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AN EXPERIMENTAL INVESTIGATION OF THE ALBITIZATION OF PLAGIOCLASE

JUDITH B. MOODY
Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201, U.S.A.

JOE E. JENKINS
Grynberg Petroleum, 5000 South Quebec Street, Denver, Colorado 80237, U.S.A.

DANN MEYER
IT Corporation, 2340 Alamo Street SE, Suite 306, Albuquerque, New Mexico 87106, U.S.A.

ABSTRACT

The process of albitization of plagioclase and associated mineralogical changes at greenschist and lower-amphibolite facies conditions were investigated experimentally at 300–600°C, 200 and 400 MPa, using powdered natural starting-materials of 1:4 and 4:1 mixtures (by weight) of labradorite and a 1:1 mixture of albite and clinozoisite, in the presence of a 0.05 M Na_2SiO_3 solution, in which solid:fluid = 1:3. The observed assemblage below 500°C includes albite + clinozoisite ± oligoclase; above 500°C, it is albite ± clinozoisite + oligoclase (or andesine) + grossular. Coexisting albite An_{0-2} and oligoclase An_{18-22} appear to outline the strain-free peristerite miscibility gap between 400 and 525°C. At higher temperatures, andesine replaces albite + oligoclase. Below 500°C, clinozoisite consumes the Ca^{2+} and Al^{3+} released in the breakdown of labradorite. Grossular production begins at 525°C and completely replaces clinozoisite as the major CaAl phase by 550°C. This study indicates that the coexistence of two sodic plagioclases is characteristic of conditions of metamorphism below the threshhold of the amphibolite facies as defined by Moody *et al.* (1983).

Keywords: albite, clinozoisite, plagioclase, greenschist facies, metamorphism, peristerite miscibility gap.

SOMMAIRE

Le processus d'albitization du plagioclase et les changements minéralogiques associés dans les conditions des facies schistes verts et amphibolite inférieur ont fait l'objet d'une étude expérimentale menée entre 300 et 600°C, de 200 à 400 MPa. Les expériences ont porté sur des mélanges 1:4 et 4:1 (en poids) de labradorite avec un mélange (à poids égaux) d'albite et de clinozoïsite, en présence d'une solution 0.05 M Na_2SiO_3. Il y avait trois fois plus de fluide que de solide pendant l'expérience. En-dessous de 500°C, on observe l'assemblage albite + clinozoïsite ± oligoclase; au-dessus, on trouve albite ± clinozoïsite + oligoclase (ou andésine) + grossulaire. Entre 400 et 525°C, l'albite (An_{0-2}) et l'oligoclase (An_{18-22}) coexistantes semblent délimiter la lacune de miscibilité sans contrainte de la péristérite. À température plus élevée, l'andésine prend la place de l'assemblage albite + oligoclase. En-dessous de 500°C, la clinozoïsite accommode le Ca^{2+} et Al^{3+} libérés par la destruction de la labradorite. Le grossulaire apparaît dès 525°C et, à 550°C, a complètement déplacé la clinozoïsite comme phase riche en CaAl. D'après ces résultats, la coexistence de deux plagioclases sodiques serait typique d'un degré de métamorphisme inférieur au seuil du facies amphibolite tel que le définissent Moody *et al.* (1983).

(Traduit par la Rédaction)

Mots-clés: albite, clinozoïsite, plagioclase, facies schistes verts, métamorphisme, lacune de miscibilité de la péristérite.

INTRODUCTION

An important consequence of the low-grade metamorphism of basalts is the albitization of plagioclase. Few experimental studies have dealt with the process of albitization because of the sluggish nature of reactions involving plagioclase under P and T conditions of low-grade metamorphism. Some experimental studies dealing with low-grade hydrothermal alteration of basalts yield plagioclase of a lower An content than the starting material (Liou *et al.* 1974, Hajash 1975, Moody & Meyer 1978, 1979, Moody *et al.* 1983). Unfortunately, there has been little characterization of the plagioclase produced, which leaves many questions unanswered with regard to the process of albitization.

Our experiments relate to the albitization reaction in the system Na_2O–CaO–Al_2O_3–SiO_2–H_2O; other minor components (FeO, Fe_2O_3, MgO, TiO_2) are present but generally do not have a major effect on the observed petrographic relationships. The conversion of plagioclase to albite necessarily requires the release of Ca^{2+} and Al^{3+}. Minerals of the epidote group (epidote, clinozoisite) are common in low-grade metamorphic rocks (Laird 1980, Turner 1981, Bird & Helgeson 1981) and are considered to be the major sink for Ca and Al. Under greenschist-facies conditions in this system, the expected product of the breakdown of plagioclase is albite + clinozoisite.

An additional area of mineralogical interest concerns the subsolidus relationships in the system Ab–An. Many versions of the phase diagram have been derived from theoretical considerations and observations of natural assemblages (Megaw 1962, Smith 1972, 1974, Nord *et al.* 1978, Carpenter 1981, Goldsmith 1982a, Ribbe 1983). The actual nature of these phase relationships has eluded researchers because of the persistence of metastable phases and complex patterns of ordering in plagioclase. Detailed characterization of the experimentally produced plagioclase may provide some information on the phase relationships in the system Ab–An relevant to low-grade metamorphic regimes.

EXPERIMENTAL METHODS

More than one reaction can be written to express the breakdown of plagioclase to albite:

$$\underset{\text{andesine}}{NaAlSi_3O_8{\bullet}CaAl_2Si_2O_8} + Na^+ + H_4SiO_4 =$$

$$\underset{\text{albite}}{2NaAlSi_3O_8} + Al^{3+} + Ca^{2+} + 4OH^- \quad \text{(Boles 1982)}$$

and

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + 2Na^+ + 4SiO_2(aq) =$$

$$\underset{\text{albite}}{2NaAlSi_3O_8} + Ca^{2+} \quad \text{(Bird \& Helgeson 1981)}$$

Both reactions require the addition of sodium and silica in a replacement process involving an equal volume of albite produced from the original plagioclase (Boles 1982). The Ca–Al-bearing mineral produced changes in response to pressure and temperature conditions: laumontite in zeolite-facies metamorphism (Boles & Coombs 1977), clinozoisite or epidote in the greenschist facies (Laird 1980, Bird & Helgeson 1981) and grossular in the amphibolite facies (Holdaway 1972, Liou 1973). The generalized reaction modeled experimentally here is:

$$\text{labradorite} + Na^+ + SiO_2(aq) + H_2O = \text{albite} + \text{clinozoisite} + H^+$$

Clinozoisite was chosen because it is the iron-poor analog of epidote. Definition of the P–T and other petrographic constraints between clinozoisite or zoisite and epidote are not yet complete (Kutty & Iyer 1977, Jenkins *et al.* 1983, Graham 1983).

