	88·02	8·163	12·892	7·119	93·57	116·48	90·18	100·68
25‡	12·847	6·352	85·85	87·92	8·165	12·881	7·106	93·60	116·32	90·27	100·54
150	12·862	6·356	86·18	88·10	8·175	12·891	7·109	93·32	116·35	90·23	100·80
300	12·879	6·363	86·37	88·37	8·187	12·905	7·117	93·25	116·39	90·02	101·17
450	12·901	6·374	86·78	88·47	8·204	12·922	7·115	92·83	116·21	90·12	101·69
600	12·921	6·387	87·30	88·72	8·210	12·935	7·126	92·38	116·20	90·10	102·09
750	12·930	6·391	87·70	88·93	8·242	12·940	7·129	92·04	116·21	90·06	102·57
850	12·940	6·394	88·25	89·18	8·255	12·946	7·129	91·55	116·20	90·05	102·83
1000	12·968	6·418	90·00	90·00	8·280	12·968	7·131	90·00	115·83	90·00	103·71

* Before; † during; and ‡ after the high-temperature measurements.

Rosenholtz and Smith (in Yoder and Weir, 1951), and Stewart and von Limbach (1967). The volume increases continuously. The coefficients of thermal expansion of the volume are smaller for the feldspars than for most tectosilicates (see Stewart and von Limbach, table 3; Taylor, 1968), and indicate the tightly bonded nature of the cations in the framework of the feldspars. The rate of thermal expansion in the plagioclase feldspars decreases with increase in anorthite content (Kozu and Ueda, 1933; Stewart *et al.*, 1966; Grundy and Brown, in preparation), presumably because of the higher charge of the calcium, which gives stronger bonds to the framework oxygens.

TABLE II. *Single-crystal data (angles in degrees, temperature in degrees centigrade)*

T	α^*	T	β^*	T	γ^*	T	α^*	T	β^*	T	γ^*
<i>F 9. Natural albite, Schyn-Schlucht, Grisons, Switzerland</i>						<i>F 9/6. Natural albite, heated for 67 hours at 1050 °C</i>					
25*	86.33	25*	63.57	25*	90.27	25*	85.99	25*	116.27	25*	89.22
25†	86.29	25†	63.55	25†	90.27	25†	86.05	25†	116.22	25†	89.27
25‡	86.27	25‡	63.53	25‡	90.27	25‡	86.05	25‡	116.22	25‡	89.27
210	86.37	250	63.65	200	90.35	1000	88.15	1000	116.43	1000	90.49
400	86.53	450	63.72	380	90.47	1050	88.36			1050	90.63
585	86.80	610	63.77	600	90.72	<i>F 9/32. Natural albite, heated for 32 days at 1050 °C</i>					
700	86.99	800	63.79	810	90.90	25*	86.05	25*	63.42	25*	87.99
800	87.30	1010	64.07	1000	91.15	25†	86.00	25†	63.40	25†	87.97
850	87.42					25‡	86.02	25‡	63.43	25‡	88.00
1000	87.65					180	86.42	180	63.50	180	88.22
<i>F 9/13. Natural albite, heated for 67 hours at 1050 °C</i>						400	86.77	400	63.62	400	88.40
25*	86.29	—	—	25*	89.97	600	87.29	580	63.62	610	88.77
25†	86.30	—	—	25†	89.97	830	88.70	835	63.79	830	89.40
25‡	86.29	—	—	25‡	89.97	910	89.50	920	63.83	910	89.77
180	86.37	—	—	590	90.37	1005	90.00	1015	63.92	1010	90.00
380	86.50	—	—	790	90.59	1070	90.00			1060	90.00
590	86.87	—	—	1020	90.92						
780	87.23	—	—	1050	90.97§						
1000	87.77	—	—								
1050	87.87§	—	—								

* Unheated specimen.

† Specimen after high-temperature mounting.

‡ Specimen on completion of the high-temperature photography.

