

Experimental delineation of the $C\bar{1} \rightleftharpoons I\bar{1}$ transformation in intermediate plagioclase feldspars

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Abstract

The $C\bar{1} \rightleftharpoons I\bar{1}$ Al/Si order/disorder transformation in intermediate plagioclase feldspars has been experimentally bracketed by dry and hydrothermal annealing of natural samples in the composition range An₅₀–An₈₀. It can be represented on the albite–anorthite binary phase diagram by a steep line passing through the points ~An₅₉, 1000°C and ~An₇₇, 1440°C (where it meets the one atmosphere solidus). The transformation appears to be characterized by a change from long range order (sharp *b* reflections in electron diffraction patterns) to short range order (diffuse *b* reflections) over a fairly narrow temperature interval. No sign of any two phase region separating the $C\bar{1}$ and $I\bar{1}$ fields was found on an electron optical scale and the observations are thus consistent with (but do not prove) non-first order properties for the transformation.

Assuming the transformation to be of higher than first order leads to some reappraisal of existing thermodynamic data for the high plagioclase solid solution. At the simplest level such data are consistent with approximately ideal mixing of albite and anorthite in both the $C\bar{1}$ and $I\bar{1}$ structures but with a continuous, non-ideal transition region between them. The apparent deviations from ideality can be ascribed to Al/Si ordering in anorthite rich compositions.

The order/disorder transformation line extrapolates at lower temperatures into the exact composition range of Bøggild exsolution, and must, therefore, be implicated in that miscibility gap.

Introduction

Although a number of experimental studies of Al/Si ordering in plagioclase feldspars have been reported in the literature, no really systematic attempts to define the stability fields of the different ordered phases appear to have been made. Much of the data on which present versions of the plagioclase subsolidus phase diagram are based (*e.g.*, Smith, 1972, 1974, 1975) are due to Gay (1954), Gay and Bown (1956) and McConnell (1974). Their experiments provide a sound basis for estimating the approximate positions of the phase boundaries but suffer from being unreversed and, in many cases, of too short duration for complete equilibration. New data are slowly becoming available (Slimming, 1976a; Wenk, 1978; Kroll and Müller, 1980; Tagai and Korekawa, 1981) which further constrain the stability limits and kinetics of the cation ordering but still do not unambiguously define the location of the equilibrium order–disorder boundaries. It is against this background that the present experimental investigation of the ordering behavior of plagioclases has been undertaken. In this paper we report the experimental bracketing of the $C\bar{1} \rightleftharpoons I\bar{1}$ transformation for the composition range ~An₅₀–An₈₀. Careful

reversals at two compositions and extended heat treatments at three others yield results which are consistent with the view that the transformation is non-first order in character, has a larger temperature variation with composition than proposed by Smith (1974, 1975) and occurs at more albite-rich compositions than shown by Grove *et al.* (1983).

In contrast with intermediate compositions the stability limits of the ordered end members, albite and anorthite, are quite well defined. Anorthite has an ordered ($I\bar{1}$) Al/Si distribution up to its melting point (Czank, 1973, in Grove *et al.*, 1983; Smith, 1974; McLaren and Marshall, 1974; Bruno *et al.*, 1976) while at high temperatures albite is essentially Al/Si disordered (Smith and Ribbe, 1969; Smith, 1974). The change in symmetry from $I\bar{1}$ to $C\bar{1}$ at some intermediate composition in the high temperature solid solution must surely be reflected in its thermodynamic mixing properties. Moreover, the nature of that transformation and its precise position must be determined before its influence on the complex phase relations at lower temperatures can be fully evaluated, since exsolution in the so-called peristerite, Bøggild and Huttenlocher miscibility gaps is inextricably associated with Al/Si ordering (Smith and Ribbe, 1969; Smith, 1974, 1975;

Table 1. Details of the starting materials used for the transformation experiments. Note that compositions are probe analyses corrected for a small systematic error at low Ab contents (see text for details).

Specimen number	Locality	Composition range	Most abundant composition	Structural state
1691	Skaergaard, E.Greenland	Ab ₄₉₋₄₆ Or ₁ An ₅₀₋₅₃	An ₅₁	"e"
101249	Duluth, Minnesota	Ab ₄₂₋₃₉ Or ₂ An ₅₆₋₅₉	An ₅₈	"e"
11044	Duluth, Minnesota	Ab ₃₉₋₃₅ Or ₂ An ₅₉₋₆₃	An ₆₁	"e"
CB	Crystal Bay, Minnesota	Ab ₃₁₋₂₉ Or ₀ An ₆₉₋₇₁	An ₇₀	I $\bar{1}$
54091	Bushveld, S.Africa	Ab ₂₅₋₂₂ Or ₁ An ₇₄₋₇₇	An ₇₆	I $\bar{1}$ + "e" (exsolved on a fine scale)

McConnell, 1974; Grove *et al.*, 1983). It is not the purpose here, however, to go beyond a simple analysis of the high temperature solid solution; the high/low albite transformation, the displacive $I\bar{1} \rightleftharpoons P\bar{1}$ anorthite transformation and the exsolution reactions will not be considered further.

Specimen description and experimental methods

Five natural plagioclase samples in the composition range An₅₀-An₈₀ were selected for the experiments on the basis of their homogeneity and comparative lack of alteration or inclusions. A summary of their compositions and structural states is given in Table 1. Sample no. 1691 (~An₅₂), from the middle gabbro zone of the Skaergaard igneous intrusion, has been described by Gay and Muir (1962). Numbers¹ 101249 (~An₅₈) and 11044 (~An₆₁) were gabbros from Duluth, Minnesota; plagioclase from the latter has already been used for experimental work by McConnell (1974). The fourth specimen (~An₇₀), an anorthosite from Crystal Bay, Minnesota, has been described by Gay (1953, 1954). The final specimen, 54091 (~An₇₆), an anorthosite from the Bushveld intrusion, was previously studied by Slimming (1976a). Small chips of plagioclase from the Crystal Bay anorthosite were heat treated without being crushed up, while feldspars from the other four samples were ground to a size range of ~50-200 μ m and separated into narrow density fractions using heavy liquids.

