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On plagioclase thermometry in island arc rocks: Experiments and theory

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Abstract—The abundant, anorthite-rich plagioclase phenocrysts of island arc lavas have often led to speculation on the importance of water in these magmas. A set of melting experiments at 1 atmosphere has been conducted on four Aleutian lavas (basalt to andesite) in order to calibrate plagioclase geothermometers and to obtain phase information that can be analytically extrapolated to higher pressures, temperatures and water contents. When considered on an 8-oxygen basis, both the melt and crystal compositions form a pseudo-binary that has a geometry (*i.e.*, liquidus and solidus slopes) very nearly the same as that found for the true binary by Bowen in 1913. The observed solidus slope is ~14% An (mole) per 100°C change in temperature. A number of geothermometers (Kudo-Weill, Mathez, Burnham, TRACE, SILMIN) applied to these data meet with varying success and are quantitatively evaluated. Overall the data and calculations agree in solidus slope. It is observed that the concentration of soda in the melt largely controls plagioclase composition and thus also whether or not plagioclase fractionation will either raise or lower the melt silica content. The addition of water to the system causes either a slight increase (Burnham's model) in An-content (~1% (mole) An per 10% (mole) water) or a slight decrease (SILMIN). It is clear, nevertheless, that water is not an important factor in deciding plagioclase composition in magmas of this compositional range.

INTRODUCTION

PLAGIOCLASE is exceedingly common in lavas of island arcs, generally being the liquidus phase and generally comprising 80 percent or more of the phenocrysts. Of all volcanic rocks, arc lavas contain plagioclase that can be unusually rich in anorthite. It is not uncommon to find compositions of An_{80} to An_{90} throughout the suite from basalts to andesites. Sometimes, large unzoned megacrysts can be found with compositions approaching An_{95} or more. Some compositional zoning is usually present; it is sharp but commonly not strong (*i.e.*, ±5%) in basaltic lavas and increases in amplitude with increasing silica content of the lava. The overall crystal composition and zoning records an intimate history of changes in magmatic intensive parameters (temperature, pressure, chemical potential) in the near-surface environment. This history is central to understanding the near surface behavior of the magma as well as characterizing the near-surface intensive parameters critical to understanding the ultimate origin of the magma itself.

A great deal has been said on the meaning of plagioclase composition in arc rocks. YODER (1969) has suggested that because the melting point of anorthite is more sensitive than that of albite to increasing water pressure, high An content reflects high magmatic water content. At the same time, however, high water content promotes normally and strongly zoned crystals whereas undersaturation with water promotes reversely and weakly zoned crystals (PRINGLE *et al.*, 1974; MARSH, 1976). The plagioclase thermometers developed by KUDO and WEILL (1970) with refinements by MATHEZ (1973) and DRAKE (1976) when applied to basaltic arc rocks sometimes give temperatures near or in excess of 1300°C, which at first seem unrealistic. To make the temperature more realistic, an arbitrary amount of water can be assumed present, but this itself begs the original question.

Much of this uncertainty in understanding plagioclase composition in basaltic arc rocks stems from the paucity of experiments explicitly designed to study plagioclase thermometry. The seminal work by EGGLER (1972; EGGLER and BURNHAM, 1973) on andesite phase equilibria has been well augmented by BAKER and EGGLER (1983; 1987), and GROVE *et al.* (1982); mainly ancillary plagioclase compositional data are available from these studies. Overall, however, there is little information on plagioclase composition in terms of understanding the influence of bulk composition, water, and pressure.

We attempt here to reconcile this need by presenting data from experiments on plagioclase equilibria in four lavas (basalt to andesite) from the Aleutian Islands, Alaska. The compositions of both the plagioclase and its host liquid (glass) have been analyzed and compared with those of the lava. In each of the four compositions, the plagioclase pseudo-binary (*i.e.*, 8-oxygen mineral and melt formula basis) is found to exist in the melt with nearly the same geometry (*i.e.*, slope of liquidus and solidus) as that originally found by BOWEN (1913) for the true binary. Comparisons with the melt compositions, suggest that plagioclase composition itself is controlled largely by the soda content of the liquid; the apparent distribution coefficient is near unity. The liquidus temperature of the melt, however, is controlled largely by alumina. The application of the common thermometers to these compositions gives fair agreement, with temperature differences ranging from 10° to nearly 100°C. The slope of the solidus (or liquidus) is difficult to predict using most thermometers, but it is matched well by the silicate solution model SILMIN (*e.g.*, GHIORSO *et al.*, 1985). Using BURNHAM's (*e.g.*, 1979) and Ghiorso's solution models, the results of these 1 atmosphere experiments have been extended to higher pressures where the effects of water can be evaluated. It is found that the liquidus is of nearly constant plagioclase composition and that with increasing water content plagioclase composition becomes slightly more anorthitic at the rate of about 1% An (mole) per 10% water (mole). This small effect suggests that plagioclase composition is primarily controlled by the soda and alumina content of the original magma. Highly anorthitic crystals probably grew from melts low (≈wt. 1%) in soda and high in alumina. If the soda content of the melt is beyond a critical amount, the plagioclase is more siliceous than the melt itself and plagioclase fractionation drives the magma to silica-undersaturation. Plagioclase fractionation in a single suite of lavas can produce both increasing and decreasing concentrations of silica.