§ Extrapolated parameters.

|| Estimated parameters.

Discussion

Relationships between the lattice constants. Before discussing the relationship between order/disorder and the lattice parameters, it is interesting to compare the changes in one parameter as a function of the changes in another.

A plot of α^* and γ^* has been frequently used for room-temperature results for the alkali feldspars (MacKenzie and Smith, 1955, 1962) and for the plagioclases (Brown, 1960). A plot of the reciprocal angles rather than the direct angles (as used for example by Orville, 1967) is to be preferred because the former angles vary more and can be more directly measured. The effect of temperature on the angles α^* and γ^* is such that the plotted points in fig. 4 for each albite lie on smooth nearly straight lines sub-parallel to the plots of the other albites. Each equal increment of temperature causes

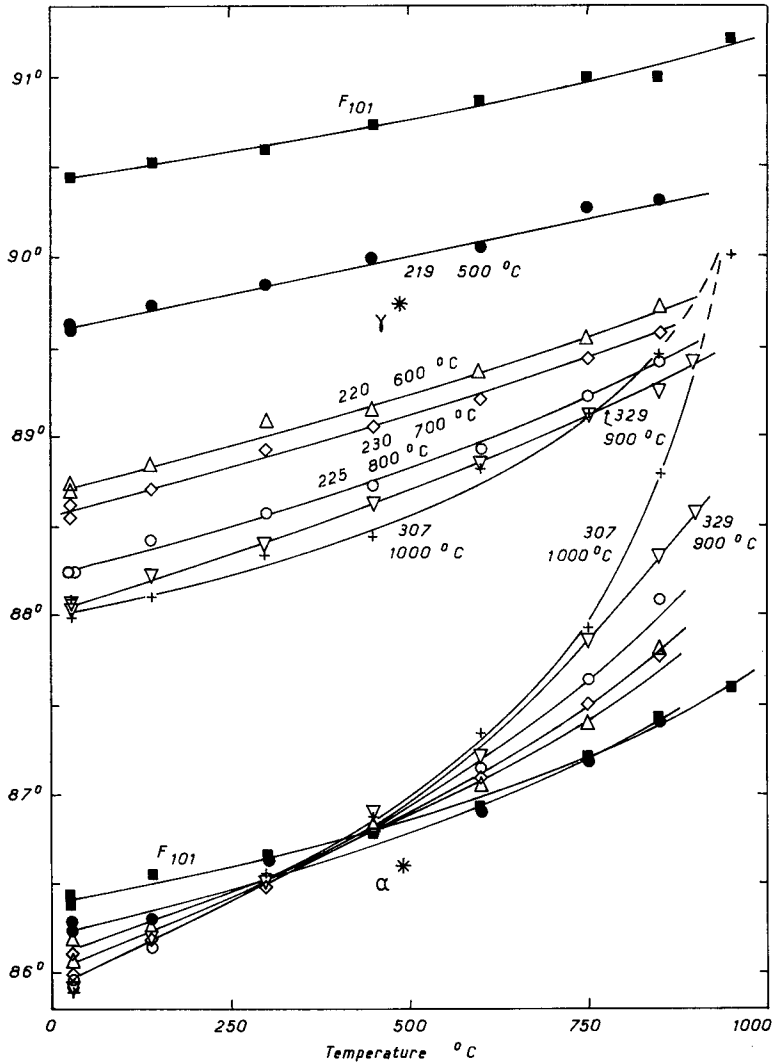


FIG. 1. Curves of α^* and γ^* against temperature for the equilibrium albites. Not all symbols have been inserted for α^* at intermediate temperatures. In this figure and all the succeeding ones only the points for the equilibrium albites have been plotted, except where expressly indicated. The temperatures indicated beside the curves in this and subsequent figures are the temperatures of synthesis of the albites.

a progressively slightly greater displacement of the plotted points for each albite. In addition, the displacement on the diagram for an increment of temperature increases progressively from low-albite to high-albite. The agreement between the results shown in fig. 4 and those obtained previously for low- and nearly high-albite (Stewart and von Limbach, 1967) is very good.