Grain mounts of all the samples were prepared for electron microprobe analysis. The microprobe used had a Harwell Si(Li) detector and pulse processor (Statham, 1976) and followed the correction procedures of Sweatman and Long (1969). Approximately ten grains per sample were analyzed giving compositions of: Ab₄₉₋₄₆Or₁An₅₀₋₅₃ (1691); Ab₄₂₋₃₉Or₂An₅₆₋₅₉ (101249); Ab₂₈₋₂₆Or₀An₇₂₋₇₄ (Crystal Bay); and Ab₂₂₋₁₉Or₁An₇₇₋₈₀ (54091). Each analysis indicated the presence of ~0.18-0.37 wt.% iron oxide (given as FeO), and the proportions of albite (Ab), orthoclase (Or) and anorthite (An) components

were calculated from the alkali ratios. Wet chemical analyses giving Ab₃₀An₇₀ for the Crystal Bay feldspar (Gay, 1953) and Ab₂₃Or₁An₇₆ for 54091 plagioclase (Slimming, 1976a) suggested that the probe data have systematically low Na contents. A series of further tests on the probe using broad electron beam techniques and longer counting times showed that this systematic error was due to incomplete stripping of the energy spectra at albite poor compositions, rather than to alkali loss. The same problem did not arise at the albite richer compositions; probe data for 1691 and 11044 feldspars correspond quite closely to independent analyses. The correct compositions are therefore considered to be an An₅₀₋₅₃, An₅₆₋₅₉, An₅₉₋₆₃, An₆₉₋₇₁, An₇₄₋₇₇.

An AEI EM6G transmission electron microscope, operating at 100 kV, was used to characterize the structural states of starting materials and experimental products. Overexposed selected area electron diffraction patterns of 10-12 crushed feldspar fragments (deposited from alcohol onto carbon film) were examined for each run. Of principal interest was the nature of diffraction maxima at $h + k = \text{odd}$, $l = \text{odd}$ positions (systematically absent in the $C\bar{1}$ structure with a $c = 14\text{\AA}$ cell, present in $I\bar{1}$, or paired in the intermediate plagioclase structure). These were noted as being either absent, weak and diffuse, weak and sharp, strong and sharp, or paired. Single reflections are usually referred to as type *b* reflections and paired reflections as type *e*. Of the starting materials, Crystal Bay plagioclase had sharp *b* reflections, 1691, 11044 and 101249 had *e*'s and 54091 had fine scale composition modulations (with a wavelength of a few hundred \AA) and both *b* and *e* reflections (plus diffuse, streaked *c*'s). Dark field images of ion thinned crystals from the initial powders showed the presence of type *b* APB's up to a few μ m apart in the Crystal Bay sample, and typical *e* APB's in 1691, 11044 and 101249. In one ion thinned crystal from 11044 inconclusive evidence of a faint composition modulation was also observed, but even if really present and pervasive, it could not have had sufficient amplitude to affect the experimental results discussed below.

Dry annealing runs were performed by wrapping a few milligrams of powder, or, in the case of the Crystal Bay sample, small ~0.5 mm chips, in Pt foil and suspending them in air in vertical Pt wound furnaces. Externally heated cold seal vessels were used for the hydrothermal runs for which a few mg of plagioclase powder were sealed in gold tubes with ~4 mg distilled water. Run times and temperatures for the dry runs were 7-34 days, 1200-1400°C and 7-104 days, 850-1000°C for the hydrothermal treatments ($P_{H_2O} = 600$ bars). Disordered starting materials used for reversing the $C\bar{1} \rightleftharpoons I\bar{1}$ transition were prepared by annealing ~50 mg batches of the separated powders or chips in air at high temperatures.

It was of some concern as to whether composition changes occurred during the heat treatments. Small portions of all the products were therefore examined optically in an immersion oil of refractive index close to that of

¹ Five and six figure numbers refer to the Harker collection, Department of Earth Sciences, University of Cambridge.

the feldspar grains. The grains usually emerged clean and unaltered but in some cases, where the gold tube had leaked during hydrothermal annealing, were clearly partly dissolved and had noticeably higher refractive indices. Such run products were discarded. In addition, polished mounts of grains from a number of heat treated samples were prepared and these then analysed with the electron probe. No significant deviations from the composition ranges of the starting materials were found.

Results

The following changes of structure were induced experimentally: e plagioclase $\rightarrow \bar{1}\bar{1}$ with sharp b reflections; $e \rightarrow C\bar{1}$, b reflections absent or diffuse; $C\bar{1} \rightarrow \bar{1}\bar{1}$ with sharp b reflections; and $\bar{1}\bar{1} \rightarrow C\bar{1}$ with diffuse or absent b reflections. Both ordering and disordering reactions were thus observed and the position of the $C\bar{1} \rightleftharpoons \bar{1}\bar{1}$ transformation defined. The complete results are given in Table 2

Table 2. Details of the transformation experiments. *The cold seal bombs could only just withstand a pressure of 600 bars at 1000°C and in some cases lost some pressure during a run.