MATERIALS AND EXPERIMENTAL PROCEDURES

The Aleutian lavas for this study (Table 1) were chosen as being typical and to span the range of silica exhibited by island arc lavas. These lavas are broadly similar with high alumina and lime, moderate soda and potash, and low magnesia. The two basaltic samples were chosen to accentuate the effect of increasing alumina and soda at a constant amount of silica. The two more andesitic compositions test the effect of increasing silica (CB-12) and the effect of low soda with high alumina and moderate silica (AD-61). A dacite (66 wt.% SiO_2) proved reluctant to crystallize regardless of run duration and history of heating.

Table 1. Rock compositions, norms, and activities

	AT-4	AT-6	AD-61	CB-12
	Bulk composition (wt.%)			
SiO_2	48.29	49.05	52.14	57.30
TiO_2	0.90	0.89	0.67	0.77
Al_2O_3	17.26	20.32	19.44	18.21
Fe_2O_3	6.17	3.31	4.79	2.93
FeO	4.16	6.52	4.25	4.54
MnO	0.18	0.18	0.19	0.16
MgO	7.61	3.91	3.73	3.06
CaO	11.56	10.44	9.79	8.01
Na_2O	2.42	3.36	2.92	3.04
K_2O	0.62	0.89	0.59	1.24
P_2O_5	0.19	0.27	0.19	0.19
Total	99.31	99.14	98.70	99.45
	8-Oxygen norm (mole%)			
Apatite	0.3	0.6	0.3	0.3
Ilmenite	1.2	1.1	0.9	1.0
Magnetite	5.5	2.9	4.3	2.5
Orthoclase	4.1	5.0	3.4	7.2
Albite	22.6	29.7	26.8	27.3
Anorthite	35.6	37.4	39.4	32.6
Diopside	16.3	5.4	5.8	3.3
Hedenburgite	1.1	3.5	1.5	1.5
Enstatite	12.5	3.0	7.0	6.4
Ferrosilite	0.8	1.9	1.8	3.1
Forsterite	—	3.1	—	—
Fayalite	—	2.0	—	—
Quartz	0.1	—	8.8	14.8
	Burnham activities			
a_{ab} =	0.226	0.297	0.268	0.273
(a_{ab})* =	0.266	0.347	0.302	0.345
a_{an}† =	0.235	0.300	0.309	0.252

* With *ad hoc* addition of orthoclase component.
† Corrected for pyroxene interaction.

All experimental runs were made at atmospheric pressure by the platinum loop method in a gas-mixing furnace (DONALDSON *et al.*, 1975) at the Johnson Space Center (by I-M.C.) and at Johns Hopkins (B.D.M.). The fugacity of oxygen was maintained (except as otherwise noted) at that described by the nickel to nickel oxide (NNO) synthetic buffer reaction. The temperature of the runs, their durations, and products are given by Table 2. Once the liquidus for each sample was determined (indicated as "rock liquidus" in Fig. 1), a sample was fused at a temperature slightly (≈5°C) above its liquidus and then dropped to the desired run temperature. The duration of each experiment was generally about a week, which resulted in plagioclase crystals of about 0.5 × 0.1 mm. Each charge was sliced and made into a thin section, and the compositions of its crystals and glass were measured with