The axial dimensions that change in the most interesting way in the albites are the b - and c -axes or the interplanar spacings d_{010} and d_{001} . A plot of b versus c has been used to demonstrate changes in both order/disorder and composition in the alkali feldspars (Wright, 1964; Orville, 1967; Wright and Stewart, 1968). Such a diagram may also be used to show the effect of temperature on these dimensions in the albites.

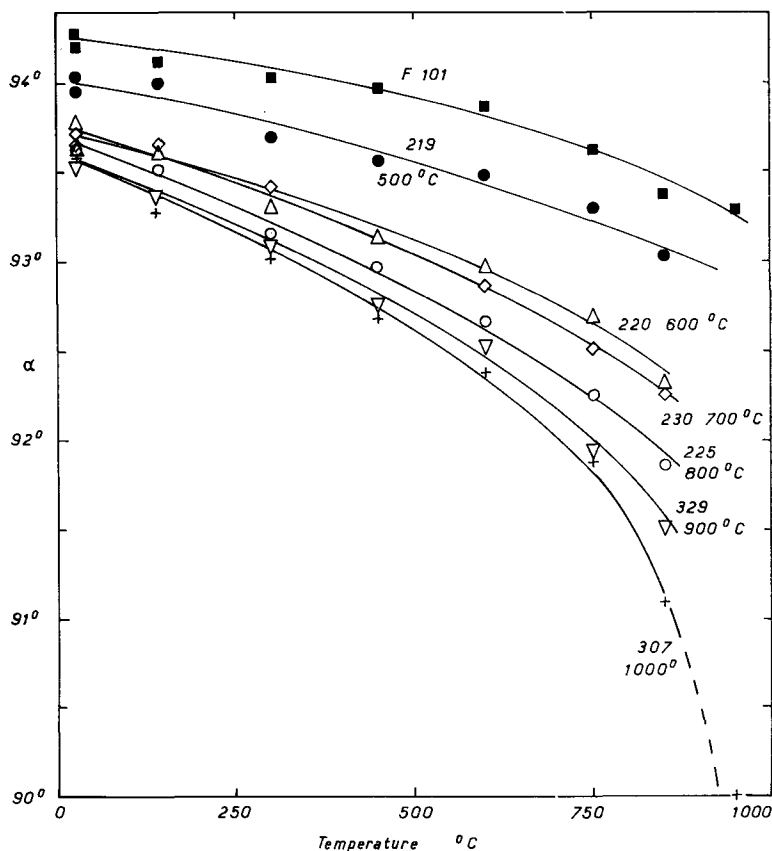


FIG. 2. Curves of α against temperature for the equilibrium albites.

On a plot of the two dimensions b and c at a series of temperatures for some of the albites studied, the trends of points for each albite at a series of temperatures are slightly curved, due to the negative or very low coefficient of thermal expansion of the c -axis at low temperatures.

The coefficient of thermal expansion of the dimension d_{001} is more nearly constant over the whole temperature range. Fig. 5 has been oriented to conform to the diagrams of α^* versus γ^* in use for many years. The interplanar spacings are also more readily determinable from either single-crystal or powder-diffraction diagrams without the need for complete determination of the lattice parameters. As can be seen from fig. 5

the trends of points for the albites are nearly parallel straight lines—thus the ratio d_{010}/d_{001} has an almost constant value for each albite (table IV). This ratio varies from albite to albite. It is also clear from figs. 4 and 5 that the influence of increase in