Run no.	Starting material	Annealing temperature (°C)	Annealing time (days)	P _{H₂O} (bars)	Product
1691 (An ₅₀₋₅₃)					
1691/H2	e (natural, untreated)	845-848	104	600	v , diffuse intensity at b positions
1691/H4	e (" ")	944-960	27	"	b 's absent, or only v , diffuse intensity around b positions
1691/1/H2	$C\bar{1}$ (annealed 13 days in air, 1255°C; diffuse/absent b 's)	845-848	104	"	v , diffuse intensity at b positions
1691/1/H4	$C\bar{1}$ (" " ")	944-960	27	"	b 's absent, or only v , diffuse intensity around b positions
101249 (An ₅₆₋₅₉)					
101249/H2	e (natural, untreated)	998-1006	14	600	b 's diffuse or absent
101249/H8	e (" ")	984-1002	24	500-600*	diffuse b 's
101249/H7	e (" ")	946-951	49	600	some crystals with sharp b 's and some with diffuse b 's
101249/1/H1	$C\bar{1}$ (annealed 14 days in air, 1275°C; diffuse/absent b 's)	996-1006	9	300-600*	b 's diffuse or absent
101249/2/H9	$C\bar{1}$ (" " ")	988-1000	24	500-600*	b 's diffuse or absent
101249/1/H7	$C\bar{1}$ (" " ")	949-955	28	600	most crystals with sharp b 's and some with diffuse b 's
11044 (An ₅₉₋₆₃)					
11044/H5	e (natural, untreated)	999-1013	7	600	most crystals with diffuse b 's and some with sharp b 's
11044/6/H1	$C\bar{1}$ (annealed 10 days in air, 1275°C; diffuse/absent b 's)	995-1010	7	"	sharp b 's
11044/1/H4	$C\bar{1}$ (" " ")	975-992	24	500-600*	most crystals with sharp b 's and some with diffuse b 's
Crystal Bay (An ₆₉₋₇₁)					
CB/5	$\bar{1}\bar{1}$ (natural, untreated)	1334-1337	11	dry, 1 atm.	diffuse intensity at b positions
CB/3	$\bar{1}\bar{1}$ (" ")	1301-1302	7	" "	diffuse intensity at b positions
CB/10	$\bar{1}\bar{1}$ (" ")	1 day 1286 + 16 days 1301-1305	"	" "	diffuse intensity at b positions
CB/4	$\bar{1}\bar{1}$ (" ")	1245-1250	7	" "	most crystals with diffuse b 's and some with sharp b 's
CB/9	$\bar{1}\bar{1}$ (" ")	1249-1259	28	" "	diffuse intensity at b positions
CB/1	$\bar{1}\bar{1}$ (" ")	1194-1201	7	" "	sharp, weak b 's
CB/8	$\bar{1}\bar{1}$ (" ")	1201-1215	34	" "	sharp, weak b 's
CB/5/10	$C\bar{1}$ (annealed 11 days in air, 1333°C; diffuse/absent b 's)	1 day 1286 + 16 days 1301-1305	"	" "	diffuse intensity at b positions
CB/5/2	$C\bar{1}$ (" " ")	1241-1250	7	" "	diffuse intensity at b positions
CB/5/9	$C\bar{1}$ (" " ")	1249-1259	28	" "	slightly diffuse b 's
CB/5/1	$C\bar{1}$ (" " ")	1206-1209	7	" "	slightly diffuse b 's
CB/5/3	$C\bar{1}$ (" " ")	1205-1208	14	" "	slightly diffuse b 's
CB/5/8	$C\bar{1}$ (" " ")	1201-1215	34	" "	sharp, weak b 's
54091 (An ₇₄₋₇₇)					
54091/1	$\bar{1}\bar{1}$ + e (natural, untreated; with fine scale exsolution)	1360-1390	10	" "	homogeneous crystals, some with diffuse b 's and some with sharp b 's
54091/1/2	$C\bar{1}$ (annealed 10 days in air, 1360-1390°C; homogeneous, sharp and diffuse b 's)	1386-1391	7	" "	homogeneous crystals with sharp, weak b 's

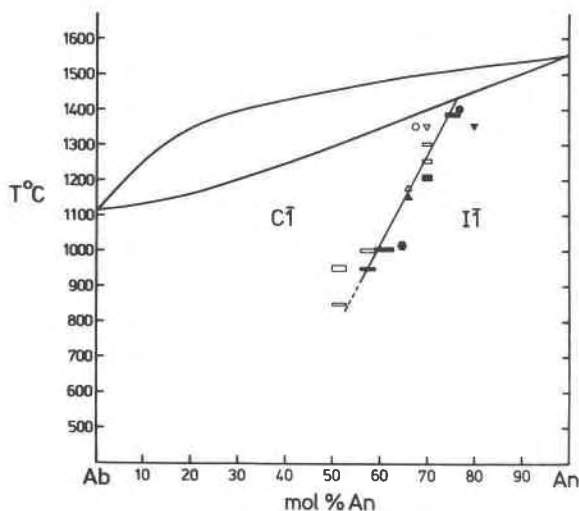


Fig. 1. Phase diagram for albite-anorthite showing only smoothed liquidus/solidus relations (from Murphy, 1977, in Henry *et al.*, 1982) and experimental bracketing of the $C\bar{1} \rightleftharpoons I\bar{1}$ transformation. Filled symbols indicate sharp b reflections ($=I\bar{1}$ symmetry) and open symbols indicate diffuse or absent b reflections ($=C\bar{1}$ symmetry). Rectangles = this study; circles = Kroll and Müller (1980); triangles = Tagai and Korekawa (1981); inverted triangles = Gay (1954); hexagon = McConnell (1974). Note that the disordering runs of Tagai and Korekawa (1981) were of relatively short duration (160 hours) for 1100–1200°C and may not have equilibrated fully.

and are summarized in Figure 1. A complete kinetic analysis of the Al/Si ordering and disordering was not attempted and only the critical experiments are described in this section. Evidence of exsolution was not observed in bright field TEM images of any of the run products. Attempts were made to obtain dark field images of antiphase textures but the b and e reflections were usually too weak. In one case (11044/6/H1), however, small, normal looking b domains were successfully imaged.

1691, An_{50-53}

Hydrothermal treatment of 1691 plagioclase crystals in both e and $C\bar{1}$ starting states for 104 days at $\sim 850^\circ\text{C}$ and for 27 days at $\sim 950^\circ\text{C}$ yielded diffuse intensity around b positions in electron diffraction patterns. Even diffuse intensity could not be detected at the b positions for some crystals annealed at 950°C . The $C\bar{1}$ material was prepared by annealing the natural sample at $\sim 1255^\circ\text{C}$ for 14 days. Both annealing temperatures are considered to have been in the $C\bar{1}$ stability field.