The decision to use a Na–Si-bearing fluid in our experiments is based on the stoichiometry of the reaction as well as petrographic observations of the natural assemblages. Such a fluid was also required in order to overcome significant kinetic barriers in the reaction (Goldsmith 1982b) by providing the necessary components for the reaction, especially at the lower temperatures typical of greenschist and amphibolite metamorphism. The choice of the fluid, its concentration and use of natural minerals as start-

TABLE 1. COMPOSITION OF STARTING MATERIALS AND MIXTURES

	Labradorite PS-S1		Amelia Albite MNMH-C-5390		Clinozoisite 112513	4:1 Bulk Composition		1:4 Bulk Composition	
	Chem*	Probe**	Chem*	Probe**	Probe**	Dry	Fluid***	Dry	Fluid***
SiO_2	52.80	52.65 (0.27)	67.42	69.12 (0.32)	39.14 (0.31)	52.96	53.28	53.18	53.88
TiO_2	0.08	0.04 (0.04)	--	--	0.10 (0.09)	0.07	0.07	0.06	0.06
Al_2O_3	29.1	29.52 (0.23)	19.65	19.37 (0.15)	27.47 (0.37)	27.25	26.37	24.67	24.05
FeO	0.44	0.41 (0.01)	0.05	--	6.74 (0.27)°	1.43	1.38	2.80	2.73
MgO	0.07	0.12 (0.01)	--	--	0.08 (0.03)	0.06	0.06	0.05	0.05
SrO	0.11	0.12 (0.09)	nd	--	--	0.07	0.07	0.02	0.02
CaO	12.8	12.92 (0.11)	0.04	0.05 (0.02)	23.93 (0.03)	12.53	12.12	12.15	11.84
Na_2O	3.96	4.13 (0.08)	11.07	11.74 (0.16)	--	4.49	6.44	5.22	7.20
K_2O	0.25	0.25 (0.01)	0.29	0.19 (0.05)	0.02 (0.01)	0.22	0.21	0.17	0.17
Total	99.61	100.13	98.25	100.47	97.48	99.08	100.00	98.32	100.00

*Gutmann & Martin (1976) for labradorite, Kracek & Neuvonen (1952) for Amelia albite. ** Atomic fractions calculated on the basis of 24 oxygen atoms for plagioclase, 13 oxygen atoms for clinozoisite. *** includes 0.05 M $Na_2SiO_3{\cdot}9H_2O$ with rock:fluid ratio = 1:3, composition normalized. ° All Fe is assumed to be Fe_2O_3, which was calculated as 1.11 of FeO from results of microprobe analysis.

ing materials are based on the results of preliminary experiments (Jenkins 1980). A low ionic-strength fluid (0.05 M Na_2SiO_3) and the seeding technique (Johannes 1968, Allen & Fawcett 1982) were utilized to facilitate reaction kinetics and discourage the production of metastable phases. Use of the seeding technique enhances growth of the stable assemblage because nucleation sites are provided (Ueda *et al.* 1980, Jenkins *et al.* 1983).

Natural starting materials (grains size 1–40 μm) were used, consisting of labradorite, albite and clinozoisite (Table 1) in the presence of 0.05 M Na_2SiO_3 solution (mineral:fluid ratio 1:3 by weight). Two mixtures were run at identical conditions and were composed of 1:4 and 4:1 mixtures (by weight) of the reactant labradorite and the products, albite + clinozoisite (1:1 mixture by weight). These different starting-material mixtures are a more definitive indicator of reaction direction than if only one of the mixtures is used (Liou 1971) because the two different mixtures provide adequate material for petrographic characterization at the completion of the experiment.

Two sets of seeded experiments were performed: the D and E series differ in the duration of an experiment and addition of fresh fluid. After emplacement in cold-seal bombs for about a month, a D-series experiment was quenched, dried, and charges reground under reagent-grade acetone, placed in new capsules using the standard procedure, with *fresh* 0.05 M Na_2SiO_3 fluid added. The formation of a reaction rim creates a diffusion barrier that effectively isolates the unreacted core from the fluid. Periodic grinding of the charge can be an effective method for reducing the formation of such a rim and increasing the surface area available for reaction. In the second series (E), charges were loaded once into Pt capsules with fluid and kept at a specified T and P for the duration of the experiment *without* intermediate quenching, regrinding, and addition of new Na_2SiO_3 fluid.

Cell parameters were refined for the starting materials; those for the labradorite (Sonora, Mexico) and the Amelia albite (Rutherford mine, Virginia) are identical to those reported in Gutmann & Martin (1976) and Stewart & von Limbach (1967), respectively. The labradorite has a composition $An_{63}Ab_{35}Or_2$ (Table 1) and is structurally intermediate between high and low plagioclase (γ 90.46°). Amelia albite has a composition of $An_1Ab_{98}Or_1$ and is structurally ordered (γ 87.41°, Kroll & Ribbe 1980). SEM analysis shows that both labradorite and albite starting-materials are typically anhedral; albite exhibits a more pronounced cleavage than labradorite. Cell parameters for the starting-material clinozoisite (Baja California, Mexico) are a 8.880(3), b 5.586(2), c 10.161(3) Å, β 115.45(2)°, V = 445.1(2) Å^3. Using the X-ray determination diagrams of