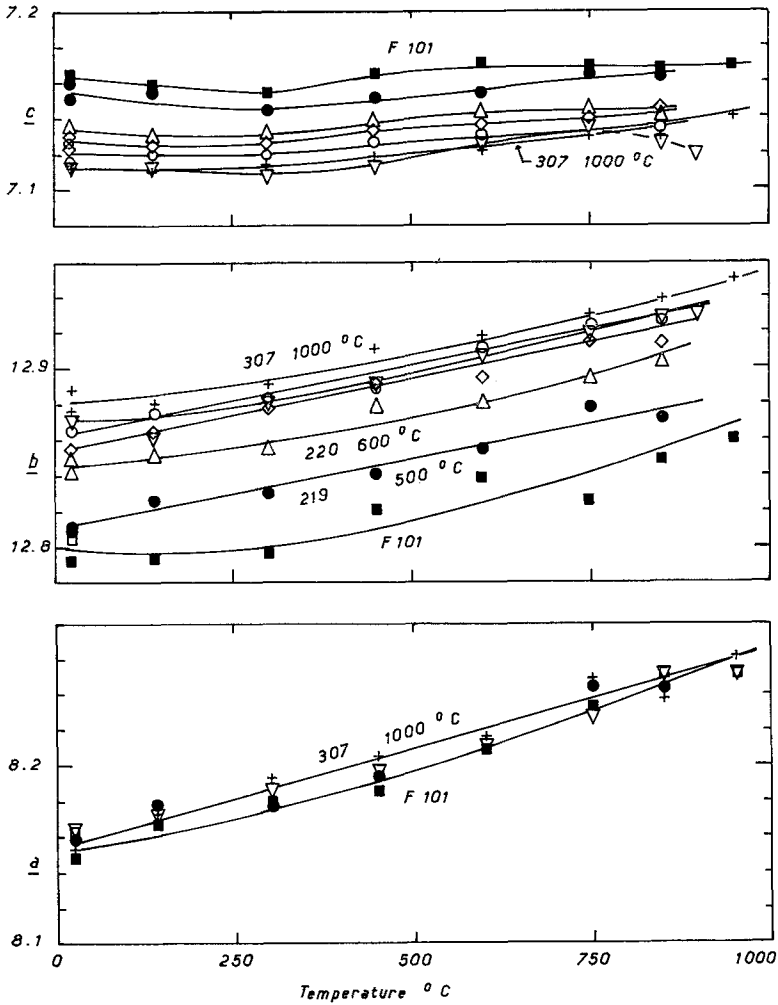


FIG. 3. Curves for the parameters a , b , and c against temperature for the equilibrium albites. Not all symbols have been inserted for the a -axis because of overlap and curves have only been drawn for F 101 and 307.

temperature of about 1000 $^{\circ}\text{C}$ on the lattice parameters of the albites is very similar to the substitution of 25–30 % Or on the room-temperature parameters.

The effect of order/disorder on the lattice parameters. One of the principal objects of this study was to determine the lattice parameters of the equilibrium albites at the temperatures of their formation, in order to obtain information about albite on the

supposed equilibrium order/disorder path. The values of the angles α^* and γ^* for each of the synthetic albites at their temperature of equilibrium are indicated in fig. 4. The curve *AFGHE* represents the supposed equilibrium order/disorder path for albite in terms of the angles α^* and γ^* . A distinct break occurs in this curve at about 600 °C or just below. It is clear from a study of the tables and the diagrams that the *equilibrium* parameters of albites change at a different rate with temperature above about

TABLE III. *Percentage changes with temperature in the axial lengths and volume of the albites and approximate linear coefficient of thermal expansion of the volume. Hand-smoothed parameters (i.e. those read from curves as shown in fig. 3) have been used in the calculations*