101249, An_{56-59}

Annealing this sample hydrothermally at $\sim 1000^\circ\text{C}$ for 24 days changed sharp e reflections into diffuse or absent b 's. Taking grains previously disordered at 1250°C for 14 days as starting material, a 24 day hydrothermal anneal at $\sim 1000^\circ\text{C}$ also produced diffuse or absent b 's. Hydrother-

mally treating disordered ($C\bar{1}$) starting material for 28 days and ordered (e) starting material for 49 days at $\sim 950^\circ\text{C}$ produced mainly sharp b 's though in some crystals the b reflections were diffuse. The $C\bar{1} \rightleftharpoons I\bar{1}$ transformation has been placed between 950 and 1000°C for this composition.

11044, An_{59-63}

The critical runs at An_{59-63} also involved ordered (e) and disordered ($C\bar{1}$, heated 10 days, $\sim 1275^\circ\text{C}$ in air) starting materials. These were annealed hydrothermally at $\sim 1000^\circ\text{C}$ for 7 days yielding sharp b 's, though some crystals from the run with initially ordered material had diffuse b 's. The $I\bar{1}$ stability field extends to above $\sim 1000^\circ\text{C}$.

Crystal Bay, An_{69-71}

All runs on the Crystal Bay plagioclase were performed dry, in air. A 17 day heat treatment at $\sim 1300^\circ\text{C}$ of both ordered ($I\bar{1}$) and disordered ($C\bar{1}$, 11 days, $\sim 1300^\circ\text{C}$) material produced crystals with diffuse or absent b 's. Sharp, though weak, b reflections were produced in $C\bar{1}$ and $I\bar{1}$ crystals annealed for 34 days at $\sim 1200^\circ\text{C}$. At $\sim 1250^\circ\text{C}$, 28 day runs yielded only slightly diffuse b reflections. The $C\bar{1} \rightleftharpoons I\bar{1}$ transformation has been placed between 1200 and 1300°C at this composition, and is probably very close to 1250°C .

54091, An_{74-77}

A batch of powder was annealed in air for 10 days at 1360 – 1390°C to homogenize the fine scale composition modulations. The product had some crystals with sharp b reflections and some with diffuse b reflections. Annealing this for a further 7 days at $\sim 1390^\circ\text{C}$ gave sharp, weak b reflections, constraining the position of the $C\bar{1} \rightleftharpoons I\bar{1}$ transformation to a higher temperature.

Uncertainties in the experiments arose principally from temperature drift of the furnaces, particularly during the longer runs, a possible error of $\pm 2^\circ\text{C}$ in temperature determinations, and from the range of compositions within each feldspar powder. During hydrothermal runs at $\sim 1000^\circ\text{C}$, the cold seal vessels tended to expand giving some pressure variations down to 500 bars. Because the volume changes associated with the cation ordering are small, however, the differences in pressure between the dry and hydrothermal runs are not likely to displace the $C\bar{1}/I\bar{1}$ boundary to a detectable degree. In addition it has been assumed that the presence of water merely influences the kinetics of the reactions without changing the relative stabilities of the structures. Further factors such as the small but variable orthoclase and iron oxide contents of the plagioclases are not likely to represent significant sources of error in placing the $C\bar{1} \rightleftharpoons I\bar{1}$ boundary, given the other uncertainties in the experimental data.

Discussion

The experiments described above have been used to define a line marking the change from sharp b reflections to diffuse b reflections in intermediate plagioclase compositions, as a function of temperature and composition. It has been assumed that this line may be equated with the $\overline{C1} \rightleftharpoons \overline{I1}$, Al/Si order/disorder transformation. Such an assumption is reasonable so long as the established boundary describes equilibrium behavior. Diffuse superlattice reflections can arise under two quite different circumstances; either they may represent equilibrium short range ordering in anticipation of a transformation, at some lower temperature, to a structure with long range ordering (*e.g.*, see Chen and Cohen, 1979), or they may be due to a non-equilibrium, intermediate state formed during the isothermal transition from a disordered to a long range ordered structure. If sharp superlattice reflections are produced from a disordered starting material, however, there are no such ambiguities and the experimental annealing conditions must have been within the equilibrium stability field of the long range ordered structure.

An important consideration in studying ordering in feldspars is the sluggishness of Al/Si diffusion. This means, at least, that the whole range of possible ordered states is quenchable, but also that even for very long heat treatments there may remain doubts over whether equilibrium really has been achieved. It is essential, therefore, either to perform a complete time-temperature-transformation analysis at each composition, so that the kinetic constraints are fully defined, or to reverse the transformations. In the present study we have followed both ordering and disordering reactions, producing sharp b reflections indicative of long range ordering at four of the five compositions (Table 2). Thus, even though a thorough kinetic analysis was not attempted, it is clear that substantial intracrystalline equilibration can be achieved in a matter of days by dry annealing at temperatures greater than $\sim 1200^\circ\text{C}$ and in a matter of weeks by hydrothermal treatment at $950\text{--}1000^\circ\text{C}$. The establishment of equilibrium at $\sim 850^\circ\text{C}$ (run nos. 1691/H2, 1691/1/H2), however, has not been unambiguously demonstrated. A further problem exists close to the equilibrium phase boundary due to the fact that the free energy driving force for the reaction may become very small, causing a slowing down of the reaction rates. It is to be expected that the heat treatments close to the boundary may not yield an equilibrium product as readily as those on either side of it.