TABLE 2. CONDITIONS OF EXPERIMENTS AND LIST OF PRODUCTS

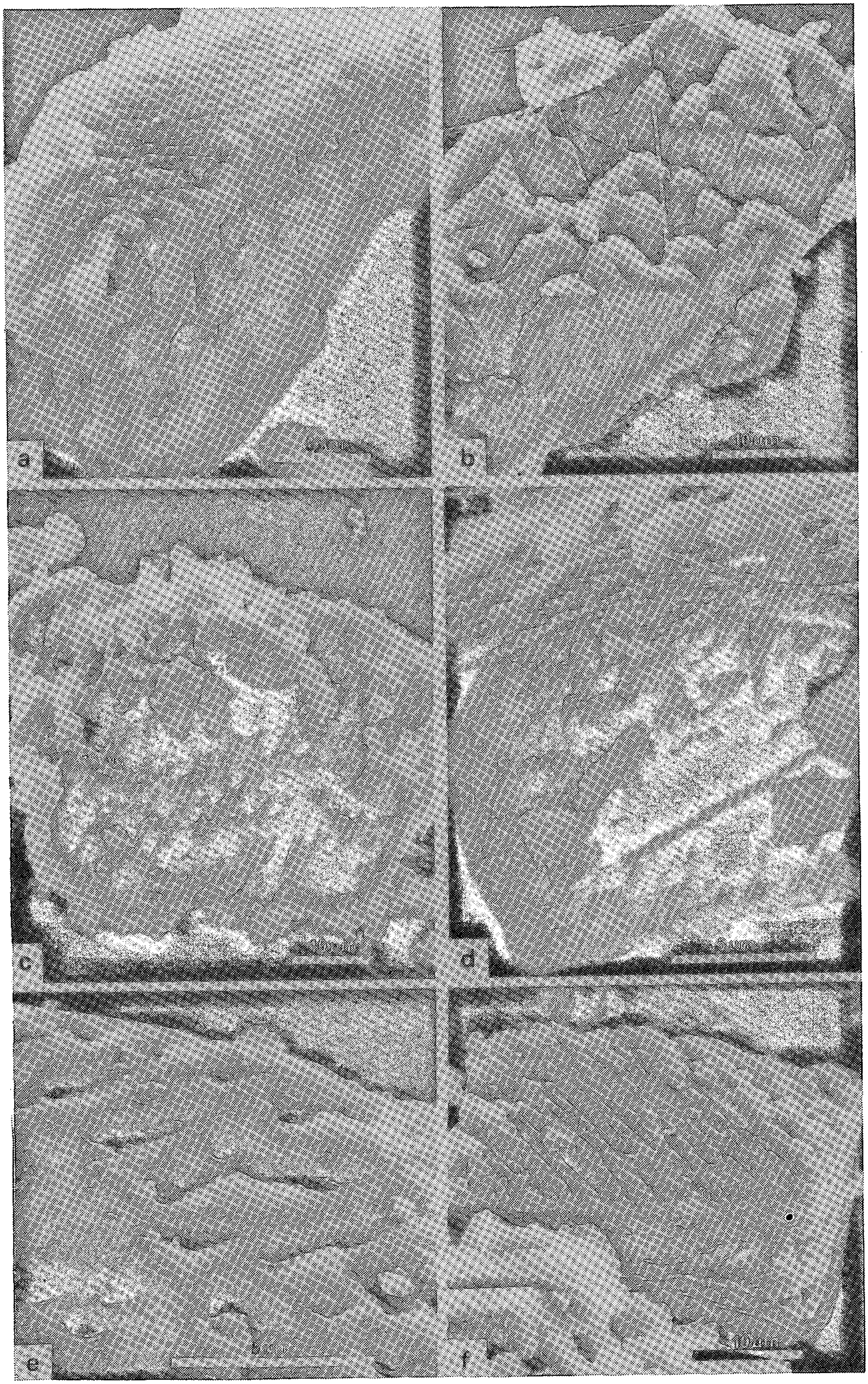
Run #	T (°C)	Duration (hr)	Run Products, 200 MPa	Run #	T (°C)	Duration (hr)	Run Products, 400 MPa
D-1-112 113	300	4644	lab(-), ab(+), cz(+), anal(+) lab(-), ab(+), cz(*), anal(+)	D-1-118 119	300	2221	lab(-), ab(+), cz(+), anal(+) lab(-), ab(+), cz(+), anal(+)
D-1-106 107	350	3586	lab(-), ab(+), cz(*), anal(+) lab(-), ab(+), cz(+), anal(+)	D-1-114 115	350	3321	lab(-), ab(+), cz(*), anal(?) lab(-), ab(+), cz(+), anal(+)
E-2-70 71	375	2759	lab(-), ab(+), olig(?), cz(*), anal(+) lab(-), ab(+), cz(*), anal(+)	E-2-78 79	375	2590	lab(-), ab(+), olig(+), cz(*) lab(-), ab(+), olig(?), cz(+)
D-1-104 105	400	2519	lab(-), ab(+), cz(*), anal(+) lab(*), ab(+), olig(+), anal(+), cz(*)	D-1-110 111	400	2661	lab(-), ab(+), olig(+), cz(*), anal(+), wo(+) lab(-), ab(+), olig(+), cz(+), anal(+)
D-1-120 121	450	3455	lab(-), ab(+), cz(*), anal(+) lab(-), ab(+), olig(?), cz(+), anal(+)	D-1-122 123	450	2804	lab(-), ab(+), cz(*), anal(+) lab(-), ab(+), olig(+), anal(+), cz(+)
				E-2-36 37	465	2157	lab(-), ab(+), olig(+), cz(+) lab(-), ab(+), olig(+), cz(+)
				E-2-38 39	485	2136	lab(-), ab(+), olig(+), cz(*), gn(?) lab(-), ab(+), olig(+), cz(+), gn(?)
D-1-102 103	500	1698	lab(-), ab(*), olig(+), cz(+), anal(+) lab(-), ab(+), olig(?), cz(+), anal(+)	D-1-100 101	500	1655	lab(-), ab(+), olig(+), cz(+), anal(+) lab(-), ab(+), olig(+), cz(+), gn(?), anal (+)
E-2-72 73	525	2732	lab(*), ab(*), olig(?), cz(+), gn(+) lab(-), ab(*), olig(?), cz(+), gn(+)	E-2-76 77	525	2659	lab(-), ab(+), olig(+), cz(+), gn(+) lab(-), ab(+), olig/and(+), cz(+), gn(+)
E-2-68 69	550	2733	lab(-), ab(+), olig/and(+), cz(+), gn(+) lab(-), ab(*), olig/and(+), cz(*), gn(+)	E-2-40 41	550	1919	lab(-), ab(*), olig/and(+), cz(-), gn(+) lab(-), ab(-), olig/and(+), cz(-), gn(+)
E-2-82 83	575	2400	lab(-), ab(-), and(+), cz(-), gn(+) lab(-), ab(-), and(+), cz(-), gn(+)	E-2-88 89	575	2731	lab(-), ab(*), olig/and(+), cz(-), gn(+) lab(-), ab(-), and(+), cz(*), gn(+)
E-2-74 75	600	2706	lab(-), ab(-), and(+), cz(-), gn(+), wo(+) lab(-), ab(-), and(+), cz(-), gn(+)	E-2-80 81	600	2252	lab(*), ab(-), and(+), cz(-), gn(+) lab(-), ab(-), and(+), cz(-), gn(+)

lab = labradorite; ab = albite (starting material + new growth); cz = clinozoisite (starting material + new growth); olig = oligoclase; and = andesine, gn = garnet; anal = analcime; wo = wollastonite.

(-) = dissolution; (*) = no change; (+) = growth; (?) = presence of phase is questionable.

The 1:4 starting mixtures are the even run numbers (e.g., D-1-112), and 4:1 mixtures are the odd run numbers (e.g., D-1-113).

See Figure 3 and Table 3 for the plagioclase microprobe compositions.


a
b
10 µm
c
d
e
f
10 µm

Myer (1965), the *a* and *b* dimensions and volume indicate Ps_5 to Ps_{12} (Ps: pistacite; Liou 1973); however, the microprobe analysis gives a Ps_{17} content (Table 1). The clinozoisite material forms anhedral grains; without an EDAX analysis, it is indistinguishable from the plagioclase when observed by SEM.

The experimental charges were not buffered with respect to oxygen fugacity. However, the Pt capsules are permeable to H_2, and it is reasonable to assume that oxygen fugacity was buffered by the walls of the cold-seal bombs, *i.e.*, the Ni-NiO (NNO) buffer assemblage (Huebner 1971).

Results of optical, X-ray diffraction, scanning-electron miscroscopy (SEM), and electron-microprobe analyses were utilized in characterizing *all* run products. Optical microscope analysis was cursory, because the reacted mixture is extremely and uniformly fine-grained; therefore, the SEM is more useful for mineral identification than the petrographic microscope (Allen & Fawcett 1982, Moody *et al.* 1983).