	<i>a</i>	<i>b</i>	<i>c</i>	Vol	α Vol	Temp range
F 101	0.26 %	0.16 %	-0.08 %	0.56 %	2.03×10^{-5}	25-300 °C
	0.82	0.41	0.22	1.59	2.88	300-850
	1.08	0.56	0.14	2.15	2.61	25-850
219	0.22	0.16	-0.15	0.52	1.88	25-300
	0.90	0.39	0.28	1.72	3.13	300-850
	1.13	0.55	0.13	2.25	2.73	25-850
220	0.16	0.10	-0.06	0.41	1.48	25-300
	0.89	0.37	0.18	1.69	3.08	300-850
	1.05	0.47	0.13	2.11	2.56	25-850
230	0.27	0.19	-0.01	0.58	2.10	25-300
	0.83	0.33	0.24	1.68	3.06	300-850
	1.10	0.52	0.22	2.27	2.75	25-850
225	0.32	0.13	-0.03	0.60	2.17	25-300
	0.87	0.38	0.22	1.70	3.09	300-850
	1.19	0.51	0.20	2.31	2.80	25-850
329	0.25	0.05	-0.07	0.42	1.52	25-300
	0.82	0.38	0.35	1.74	3.17	300-850
	1.07	0.43	0.28	2.17	2.63	25-850
307	0.37	0.10	0.00	0.71	2.57	25-300
	0.78	0.35	0.28	1.66	3.02	300-850
	1.15	0.45	0.28	2.38	2.88	25-850

600 °C than below it. This break in the influence of temperature on the equilibrium parameters is very strong evidence in favour of a two-stage ordering process in albite (Laves, 1960; Brown and Grundy, in preparation). A similar break is seen at the same temperature in fig. 6. It was suggested by Jones (1966) that the ratio c^*/b^* or d_{010}/d_{001} can be used as an order parameter in the alkali feldspars. In the case of albite this ratio (table IV and fig. 6) clearly indicates a two-step ordering process.

Crystals of F 9 were examined to determine the non-equilibrium disordering path of albite at high temperature. The crystals were sealed in platinum tubes during the heat treatment and subsequently studied by single-crystal and powder methods at elevated temperatures (tables I and II). The results are plotted in fig. 4—the points

I, J, K, and E represent extrapolations to 1050 °C for F 9, F 9/13, F 9/6, and F 9/32 respectively. The curve *IJKE* represents the non-equilibrium disordering path for F 9 on prolonged heating at 1050 °C, in terms of the angles α^* and γ^* .

The effect of an increase in disorder on the lattice angles of albite at room temperature is to produce a decrease in both α^* and γ^* (fig. 4); under the same conditions

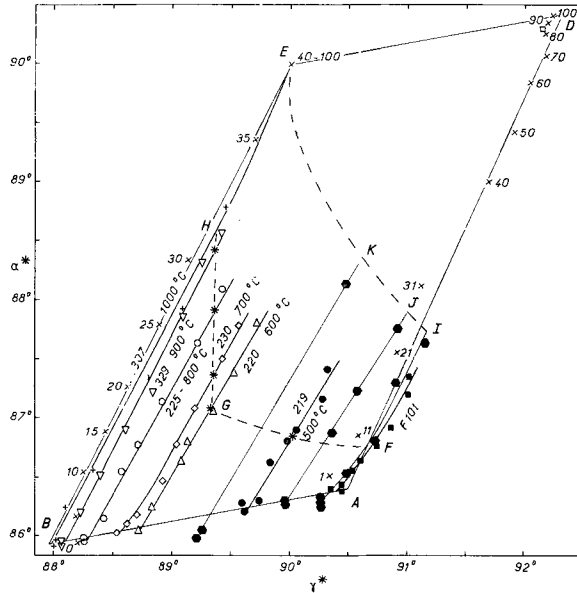


FIG. 4. Plot of α^* against γ^* at a series of temperatures for the equilibrium albites. The values near the line *AB* are at 25 °C; subsequent points on each of the lines for the albites are at 140, 300, 450, 600, 750, 850, and in some cases at 900 or 950 °C. The stars * on these lines represent the value of α^* and γ^* for the synthetic albites at their temperatures of synthesis—for an explanation of the curve *FGHE* see the text. Points *ABDE* are from Brown (1960). The data at room temperature for solid solutions between albite and potassium feldspar from Orville (1967) are indicated by a cross \times , the number indicating the percentage of Or. The average value of α^* and γ^* for microcline at 25–1000 °C from Grundy and Brown (1967) is given by \square . Data for the albites F 9, F 9/13, and F 9/6 from precession photographs are given by \bullet . Slightly smaller values were obtained for F 9 using the diffractometer furnace. The broken line *IJKE* represents the non-equilibrium disordering path for the particular albite F 9 at 1050 °C.