At An_{69-71} (Crystal Bay) the transformation was bracketed between 1200 and 1300°C by following both $\overline{C1} \rightarrow \overline{I1}$ and $\overline{I1} \rightarrow \overline{C1}$. Gay and Bown (1956) reported that b reflections were absent after heating the same sample at $\sim 1200^\circ\text{C}$ for three days but, in the present study, 7-34 day annealing gave sharp but weak b 's at the same temperature. Electron diffraction is generally a more sensitive technique for detecting weak reflections than X-

ray diffraction and it is possible that Gay and Bown were unable to detect these reflections in their single crystal X-ray photographs. At $\sim 1250^\circ\text{C}$, long anneals (28 days) gave diffraction intensity at the b positions which was only slightly diffuse and these runs are presumed to have been very close to the $\overline{C1} \rightleftharpoons \overline{I1}$ boundary. At An_{56-59} (101249) and An_{59-63} (11044) sharp b reflections were produced from crystals which had been initially ordered (e) or disordered ($\overline{C1}$) giving unequivocal temperatures for $\overline{I1}$ ordering of greater than or approximately equal to 950°C and 1000°C respectively for the two compositions. Also present in these runs, however, were some crystals with diffuse b reflections, indicating that the composition ranges either straddle or come very close to the $\overline{C1}/\overline{I1}$ boundary at such temperatures. The time scale of 950°C treatments at An_{50-53} (1691) was similar to that for An_{56-59} runs which yielded crystals with long range ordering. It is concluded that the diffuse b reflections which resulted represent an equilibrium (or near equilibrium) state of short range ordering, and are not due to kinetic problems of ordering.

As shown in Figure 1 the suggested position for the $\overline{C1} \rightleftharpoons \overline{I1}$ boundary is consistent with experimental data from other sources. Kroll and Müller (1980) annealed a range of synthetic plagioclases at high temperatures and found a change from sharp to diffuse b reflections (also using electron diffraction) between $\text{An}_{67.5}$, 1350°C and An_{77} , 1400°C . Gay (1954) effectively bracketed the transformation between An_{70} and An_{80} at 1350°C . Tagai and Korokawa (1981) produced disordered crystals of composition An_{66} at 1180°C from an $\overline{I1}$ starting state but at 1150°C sharp b reflections remained. Their experiments were of relatively short duration (160 hours), however, and they reported the presence of diffuse e reflections in diffraction patterns both before and after the heat treatments. McConnell (1974) transformed e reflections into b 's at 1010°C , An_{65} .

With increasing temperature, at a fixed composition, there appears to be a gradation in the nature of the b reflections in samples annealed on either side of the $\overline{C1} \rightleftharpoons \overline{I1}$ boundary. At relatively low temperatures the b reflections are sharp, but weaken as the annealing temperature is raised and then become diffuse. The diffuseness increases until at high temperatures the reflections cannot easily be detected. This is consistent with a thermodynamically non-first order transformation in which long range ordering (sharp reflections) gives way to short range ordering (diffuse reflections) over a narrow temperature interval but in a continuous way. Kroll and Müller (1980) noted that the transformation as a function of composition also appears to have no obvious discontinuity. Evidence for a high order transformation is necessarily negative, *i.e.*, first order properties are not detected (see Carpenter and Smith, 1981, for a discussion of this problem). $\overline{I1}$ is a normal subgroup of $\overline{C1}$ and fulfills the Landau-Lifschitz (1958) criteria for a second order transformation, and the apparent absence of exsolution in any

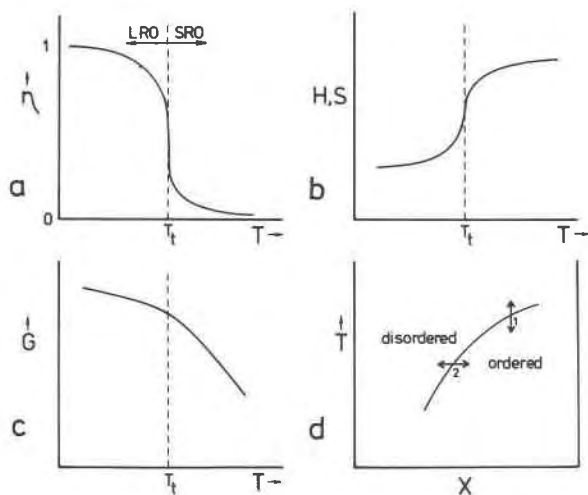


Fig. 2. (a–c) The forms of ordering parameter (η), enthalpy (H), entropy (S) and free energy (G) as functions of temperature (T) through a non-first order phase transformation (at temperature T_t) with short range ordering (SRO) and long range ordering (LRO). (d) Composition (X)–temperature (T) relations for a solid solution with a non-first order transformation. The forms of η , G , H , S should be similar when crossing the boundary by varying temperature (1) or by varying composition (2).

of the annealed samples is also consistent with, but not proof of, other than first order transformation behavior. It can safely be stated, therefore, that the $C\bar{1} \rightleftharpoons \bar{1}\bar{1}$ transformation shows no signs of being first order but has the appearance, at least, of being non-first order and truly continuous in the thermodynamic sense.

Plagioclase mixing properties

As stated earlier, the $C\bar{1} \rightleftharpoons \bar{1}\bar{1}$ transformation occurring at some composition (depending on the temperature) between albite and anorthite must surely affect the thermodynamic mixing properties of the high temperature solid solution. With the added insight into the ordering behavior provided by the experiments it is instructive to reconsider data relating to plagioclase mixing from this point of view. It is necessary first, however, to discuss what form the principal parameters might have. The evidence outlined above favors a non-first order transformation with short range ordering above the transition temperature. Free energy (G), enthalpy (H), entropy (S) and an order parameter (η), as functions of temperature, should therefore have the forms given in Figure 2, which Thompson and Perkins (1981) define as being due to a “mixed or λ ” transition. Crossing the transformation line by varying composition rather than temperature should give an analogous series of relations (Fig. 3). Because the end members of the solid solutions have different symmetries the conventional free energy (ΔG_m), enthalpy (ΔH_m) and entropy (ΔS_m) of mixing, which formally should go to zero at pure albite and pure anorthite, could be mislead-

ing. A clearer picture of the order/disorder contribution to the mixing at high temperatures is most easily illustrated by referring to $C\bar{1}$ (*i.e.*, disordered) end members as the standard states. The new mixing parameters ($\Delta G_{m'}$, $\Delta H_{m'}$, $\Delta S_{m'}$), as shown in Figure 3, do not then go to zero at An_{100} . In the simplest possible case the $C\bar{1}$ solid solution could be represented by ideal mixing of albite and anorthite, with G , H and S displacements due solely to a non-first order Al/Si ordering transformation (Fig. 3). $C\bar{1}$ albite is defined as having $\eta = 0$ and $\bar{1}\bar{1}$ anorthite as having $\eta = 1$. The $C\bar{1} \rightleftharpoons \bar{1}\bar{1}$ transformation in pure