A Guinier–Hägg (model XDC-700) powder pattern with $CuK\alpha_1$ radiation was obtained (8-hour exposure) on all starting materials and products, with Si (NBS #640) as an internal standard. The resulting films were read manually to 0.01 mm, with intensities estimated visually. The X-ray data were reduced and corrected with respect to the Si standard by computer. The X-ray data gave the following information: (1) mineral identification, (2) growth or disappearance of phases, detected through a comparison of reflection intensities and total number of lines in the starting-material mixture *versus* those in run products, and (3) unit-cell data, generated for some minerals by least-squares refinement with the program of Appleman & Evans (1973).

An Etec Autoscan scanning electron-microscope (SEM) was employed routinely with a Kevex X-ray energy-dispersion spectrometer (EDAX) for the study of all phases. The samples were prepared according to the method described by Walker (1976) and carbon-coated before analysis. The SEM was crucial for distinguishing mineral growth (development of euhedral habits and increase in crystal size) or dissolution (etching of grains) and for detection of phases present in amounts less than 5% of sample (Allen & Fawcett 1982, Moody *et al.* 1983). The EDAX was necessary for definitive identification of minerals in these complex multiphase mixtures.

The powdered samples were mounted in epoxy and hand-polished using a method developed at NASA for lunar fines (G. Lofgren, pers. comm. 1976), then carbon-coated before electron-microprobe analysis. The microprobe analyses were performed using a nine-spectrometer ARL–SEMR microprobe at Virginia Polytechnic Institute and State University (VPISU) operated at 15 kV, 10 nA with a fixed counting time of 10 s. The fine grain-size of most samples necessitated using a small beam-spot (~ 1 μm). Chemically analyzed minerals available at VPISU were utilized as microprobe standards: albite TAB for Na, Al, Si; olivine MARJ for Mg, Fe; orthoclase ORTHO for K; anorthite AN for Ca, and strontium titanite SRTI for Sr, Ti. Data reduction utilized Bence & Albee (1968) procedures. The VPISU electron microprobe also has SEM and EDAX capability, which aided in quick recognition of phases to be analyzed. Characteristic habits, new growth and dissolution features could be recognized with this SEM feature and correlated with the grains analyzed. The SEM capabilities were a necessity for analysis of finer growth-features and small euhedral crystals (new growth), which could not be detected using the microprobe's standard light-optics system.

Selected transmission-electron microscopy (TEM) was performed on some run products by Professor H.-R. Wenk at the University of California, Berkeley. Indexing of electron-diffraction patterns was done by Dr. G.L. Nord, U.S. Geological Survey, Reston.

RESULTS

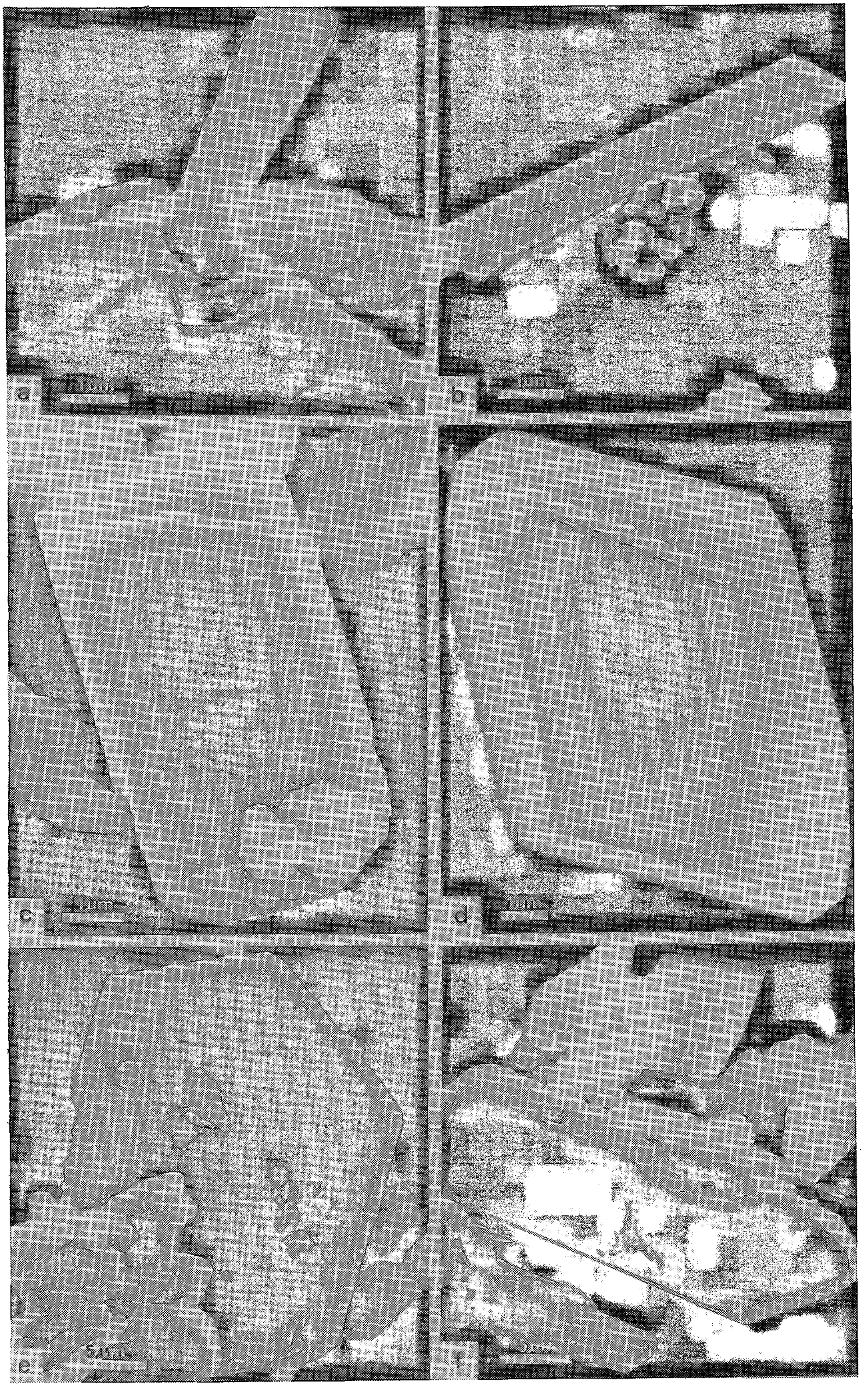
All critical data relating to the experimental products are presented in Table 2, which includes a record of temperature and pressure of the experiments. A discussion follows combining all analytical data for each phase in the starting materials and in the products.

Starting materials in the reaction products

The cell parameters are not reported since no significant change was noted from their initial values. Since γ remains constant for both albite and labradorite in the products, no significant ordering of Si and Al (Kroll & Ribbe 1980) occurred during the hydrothermal treatment.