α decreases and γ increases (Baskin, 1956; Smith, 1956; Schneider, 1957). The angles β^* and β hardly change at all.

As was first shown by Cole, Sørum, and Kennard (1949) the effect of disordering orthoclase is to produce an increase in *b* and a decrease in *c* at room temperature. The albites show the same effect with disorder at both room and elevated temperatures. Whereas the properties of the intermediate albites are in general intermediate between those of low- and high-albite, this may possibly not be the case for the *a*-axis and the volume, which appear to be greater at room temperature for intermediate albites.

High-albite and the triclinic/monoclinic transformation. As was pointed out at the

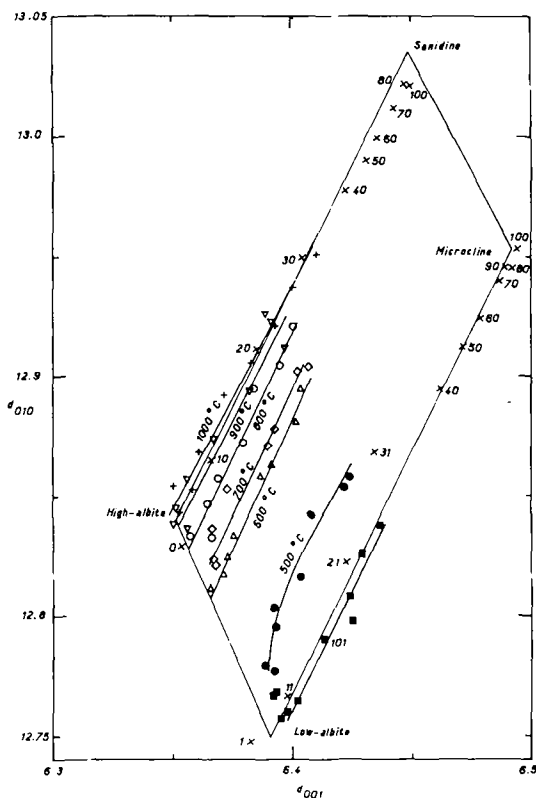


FIG. 5. Plot of d_{010} against d_{001} at a series of temperatures for the equilibrium albites studied. The values for low- and high-albite are from Smith (1956), those for microcline and sanidine from Gubser and Laves (1967).

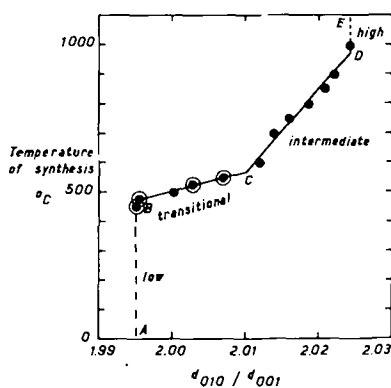


FIG. 6. Plot of the value of the ratio d_{010}/d_{001} at 25 °C against the temperature of synthesis of the equilibrium albites. The encircled values at 450, 475, 525, and 550 °C have been estimated on the basis of the extrapolated values for the separation of the lines $1\bar{3}1$ and $1\bar{3}\bar{1}$ calculated by McConnell and McKie (1960) and are thus less accurate.

beginning of the section on high-temperature results, certain difficulties arose in the measuring and interpreting of the diffraction patterns of high-albite at temperatures above 900 °C, due to the merging of diffraction peaks of the type hkl and $h\bar{k}l$. Evidence has been presented elsewhere (Grundy, Brown, and MacKenzie, 1967), which in our view suggests that material that we believe to be nearly pure albite becomes monoclinic at temperatures above about 930–50 °C. This problem will be briefly discussed again because data for a series of albites is now available, and because of the evidence presented by Stewart and von Limbach and their discussion of it (1967, pp. 391–3, 395–7, and 403–5).