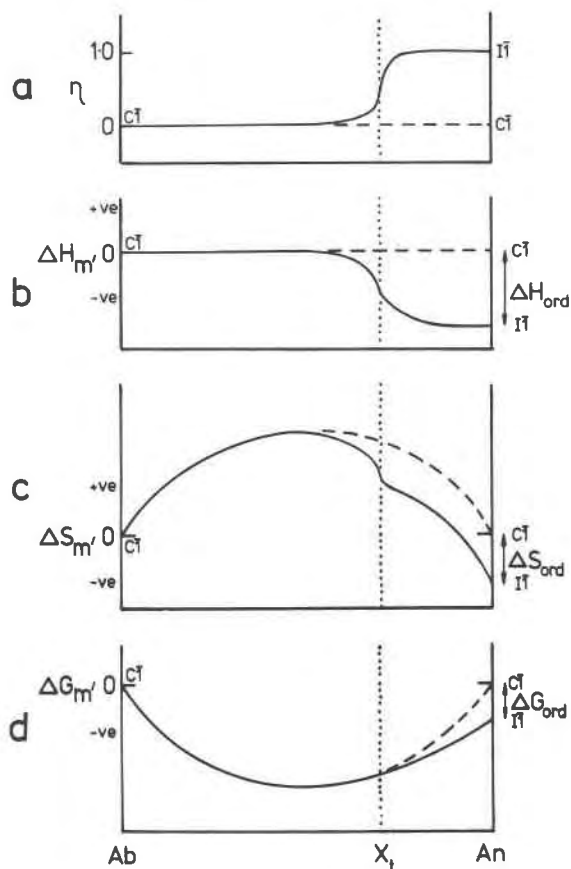


Fig. 3. Schematic thermodynamic functions for albite-anorthite mixing assuming ideal mixing in the $C\bar{1}$ and $\bar{1}\bar{1}$ structures and a non-first order transformation (as characterized in Fig. 2) between them. (a) An arbitrary order parameter, η , which varies from 0 in the disordered $C\bar{1}$ structure to 1 in the ordered $\bar{1}\bar{1}$ structure. (b) Enthalpy of mixing; the dashed line represents an extension of the $C\bar{1}$ solid solution to a “fictive” pure anorthite end member. (c–d) Entropy and free energy of mixing; the dashed line represents the extension to “fictive” $C\bar{1}$ anorthite. At the transformation composition, X_t , there is only a change in slope of the free energy curve. ΔH_{ord} , ΔS_{ord} and ΔG_{ord} are respectively the enthalpy, entropy and free energy associated with Al/Si ordering ($C\bar{1} \rightarrow \bar{1}\bar{1}$) in pure anorthite. Note that the mixing parameters designated by m' refer to standard end member states which have $C\bar{1}$ symmetry, and thus do not go to zero at $\bar{1}\bar{1}$ An_{100} .

anorthite has a free energy, enthalpy and entropy of ordering indicated by ΔG_{ord} , ΔH_{ord} and ΔS_{ord} in Figure 3.

As an aside before considering the activity data of Orville (1972) and the enthalpies of solution measured by Newton *et al.* (1980), it is worth highlighting a difference in their sample characterization methods compared with those of the present study. X-ray powder diffraction, and in particular the $\Delta 2\theta(131-1\bar{3}1)$ parameter, is useful for distinguishing between "high" and "low" plagioclases (Ribbe, 1975; Kroll and Ribbe, 1980) but, unfortunately, is rather insensitive to changes of ordering in An rich compositions, and does not lead to a distinction between $I\bar{1}$ and $C\bar{1}$ structures. To be sure of the state of order of synthetic crystals with compositions of An_{50} - An_{100} it is necessary to use single crystal X-ray or electron diffraction. Both Orville (1972) and Newton *et al.* (1980) used only powder diffraction to characterize their experimental products and there remains some uncertainty as to the state of Al/Si order in them. This represents an important limitation on the degree of confidence with which their data may be discussed in the present context.

Enthalpy of mixing

Enthalpies of mixing for a high plagioclase series were measured by Newton *et al.* (1980) using oxide melt solution calorimetry. Their crystalline samples were prepared by annealing glasses at 1200°C, 20 kbar, for 3 hours. In spite of their careful characterization by X-ray powder diffraction it is not clear whether their An rich samples achieved short range or long range ordering on an $I\bar{1}$ basis or retained a metastable $C\bar{1}$ structure. The enthalpy of solution (ΔH_{soln}) values they quote for An_{100} are the same, within experimental error limits, for natural crystals and for samples annealed at 1200°C, 20 kbars, or 1300-1400°C, 1 bar, for 3 hours. Since Kroll and Müller (1980) showed that synthetic anorthite orders in less than 3 hours at 1400°C, 1 bar, and no natural disordered anorthites have yet been reported, it may be concluded that the ΔH_{soln} is for $I\bar{1}$ anorthite. Similar predictions of the state of order for intermediate compositions are rather less certain because the rate of ordering varies with composition, typically requiring ~5 days to reach a steady value of $\Delta 2\theta(131-1\bar{3}1)$ at $T = 1060$ - 1380°C , 1 bar (Kroll and Müller, 1980). For the sake of continuing this discussion it will be assumed that some consistent degree of order occurred under the synthesis conditions in compositions where it was energetically favored. Newton *et al.* (1980) interpreted their data (reproduced in Fig. 4) in terms of a small, positive excess ΔH_m and used a two parameter Margules expression to describe the effect. It is not strictly valid, however, to treat a solid solution in this way if the end members have different symmetries and there is a distinct phase transformation at some intermediate composition.