Each phase exhibits dissolution features indepen-

FIG. 1. Relict grains and dissolution features. (a) Structurally controlled etching of labradorite (An_{63}) from D-1-119. (b) Etching of labradorite (An_{63}) from D-1-121. Etching and rounding of the grain are extensive, but crystallographic control is less evident. Note the development of fibrous clinozoisite. (c) Highly pitted relict albite (An_1) from D-1-114, with a sieve-like appearance. (d) Stair-step pattern of etching seen in some experiments. Crystallographic control of etching is obvious for this albite from D-1-120 (An_1). Note two albite laths (An_1) apparently growing from this grain in the upper right-hand corner. A few fibres of clinozoisite are present. (e) Pitted clinozoisite from D-1-114. (f) Crystallographically controlled etch-pattern on clinozoisite from E-2-40.


a
b
1μm
c
1μm
d
1μm
e
5μm
f

dent of the T and P of the experiment. In some lower-temperature experiments labradorite was not detected, implying complete dissolution. Relict albite and clinozoisite can be found at all conditions except for albite in the 4:1 mixture at 200 MPa above 400°C, and clinozoisite in the 1:4 mixture at 400 MPa above 550°C.

All relict phases display crystallographically controlled etching. This style of dissolution is most prominent at lower temperatures (300–400°C) for labradorite (Fig. 1a), and at higher temperatures (>400°C) for albite (Figs. 1c, d). Crystallographically controlled etching has also been observed in plagioclase in the experiments of Meyer (1978) and Allen & Fawcett (1982). Berner & Holdren (1979) observed dissolution features similar to the "stair-step-like" etch pattern (Fig. 1d) for albite, etched in acid at 25°C, one atmosphere. Etching of relict clinozoisite also appears to be crystallographically controlled (Figs. 1e, f), giving grains a striated or sieve-like appearance.

A reaction rim of oligoclase or andesine composition has been observed, especially on relict labradorite, above 400°C. The core of labradorite altered in this fashion is highly etched (Fig. 1b), and exhibits apparently less crystallographic control than with the etch pattern on intact plagioclase (Fig. 1a). Alteration occurs as an abrupt compositional change from the original starting-material labradorite composition (An_{60-65}) to that of oligoclase (An_{18-25}). These rims are approximately 2–4 μm thick. At higher temperatures (>525°C, both 200 and 400 MPa), a rim is also developed on labradorite, with an abrupt compositional change from labradorite to oligoclase or andesine (An_{28-45}).

Reaction rims on starting-material albite and clinozoisite are limited. Only one anhedral grain of albite was observed with a rim composition (An_4) different from that of the starting-material albite (An_1) (D–1–114). Between 400 and 485°C at 400 MPa and at 375°C at 200 MPa, compositional zoning was found in clinozoisite. Zoned clinozoisite shows Fe^{3+} decreasing and Al^{3+} increasing from core (Ps_{17}) to rim (Ps_1, Jenkins 1980). In all other cases, the clinozoisite produced is unzoned and has the starting-material composition.

Growth of new albite

Albite laths (Figs. 1d, 2a) representing growth occur more abundantly in the 1:4 than in the 4:1 mixtures. In the 1:4 mixture, laths can be found from 300 to 550°C in 200 MPa runs and to 575°C in 400 MPa runs. In the 4:1 mixture, laths are observed from 300°C to 500°C at 200 MPa runs and to 525°C in 400 MPa runs. Compositionally, these laths are consistently 0–1 mole % An. In two cases, the laths do exhibit compositional zoning [An_0 core and An_{21} (D–1–105) and An_{30} (E–2–88) rim]. This lath habit (Fig. 2b) has also been demonstrated in diagenetic alteration of plagioclase (Boles 1982, Plate 2).

The run-product albite is ordered (Kroll & Ribbe 1980), equivalent to the starting material. Since powder-diffraction techniques were used, no definitive determination of the structural state of lath albite could be made owing to the persistence of starting-material albite in the products.

Growth of oligoclase or andesine

Oligoclase or andesine is found in most experiments at or above 375°C. These plagioclase compositions occur as a rim on labradorite, as discrete laths, or platelets, and infrequently on zoned, euhedral albite. Figures 2c and 2d show discrete, intermediate plagioclase euhedra from experiments D–1–123 and E–2–68, respectively. Similarities between the two grains can be seen, although the plagioclase from the higher-temperature experiment (E–2–68) exhibits a more euhedral habit.

Compositions of intermediate plagioclase appear to fall into three groups according to temperature (Fig. 3). Between 400°C and 525°C, oligoclase forms discrete grains that have a nearly consistent composition (An_{21-23}). Oligoclase (An_{18-24}) also rims labradorite except at 525°C, where rim compositions of An_{29} and An_{34} have been noted. Above 550°C, no intermediate plagioclase exists with a composition less than An_{40} (Fig. 3).

Refining cell parameters of oligoclase or andesine was a distinct problem since powder-diffraction methods average similar crystal-structures (Kroll & Ribbe 1980, Ribbe 1983) and compositions. We used a designated series of 15 reflections that exhibit the greatest shift in 2θ as composition changes (Smith 1956). Refinements were made only for products in which microprobe data supported the existence of an intermediate plagioclase phase. Comparison of γ and the mole % An content of plagioclase (Table 3) with the curve of Kroll & Ribbe (1980) indicates

FIG. 2. Growth features in albite, oligoclase or andesine, and clinozoisite. (a) Lath-like albite (An_1) growing from a rounded, anhedral albite in E–2–78. (b) Well-formed lath of albite (An_1) from D–1–123. The left-hand end of the lath is broken, and exhibits no crystal face. (c) Oligoclase (An_{20}) from D–1–123. The edges are rounded, but some crystal faces are present (lower left). (d) Euhedral andesine (An_{30}) from E–2–68. Note presence of fibrous clinozoisite. (e) Euhedral clinozoisite (new growth) from D–1–123. (f) Prismatic clinozoisite from E–2–77 that formed around a seed grain of starting-material clinozoisite. The seed grain protrudes from the prismatic grain at right of centre. Platelet at the top-centre of the photomicrograph is new albite (An_1).

that most intermediate compositions are relatively well ordered. However, intermediate plagioclase produced at or above 575°C is more disordered (Jenkins 1980). Preliminary TEM data (H.-R. Wenk pers. comm., 1980) show that the intermediate plagioclase from the 550°C, 400 MPa experiment (E-2-40) is homogeneous, exhibiting no domain textures or lamellar microstructures.