TABLE IV. *The variation of the ratio d_{010}/d_{001} with temperature in the supposed equilibrium albites*

	25 °C	150 °C	300 °C	450 °C	600 °C	750 °C	850 °C	950 °C
F 101	1·995	1·995	1·994	1·994	1·994	1·992	1·995	1·995
219	2·000	2·002	2·003	2·001	2·004	2·001	2·002	—
220	2·012	2·012	2·013	2·013	2·013	2·012	2·014	—
230	2·014	2·016	2·017	2·014	2·014	2·015	2·014	—
225	2·018	2·018	2·019	2·018	2·020	2·019	2·019	—
329	2·022	2·020	2·023	2·022	2·020	2·018	2·022	2·023 *
307	2·023	2·021	2·023	2·023	2·022	2·021	2·021	2·020

* At 900 °C.

MacKenzie (1957) showed clearly that the properties of albite synthesized hydrothermally depend on the temperature of crystallization and on the length of time. Albite synthesized at 900 °C, even for as short a time as two hours, is not identical to that formed at 1000 °C. Thus, neither the albite studied by Stewart and von Limbach nor that studied by Orville is equivalent to the highest albite made by MacKenzie. From an examination of the trends of the lines in fig. 4, it seems improbable that the intermediate albites synthesized between 600 and 800 °C would become monoclinic even if they could be heated well above their melting-point. The albite synthesized at 900 °C might trend towards a monoclinic state at about 1150 °C (compare fig. 1), but the evidence from Stewart and von Limbach (1967) from very similar material does not suggest that it becomes monoclinic before melting. Their high-temperature study of this albite does not, however, exclude the possibility that an albite synthesized at a higher temperature might become monoclinic before melting.

The negative evidence presented by Dietz (1965) and by Kayode (in Stewart and von Limbach, 1967, p. 405) from a high-temperature study of albites prepared by long heating of very pure natural albites is of a different nature. It may perhaps be related to the kinetics of the disordering process. As was shown by Schneider (1957), the rate of disordering at high temperature of a large number of albite samples varies greatly. It is possible that the materials studied by Dietz and by Kayode had not been fully disordered by heating. Alternatively, it is possible that both the synthetic albites 307 and 901 contain sufficient Or in solid solution to lower the temperature of the

monoclinic/triclinic transformation. This argument cannot be applied to the single crystal of F 9, a very pure glass-clear albite, with only about 0.5 % Or.

As reported by Grundy, Brown, and MacKenzie (1967) a small crystal of albite F 9/32 weighing probably less than 10 μg (which had been prepared by heating low-albite sealed in a platinum tube for 32 days at 1060 °C) was found to become monoclinic above about 930 °C by the single-crystal precession method. A powder was made from some of the rest of the same heated material and examined in the diffractometer furnace (table I). It was noted that the diffraction peaks were broad at all temperatures. An examination of a coarse fraction of the powder with a polarizing microscope showed it to contain crystals with variable extinction angle suggesting that it was made up of a number of similar but not identical highly disordered states. The best estimate for its transformation temperature is just above about 950 °C. The most reasonable value for the temperature of the monoclinic/triclinic inversion for the non-equilibrium albite 901 is about 1000–50 °C. The behaviour of these highly disordered albites suggests the possibility of various slightly different states of disorder for the highest albites.