According to the present analysis, the $C\bar{1} \rightleftharpoons I\bar{1}$ transformation at 1200°C (1 bar) would occur at ~ An_{67} . Pressure is unlikely to change this significantly because

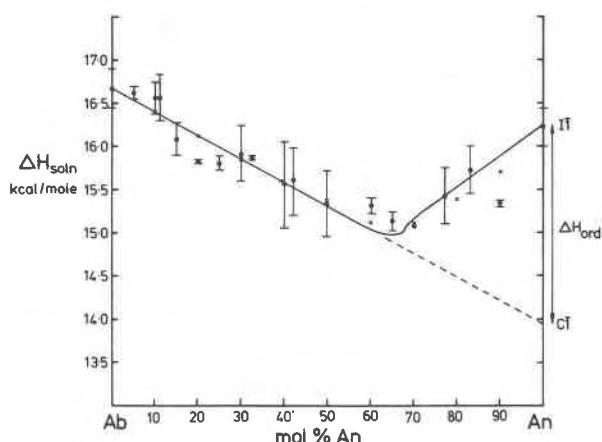


Fig. 4. Enthalpy of solution data for synthetic plagioclases crystallized at 1200°C, 20 kbar, for 3 hours (from Newton *et al.*, 1980). The crosses represent the two parameter Margules expression used by Newton *et al.* to describe a small positive excess enthalpy of mixing. The solid line represents an alternative interpretation in which approximately ideal (enthalpy of mixing = 0) mixing occurs in the $C\bar{1}$ structure over the composition range An_0 - An_{55} with a non-first order Al/Si ordering transformation at ~ An_{70} . The broken line represents the extension of the ideal $C\bar{1}$ solid solution to "fictive" $C\bar{1}$ anorthite. ΔH_{ord} is then the enthalpy of ordering for pure anorthite ($C\bar{1} \rightarrow I\bar{1}$), and is $\sim 2.3 \pm 0.6$ kcal/mole.

the volume change associated with ordering is small. An alternative explanation of the observed enthalpy effects ascribes the non-ideality to ordering at An rich compositions leaving the $C\bar{1}$ structure with a linear ΔH_{soln} /composition relationship, that is, with ideal mixing (Fig. 4). The form of ΔH_m should then, in the simplest case, be that shown in Figure 3b. Extrapolation of the ΔH_{soln} line for the $C\bar{1}$ structure to An_{100} gives an estimate for the $C\bar{1} \rightarrow I\bar{1}$ ordering enthalpy in pure anorthite (ΔH_{ord}) of 2.3 ± 0.6 kcal/mole (Fig. 4).

Activities

Orville (1972) determined activities of the end member components, Ab and An, in the plagioclase solid solution (Fig. 5) by considering ion-exchange equilibria between synthetic crystals and a fluid. His data do not necessarily reflect equilibrium Al/Si order because the feldspars were synthesized hydrothermally from glasses at only 800°C, 1 kbar, and then annealed in the ion exchange experiments at 700°C, 2 kbar, for up to 12 days. Significant Al/Si ordering clearly did occur, however, as evidenced by variations of $\Delta 2\theta(131-1\bar{3}1)$ with annealing time. For the composition range An_0 - An_{55} ideal mixing was inferred and presumed to be of the $C\bar{1}$ high albite structure. For An_{85-90} - An_{100} the activities were also consistent with ideal mixing, but in the $I\bar{1}$ structure. The continuous, non-ideal range between these two states was then taken to represent the transition from $C\bar{1}$ to $I\bar{1}$ symmetry. Orville also pointed out that the solid solution for An_0 - An_{55} may be

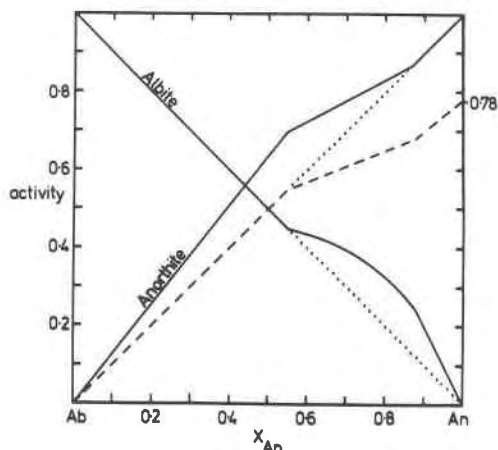


Fig. 5. Smoothed activity-composition relations from Orville (1972), obtained using ion exchange between crystals and a fluid at 700°C (solid lines). The straight segments correspond to ideal mixing in the $C\bar{I}$ and $\bar{I}\bar{I}$ structures with a non-ideal transitional region between them (Orville, 1972). The dashed activity line for anorthite has been recalculated for a "fictive" $C\bar{I}$ anorthite end member assuming ideal mixing ($a_{An} = X_{An}$) for the composition range An_0 - An_{55} ; on this scheme pure ordered $\bar{I}\bar{I}$ anorthite has an activity of 0.78.

represented by an ideal $C\bar{I}$ structure having a "fictive" high albite structure, An_{100} end member. Recalculating the activities in terms of an ideal $C\bar{I}$ solid solution, with disordered albite and anorthite as standard end member states, reduces the activity of $\bar{I}\bar{I}$ ordered anorthite to 0.78 (Fig. 5). This corresponds to a ΔG_{ord} of ~ 480 cal/mole (at 700°C).

Saxena and Ribbe (1972) calculated very similar activities from Orville's data but chose to apply a continuous mathematical function to describe them. They justified their choice on the basis that there is "no reason to suppose that the structural changes are anything but continuous." A non-first order transformation allows for such changes to be continuous and Orville's interpretation is consistent with the simple analysis, illustrated in Figure 3, in which deviations from ideality are concentrated into the composition range of an order-disorder transformation. Similarly, in their reinterpretation of Orville's data Blencoe *et al.* (1982) also did not take into account the presence of a distinct order/disorder transformation.

Free energy and entropy of mixing

Orville's activity data, with $C\bar{I}$ end member standard states, may be used to calculate $\Delta G_m'$ (Fig. 6). In form, $\Delta G_m'$ is wholly consistent with the free energy of mixing shown in Figure 3d, *i.e.*, ideal mixing in the composition range An_0 - An_{55} with a continuous (non-first order) transformation to $\bar{I}\bar{I}$ at calcic compositions. Assuming $\Delta H_m' = 0$ for the $C\bar{I}$ solid solution leads to a form of $\Delta S_m'$ which

corresponds to Figure 3c, with ideal mixing of $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ molecules from albite to An_{55} .