Growth of clinozoisite

Some grains exhibit partial growth, portions of one grain being euhedral, other portions being anhedral with etch features. Euhedral, prismatic clinozoisite (Fig. 2e) represents this growth process taken to completion. Prismatic clinozoisite is found in most experiments between 450 and 525°C and occurs at 575°C in the 400 MPa experiments. In the 200 MPa experiments, prismatic clinozoisite is found at 500 and 525°C only. X-ray-diffraction analysis for clinozoisite indicates growth or no change from 300 to 500°C at 200 MPa, and from 300 to 525°C at 400 MPa. The X-ray data suggest that the growth of clinozoisite is well below the detected SEM occurrence of prismatic clinozoisite because clinozoisite also occurs in a fibrous habit (Figs. 1b, d).

Growth of garnet

Garnet has been produced in both 200 MPa and 400 MPa experiments above 500°C and 480°C, respectively. Garnet becomes distinctly euhedral at higher temperatures. Common habits for garnet include dodecahedra and dodecahedra modified by an octahedron or trapezohedron (Jenkins 1980). Compositionally, the garnet is grossular with minor substitution of andradite and pyrope. In three cases, E-2-74, E-2-88 and E-2-80, the garnet is zoned,

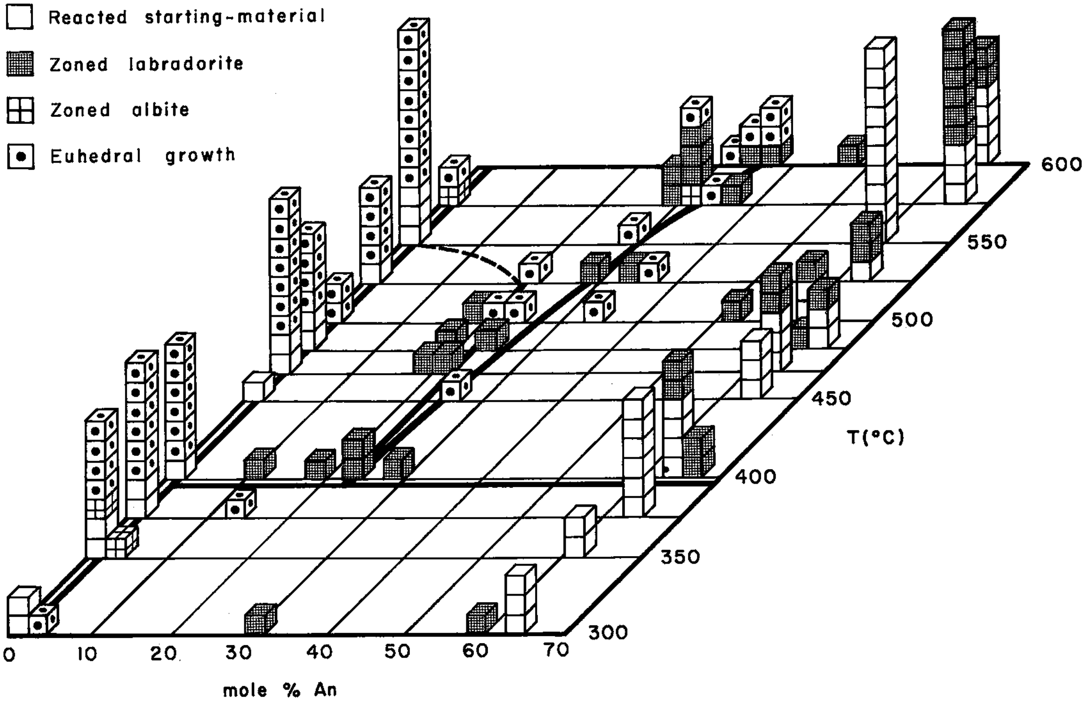


FIG. 3. Temperature–composition*–frequency** diagram for plagioclase from 400 MPa (4 kbar) experiments (Jenkins 1980). The heavy lines represent proposed plagioclase subsolidus phase-relationships of Grove *et al.* (1983), constrained by the data available. The dashed line represents extrapolated closure of peristerite miscibility-gap. The identification of habit of the analyzed grain was done at time of analysis with SEM/EDAX attachment to the electron microprobe. *Shaded boxes or boxes marked with a cross indicate core and rim compositions from the same grain. For some samples, data on more than one grain have been obtained, and no attempt has been made to distinguish these grains on this diagram. Occasionally, two or more distinctly different rim-compositions were obtained from the same grain. Where this occurs, each rim composition has been depicted on the diagram. **Microprobe analyses for all runs at each temperature were obtained in a standardized time-period (1 hr.). Plagioclase from 450, 500, 550°C runs was analyzed before this time constraint was utilized, and frequencies at these temperatures more probably reflect the total number of grains with a given composition rather than their relative abundance in the sample.

TABLE 3. UNIT-CELL REFINEMENTS AND COMPOSITIONS† FOR RUN-PRODUCT OLIGOCLASE AND ANDESINE

Sample	An(mole(%)	a(Å)	b(Å)	c(Å)	(α)°	(β)°	(γ)°	vol(Å^3)
D-1-111	19(6)	8.16(1)	12.85(1)	7.12(4)	93.6(1)	116.8(1)	89.9(1)	666(1)
E-2-37	26(5)	8.17(3)	12.84(2)	7.13(1)	93.5(2)	116.5(2)	89.6(3)	668(2)
E-2-38	19(1)	8.140(6)	12.902(7)	7.114(2)	93.63(9)	116.48(4)	89.41(9)	667.2(5)
E-2-39	24(1)	8.19(1)	12.83(1)	7.108(3)	93.43(9)	115.8(1)	89.4(2)	672(1)
D-1-100	21(3)	8.16(2)	12.83(2)	7.14(3)	93.1(4)	115.9(3)	89.2(2)	671(3)
D-1-101	22(1)	8.179(9)	12.825(7)	7.104(3)	93.34(8)	116.0(1)	89.10(7)	668.5(9)
E-2-76	22(1)	8.16(1)	12.852(8)	7.126(7)	93.5(2)	116.7(1)	89.2(2)	666(1)
E-2-77	29(1)	8.18(2)	12.82(2)	7.104(8)	93.3(2)	115.5(3)	89.6(3)	672(2)
E-2-68	34	8.16(1)	12.855(8)	7.108(3)	93.6(1)	116.14(9)	89.5(2)	668.1(1)
E-2-69	28(1)	8.168(4)	12.869(4)	7.104(1)	93.47(4)	116.07(2)	90.38(5)	669.1(4)
E-2-40	30	8.16(2)	12.80(2)	7.114(8)	93.5(2)	116.6(2)	89.3(2)	664(2)
E-2-82	40(2)	8.17(2)	12.85(1)	7.107(6)	93.5(2)	116.1(2)	89.3(2)	670(2)
E-2-83	38(4)	8.17(2)	12.83(1)	7.127(6)	93.6(1)	116.30(9)	90.1(2)	668(1)
E-2-88	31(3)	8.17(2)	12.86(2)	7.109(8)	92.8(2)	116.6(1)	89.8(2)	668(2)
E-2-89	36(3)	8.18(1)	12.817(8)	7.103(4)	93.4(1)	116.06(9)	89.2(2)	667.9(9)
E-2-74	37(4)	8.159(6)	12.873(5)	7.112(2)	93.52(5)	116.25(3)	90.19(6)	668.3(5)
E-2-80	33(3)	8.159(9)	12.857(6)	7.108(3)	93.4(1)	116.30(5)	90.2(1)	666.9(7)
E-2-81	36(3)	8.17(1)	12.86(1)	7.104(4)	93.7(2)	116.04(7)	90.1(1)	669(1)

* Determination of An content via microprobe, if no standard deviation given, then only one analysis available.
† Jenkins (1980).

always with grossular content increasing and andradite and pyrope contents decreasing from the core to the rim. The garnet has a cell dimension 11.885(8) Å [V 1666(2) Å^3], which compares well with values reported for grossular by Deer *et al.* (1962) and Liou (1973).