APPENDIX

Twining in albite

The purely geometrical aspects of twinning in albite can be discussed in relation to the changes in lattice parameters. The genesis of twins in feldspars depends on more than the geometry of the lattice, so the results of this study are not directly applicable to the origin or frequency of twins. The changes in obliquity $\phi = (010) \wedge [010]$ and the angle σ of the rhombic section ($\cot \sigma = \cos \alpha^*/\cot \gamma$) of the albites can be calculated from the lattice parameters. The effect on the obliquity due to changes in order/disorder or increase in temperature is small, the maximum change amounting to just over 4°. The effect of the same changes on the position of the rhombic section is more marked, here the greatest change is 14° (table V and fig. 7).

TABLE V. *Variation of the rhombic angle (σ) with temperature of the supposed equilibrium albites. Hand-smoothed angles read from curves have been used in the calculations. For F 101 $\sigma = 47.42^\circ$ at 950 °C and for 329 $\sigma = 3.82$ at 900 °C*

	25 °C	150 °C	300 °C	450 °C	600 °C	750 °C	850 °C
F 101	33.32°	34.42°	36.90°	37.17°	40.87°	42.35°	44.32°
219	22.93	23.67	24.17	26.22	28.07	31.60	33.72
220	8.75	9.67	11.82	12.09	15.80	17.50	19.19
230	6.42	7.25	9.87	10.20	12.69	14.53	16.72
225	2.99	2.80	3.97	3.15	5.63	8.37	9.32
329	-1.72	-1.52	-0.80	-0.15	1.29	2.29	1.97
307	-4.82	-4.79	-3.05	-3.09	-3.93	-2.37	-2.00

Theoretically, the pericline composition plane and the rhombic section coincide on the formation of a pericline twin. If after the formation of the twin the lattice angles of the crystal change, the current position of the rhombic section is unlikely to coincide with the composition plane of the original pericline twin (Mügge, 1930; Smith, 1958; Brown, 1962, p. 362). Subsequent cooling from the temperature of formation by any path will have very little effect

on the angle σ of the fossil pericline composition plane, as the angle β only changes by about 0.5° in 1000°C . Therefore, the orientation of the pericline composition plane is a possible clue to the temperature and structural state of the crystal at the time of formation of the twin.

Values of the angle σ of the pericline composition plane measured at room temperature can be used to deduce a temperature of formation from fig. 7 only if it can be assumed that the albite was in equilibrium at the time of twinning. Above about 475°C it would seem possible

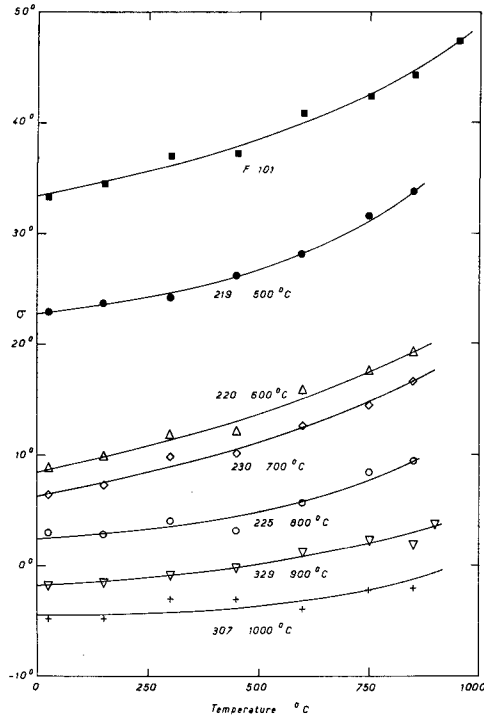


FIG. 7. Variation of the angle of the rhombic section (σ) with temperature for the supposed equilibrium albites studied. The values for the angle σ for each albite at its temperature of synthesis can be obtained from the curves.

to give a reasonably accurate estimate of the temperature (and hence the structural state) on the above assumption at the time of formation of the pericline twin. As it is probable that most pure albites in rocks formed at temperatures below about 500°C , it is clear that the position of the pericline twin plane gives little information about the temperature at the time of formation of the twin. The effect of pressure and substitution of Or and An will make it of even less use.

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