Given $\Delta G_{ord} \approx 480$ cal/mole at 700°C, and $\Delta H_{ord} \approx 2.3 \pm 0.6$ kcal/mole the entropy of ordering for pure anorthite (ΔS_{ord}) is ~ 1.3 - 2.5 cal/deg/mole (see Fig. 3c). This may be compared with an extreme value for complete disorder to complete order of $4R(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}) = 5.5$ cal/deg/mole.

Implications and conclusions

It has not been the purpose here to present a new model for plagioclase mixing. Rather, the intention has been simply to demonstrate that deviations from ideality in the high temperature solid solution may be ascribed to cation ordering. Possible values for the free energy, enthalpy and entropy of ordering for pure anorthite have been extracted and, in principle, data can be obtained in a similar manner for $C\bar{I} \rightleftharpoons \bar{I}\bar{I}$ ordering in more albitic compositions. Too much credence should not necessarily be attached to these numbers, however, because of the uncertainties relating to the state of order of the experimental material from which the data were derived. As pointed out by Newton *et al.* (1980), for thermodynamic calculations it is not actually too critical what kind of

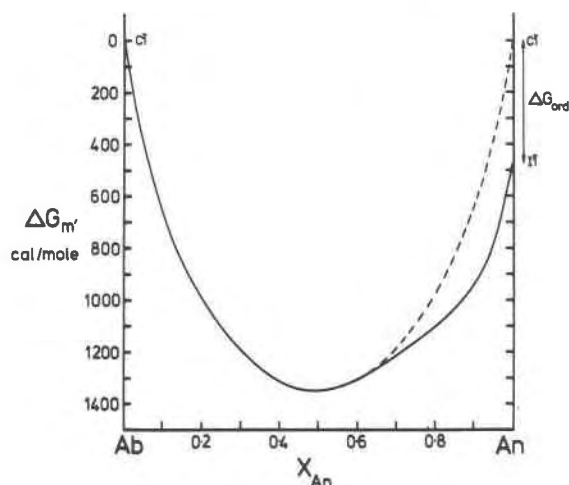


Fig. 6. Free energy of mixing for albite-anorthite at 700°C, calculated from the smoothed activity data of Orville (1972) and using a "fictive" $C\bar{I}$ end member for anorthite. Ideal mixing occurs for much of the composition range, and deviations in anorthite rich compositions are ascribed to Al/Si ordering ($C\bar{I} \rightleftharpoons \bar{I}\bar{I}$). The dashed line represents a continuation of the ideal mixing curve. The free energy of ordering for pure anorthite (ΔG_{ord}), is ~ 480 cal/mole at 700°C. In principal, free energies of ordering could be estimated for each composition in the range An_{60} - An_{100} , but no great credence should be attached to the numbers in view of uncertainties concerning the structural state of the experimental samples. The change in slope of the free energy curve at $\sim An_{60}$ is, within experimental error, similar in appearance to that expected for a non-first order transformation (Fig. 3d).

model is used for a solid solution so long as it predicts correct enthalpies and entropies under changing P, T conditions. Unfortunately, although straight-forward non-ideal enthalpies of mixing are expected to be fairly constant with temperature, the effects of cation ordering are generally strongly temperature dependent. Thus the heat of mixing data of Newton *et al.* may apply strictly only to 1200°C (assuming no large ΔC_P effects between 1200°C and the calorimeter temperature, $\sim 700^\circ\text{C}$).

The existence of a non-first order transformation at an intermediate composition between albite and anorthite also illustrates a limitation of the Al avoidance model for the entropy of mixing terms. The expression given by Kerrick and Darken (1975) for Al avoidance effectively averages out the contributions of a true order-disorder transformation by producing a completely smooth transition between high albite and fully ordered anorthite. Probably for this reason, it fails to predict the correct composition ranges for miscibility gaps at low temperatures (Henry *et al.*, 1982).

The position of the $C\bar{1} \rightleftharpoons \bar{I}1$ transformation line is interesting from two further points of view. First, it intersects the solidus determined by Murphy (1977, given by Henry *et al.*, 1982) for the binary system Ab–An at $\sim \text{An}_{77}$, 1440°C. At this point the experimental solidus appears to vary quite smoothly. A marked effect would not be expected for the case of a non-first order transition, however, because the free energy of mixing for the crystalline phase would be a continuous function. Only a change in slope of the solidus might be anticipated. Second, extrapolating the $C\bar{1} \rightleftharpoons \bar{I}1$ transformation line to lower temperatures takes it exactly into the region of the Bøggild miscibility gap. It would pass through An_{50} at $\sim 750^\circ\text{C}$ and, given the steep slope, would probably not reach compositions which are much richer in albite. This coincidence with the Bøggild gap and also, incidentally, with the break in structural parameters observed in natural low plagioclases (Smith and Gay, 1958; Doman *et al.*, 1965; Bambauer *et al.*, 1967a,b; Slimming, 1976b), must imply some involvement of the transformation in the observed exsolution behavior. It is interesting to note that in sodic pyroxenes (Carpenter, 1980) and in the peristerite range of plagioclases (Carpenter, 1981) it may be possible to relate exsolution to non-first order cation ordering reactions. Speculation along these lines raises a number of further issues, however, as outlined, for example, by Grove *et al.* (1983), and is unlikely to be convincing until a clearer understanding of the relationship between the e and $\bar{I}1$ ordering schemes has been established. It is notable that the Huttenlocher miscibility gap is located entirely below the $C\bar{1} \rightleftharpoons \bar{I}1$ transformation.

In conclusion, it seems likely that the key to the plagioclase solid solution lies in the order–disorder phenomena. Further experiments and thermochemical data, which define the stability limits of the different ordered phases (and of $C2/m$, monoclinic albite) as functions of temperature, pressure and composition, are required.

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