Other phases

Analcime was observed in the D series of experiments from 300 to 500°C, 200 and 400 MPa (Table 2). Analcime is characteristically euhedral and commonly is found to be slightly etched. The cell dimensions determined suggest a slightly to moderately Si-deficient analcime, with Si ranging from 31.6 to 30.6 on the basis of 96 oxygen atoms (Saha 1959, Coombs & Whetten 1967). Attempts to obtain an electron-microprobe analysis of analcime were not satisfactory owing to Na volatilization during the analysis. However, analcime is a metastable phase in this bulk composition because of its lack of appearance in E-series experiments (see also Matthews 1980). Analcime was not produced in any E-series experiments at 400 MPa below 500°C but occurs in all D-series experiments. Analcime may crystallize early once the breakdown of the labradorite occurs. If no new sodium metasilicate fluid is added, as in the E-series runs, the easily nucleated analcime can break down to form albite. If new fluid is added, as in the D series, this new fluid reinforces the previously nucleated analcime by the addition of Na$^+$ and SiO$_2$(aq) to the system, and this analcime then persists metastably in the experiment.

Wollastonite (Table 2) was positively identified by lack of Al in SEM/EDAX analysis of trace occurrences of fibres in two experiments at widely different temperatures and pressures. Characteristic reflections in the X-ray films are absent.

A total study of this system would have included an analysis of the fluid phase present at the end of each experiment. Unfortunately, a technique for analyzing the minute amount of fluid (~30 μL) present was not available. Quench products observed in trace amounts *only* in some of the higher temperature runs (>550°C) have compositions (*via* SEM/EDAX) that are highly aluminous. These high-temperature quench products also contain small amounts of silica and, infrequently, minute amounts of Na$^+$ and Ca^{2+}. Zoning trends in clinozoisite and garnet indicate that the minor mafic components (Fe, Mg, Ti) are enriched in the fluid phase at temperatures below 500°C and readily removed from the fluid phase above 500°C.

Phase relationships

Figure 3 is a temperature – composition – frequency diagram illustrating plagioclase compositions from 400 MPa experiments determined by microprobe. A consistent duration of analysis (1 hr. per mounted specimen) is a constraint on the frequency of observed compositions. The significant features of this diagram and data in Table 2 are:

1. labradorite dissolves at temperatures below 525°C at both 200 and 400 MPa and is found to have a reaction rim along the edge of grains; the altered grains exhibit zoning with a core of original labradorite and a rim richer in Na;

2. albite dissolves and grows between 300 and 350°C, producing lath-shaped euhedra;
3. intermediate plagioclase (oligoclase or andesine) and albite are observed to coexist between 375 and 550°C at 200 MPa and 400 MPa; the intermediate plagioclase is predominantly oligoclase up to 500°C, and predominantly andesine from 500 to 600°C;
4. the amount of intermediate plagioclase increases greatly with increased dissolution of albite;
5. below 525°C, Ca placed into solution from the dissolution of labradorite is taken up by the growth of clinozoisite; clinozoisite and grossular coexist over a small range in temperature (~50°C), and finally the amount of grossular increases as the amount of clinozoisite decreases (>550°C).

DISCUSSION OF RESULTS

Petrological constraints in the system Na_2O-CaO-Al_2O_3-SiO_2-H_2O

Albite and clinozoisite are the observed phases present between 300 and 350°C (Table 2). Little or no effect of pressure has been noted between the 200 and 400 MPa runs except that fibrous clinozoisite occurs more commonly in the 200 MPa experiments than prismatic clinozoisite.

The observed assemblage over the temperature range 375–500°C is albite + oligoclase (Fig. 3, $\sim An_{20}$) + clinozoisite. The production of oligoclase reduces the amount of Na^+ and Ca^{2+} available for the production of albite and clinozoisite. The composition of the oligoclase is controlled by the peristerite miscibility gap in the system Ab–An. This control is supported by the fact that new grains (of intermediate plagioclase) produced (Moody & Jenkins 1981) have nearly the same composition as the alteration rim on relict labradorite (Fig. 3).

The assemblage albite + andesine (An_{30}) + clinozoisite + grossular is observed between 525 and 550°C. Closure of the peristerite miscibility-gap is necessary topologically near this temperature (Grove *et al.* 1983). However, closure of this solvus has not been demonstrated from either laboratory or field data (Smith 1972, Grove *et al.* 1983). Instead of oligoclase, andesine ($\sim An_{30}$) is the predominant intermediate plagioclase observed in this temperature range.

The significant difference between this higher-temperature assemblage and the assemblages at lower temperatures is the introduction of a new Ca-rich phase, grossular. The production of grossular necessarily consumes available Ca^{2+} used in the production of clinozoisite but consumes less Al^{3+} than clinozoisite. By increasing the temperature between 500 and 550°C, grossular production increases as clinozoisite production decreases, implying a transition zone between the assemblages below 525 and above 550°C.

Above 550°C, the assemblage includes andesine ($\sim An_{35}$) + grossular (Fig. 3). Anorthite is not an observed phase in any product assemblage; however, its coexistence with andesine or labradorite is defined by inferred phase-relations in the plagioclase system (Carpenter 1981, Grove *et al.* 1983). A major increase in the amount of intermediate plagioclase with respect to the lower-temperature assemblages is expected, and this feature is evident from the temperature - composition - frequency diagram (Fig. 3). With the disappearance of clinozoisite from the system, grossular was observed to be enriched in the andradite component. In experiments where clinozoisite was not detected (E-2-74, E-2-88, E-2-80), grossular is found to be zoned, with Fe^{3+} and Ti enrichment in the core (Jenkins 1980). This zoning indicates that these ions are incorporated into the garnet in the form of andradite and that consumption of Fe^{3+} and Ti from the fluid phase occurs.

Albitization in metamorphic rocks

Plagioclase is a major mineral in tholeiitic basalts, but albite is the stable plagioclase found in low-grade metabasalts (Vallance 1960, 1974, Coombs 1974, Liou *et al.* 1974, Vernon 1976, Kuniyoshi & Liou 1976, Laird 1980). Epidote is commonly found coexisting with the sodic plagioclase, and forms owing to the release of Ca^{2+} and Al^{3+} during the breakdown of plagioclase. These features of the low-grade metamorphism of mafic rocks have been successfully reproduced in this experimental study; albite and an intermediate plagioclase have been produced through the breakdown of labradorite (An_{63}), and clinozoisite takes up the excess Ca^{2+} and Al^{3+} from the system. At the higher temperatures, garnet replaces clinozoisite as the major calcium-rich phase.

Albitization implies the replacement of calcium-bearing plagioclase by albite and does not infer any textural relationships between the plagioclases. Is calcium-bearing plagioclase altered to albite through diffusional processes or does it dissolve and form new plagioclase with formation of albite as a pseudomorph after calcium-bearing plagioclase? Na-rich plagioclase produced in this study forms by nucleation and growth, as indicated by new discrete grains and by the abrupt change in composition observed in the zoning of reacted grains of starting material (Fig. 3). During metamorphism, fluid migration occurs along grain boundaries and facilitates metamorphic reactions, with dissolution and new growth occurring in response to changing temperature and pressure conditions. This new growth accounts for the occurrence of albite-filled vesicles and veinlets in metabasalts. In the presence of fluids, then, the rate-controlling step for albitization is grain-surface dissolution, because the major mechanism of replacement is solution followed by precipitation. This mechanism of albitization has also been observed in sedimentary rocks (Boles 1982).

Intimately associated with the process of albitization is the formation of Ca-Al silicates in low-grade metabasalts (Vallance 1960, 1974) and metamorphic rocks of other bulk compositions [see Bird & Helgeson (1981) for a recent review of the petrological literature]. Clinozoisite crystallization has also been modeled in these experiments on plagioclase. Clinozoisite production consumes excess Ca and Al produced by the breakdown of labradorite. Subsequently, grossular is the major consumer of Ca + Al at temperatures above approximately 550°C, the thermal stability limit of clinozoisite in this system.

The peristerite miscibility-gap

Depending on the metamorphic regime and bulk-rock composition, certain compositions of metamorphic plagioclase do not occur as a result of a miscibility gap. This miscibility gap (*i.e.*, peristerite gap) can be represented in the natural environment as (1) a discontinuous increase in Ca-content of a single plagioclase grain from approximately An_5 to An_{20} (Laird 1980), (2) the occurrence of two discrete plagioclase phases of different composition (*e.g.*, An_{0-2} and An_{20-25}) (Crawford 1966, Steck 1976, Wenk & Wenk 1977), or (3) the occurrence of a single plagioclase with a bulk composition between An_2 and An_{17} that exhibits an exsolution texture. These grains of exsolved plagioclase exhibit discrete domains or lamellae of two different Na-rich compositions (An_1 and An_{25}).

Commonly, petrologists have considered the solvus model of Crawford (1966) to be an accurate representation of the phase relationships represented by the coexisting discrete Na-rich plagioclases, whereas others (Smith 1972, 1974, Orville 1974) proposed the two-phase binary-loop model as a better representation of these subsolidus phase-relationships. The resolution of this choice of models appears to be imminent, considering the recent mounting evidence in support of spinodal decomposition (Christie 1968, 1969, McLaren 1974, Nord *et al.* 1978, Carpenter 1981). Spinodal decomposition is possible only in the solvus model (Nord *et al.* 1978), where the requirement of a continuous free-energy surface between albite and oligoclase is met. The binary-loop model involves a discontinuous free-energy surface; in this case, spinodal decomposition is not possible.

The shape of the strain-free solvus could be extrapolated in a manner consistent with the experimental data by drawing a closure loop from the composition maxima at An_{18-22} at about 550°C to An_{0-2} (Fig. 3). The compositions of the two coexisting plagioclases place the experimental compositions of plagioclase outside the coherent spinodal (Nord *et al.* 1978) but within the strain-free solvus, which is substantiated by the formation of oligoclase without any exsolution features (H.-R. Wenk 1980, pers. comm.). Placement under the strain-free solvus (Crawford 1966) is also consistent with SEM observations of nucleation and growth of both albite and oligoclase. This peristerite gap is consistent with the plagioclase phase-diagrams deduced by Grove *et al.* (1983), based on petrographic observations of natural metamorphic plagioclase. The chief difference is the position of the tricritical point of the peristerite solvus (first proposed by Carpenter 1981), which could be placed at 525 or 550°C rather than 500°C in the Grove *et al.* (1983) diagram. Carpenter (1981), as well as Nord *et al.* (1978) and Laird & Albee (1981), would place the peak temperature for the peristerite solvus at 550°C rather than 500°C. This higher temperature for the solvus is based on a reassessment of staurolite stability (Thompson 1976) and the occurrence of garnet–albite and garnet–oligoclase assemblages for medium-pressure assemblages (Laird & Albee 1981). The plagioclase compositions outlining the peristerite solvus itself and the one limb of the Bøggild solvus are within experimental error of those compositions determined by Grove *et al.* (1983). The experimental results cannot be extrapolated to more Ca-rich compositions owing to limitations imposed by the total bulk-compositions of the experimental system (Table 1).

Maruyama *et al.* (1982) have proposed that the consolute temperature for the peristerite solvus is dependent on pressure, with the asymmetry of the solvus and its peak temperature increasing with increased pressure for a variety of rock bulk-compositions. The experimental data presented in this study show no difference in the plagioclase compositions coexisting with clinozoisite or garnet for both the 200 and 400 MPa experiments (Table 2). Interestingly, there is a strong correlation between the asymmetry proposed by Maruyama *et al.* (1982) in their T-X_{An} diagram for pressures above 350 MPa (their Fig. 7) and that proposed by Grove *et al.* (1983). These results (Fig. 3) indicate agreement on the shape of the solvus, the expected plagioclase compositions within the constraints of bulk compositions and determinations of temperatures and pressures in a variety of metamorphic terranes.

Data from this experimental study provide a second parameter for the determination of metamorphic grade in greenschist-to-amphibolite rocks. Occurrence of two coexisting, discrete Na-rich plagioclase phases representing peristerite immiscibility indicates temperature conditions less than 550°C (Fig. 3) and is thus clearly below amphibolite-facies conditions. The occurrence of two discrete plagioclases defining the transition zone between greenschist and amphibolite facies was also postulated by Maruyama *et al.* (1982) in their review of plagioclase in metamorphic assemblages. Occurrence of a single plagioclase phase will not, however, conclusively determine the conditions of metamorphism. Wenk & Wenk (1977) have shown albite to be stable well into the amphibolite facies in Na-rich, Ca-depleted rocks of the central Alps; however, structural determinations can indicate if the albite was produced above or below the temperature of the high-to-low transition, 575 ± 50°C (Smith 1972). Crawford (1966) and Wenk & Wenk (1977) have shown that the shift from a two-plagioclase assemblage (*i.e.*, peristeritic plagioclase) to a single-plagioclase phase of higher anorthite content can occur at different temperatures depending on the bulk composition of the system, thus enabling the occurrence of andesine below amphibolite-facies conditions, for the same bulk compositions.

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