Table 2. Summary of experimental runs

Rock	Run no.	Temp. (°C)	Duration (days)	Average compositions (An, Ab, Or; mole%) Crystal	Liquid
AT-4	16	1233	4	79.3, 20.4, 0.3	68.9, 26.8, 4.3
	17	1223	3	78.0, 21.6, 0.4	68.2, 26.8, 4.3
	18	1213	3	75.7, 23.9, 0.4	66.0, 29.5, 4.6
	19	1204	4	75.6, 23.9, 0.5	67.8, 27.4, 4.8
	23	1177	6	72.0, 27.2, 0.7	66.2, 28.5, 5.4
	24	1165	6	72.6, 26.4, 1.0	65.2, 28.9, 5.9
	26	1192	1 hr.*	73.4, 25.9, 0.7	65.7, 29.8, 4.6
	27	1153	4	71.7, 27.3, 1.1	67.3, 27.3, 5.5
AT-6	4	1262	2	79.2, 20.4, 0.5	
	5	1262	4	79.8, 19.7, 0.5	63.2, 31.1, 5.7
	6	1226	3**	74.5, 24.7, 0.8	60.3, 32.3, 7.4
	7	1244	6	76.7, 22.8, 0.5	61.6, 31.9, 6.6
	8	1225	6	72.9, 26.3, 0.8	60.1, 32.7, 7.2
AD-61	10	1265	7	77.6, 22.1, 0.3	63.1, 32.0, 4.8
	11	1233	7	73.7, 25.9, 0.4	60.6, 33.7, 5.7
	12	1250	5	76.0, 23.6, 0.4	60.7, 34.0, 5.3
CB-12	11	1233	4	70.1, 20.3, 0.6	50.9, 30.4, 4.7
	12	1223	5	67.1, 31.1, 1.7	48.1, 41.7, 10.2

*: power failure.

**: NNO buffer for 2 days and 1 day at 2 log units higher.

the electron microprobe at the Geophysical Laboratory, Washington, D.C. (by J.D.M.). The procedures of data reduction of this instrument are described by FINGER and HADIDIACOS (1972).

Five crystals in each thin section were analyzed, each in five areas, and the glass was randomly analyzed in at least five areas. Generally no more than about 1% (mole) zoning was detected in any of the crystals; in the andesite slightly more variation occurred. The glass appears for the most part homogeneous, but losses of sodium and iron were heterogeneously distributed about the charge due to surface loss of sodium and absorption of iron by the platinum loop. Apparently, even with substantial surface loss of sodium in one run, the composition of the crystals seems unaffected.

The modal amount of crystals in each thin section was measured by point counting, and these modes were checked by mass balance calculations utilizing the known composition of the crystals, glass, and the initial (crystal-free) composition. This check generally shows fair to poor agreement between the counted and calculated modes, presumably due to the difference between surface and volumetric estimates of crystal content.

EXPERIMENTAL RESULTS

For purposes of comparison, each average glass analysis is cast into an equivalent feldspar-like mineral formula based on eight oxygens. (For convenience, iron is treated as being solely ferrous. It could just as easily be distributed according to the NNO buffer, but this makes little difference as will later be seen.) Each experiment provides a single average glass and crystal composition that are plotted in Fig. 1 on a plagioclase pseudo-binary for each rock. The seven runs on AT-4 are the most complete and above 1185°C they define a straight solidus having a slope ($\approx$14% An (mole)/100°C), which is similar to that determined by BOWEN (1913) in the true plagioclase binary itself. We will see that generally this same slope is a central ingredient of all plagioclase geothermometers, but its similarity to Bowen's original binary has apparently not been previously noticed. Although only three independent runs were made for two of the lavas and two for another, they are sufficiently separated in temperature to suggest solidus and liquidus slopes similar to those of AT-4. We thus assume that the following general description of crystallization holds true for each of these lavas.

Below about 1185°C the solidus and (pseudo-)-liquidus of AT-4 become vertical; the crystal composition becomes invariant with decreasing temperature. At first this might seem to reflect disequilibrium, but recalling the basic mass conservation law for crystallization in binary solid-solutions, this is to be expected. That is, equilibrium crystallization in a binary solid solution produces a solid whose final composition is the same composition as that of the initial (*i.e.*, crystal free) liquid. At this point the liquid is exhausted of one or more of the components necessary to produce a crystal of a given stoichiometry; here the melt becomes exhausted of lime and alumina. Below this temperature further crystallization is prohibited unless the melt is replenished in the exhausted feldspar ingredients. Since in these rock compositions plagioclase crystallizes alone over a temperature interval of about 100°C, the point of exhaustion comes before the appearance of a second solid phase. When there is multiple saturation with, say, plagioclase, olivine, and/or pyroxene, the mass of melt shrinks faster and this point of exhaustion is progressively (depending on the rate of appearance of other phases) shifted to lower temperatures. In addition, the width (ΔW) of the liquidus-solidus loop also influences when this invariance is reached, and ΔW is directly proportional to the "albite" content of the melt as shown by Fig. 2.

Of the experiments themselves, no crystal is more anorthitic than about An_{80} (AT-4 at 1233°C, AT-6 at 1262°C), but if the respective solidi are extrapolated to the liquidus temperature of each rock (determined independently), the earliest plagioclase compositions can potentially become unusually anorthitic. We find for AT-4 at 1250°C, $\mathrm{An}_{81.5}$; for AT-6 at 1300°C, An_{85}; for AD-61 at 1300°C, An_{83}; and for CB-12 at 1290°C, An_{78}. These projected

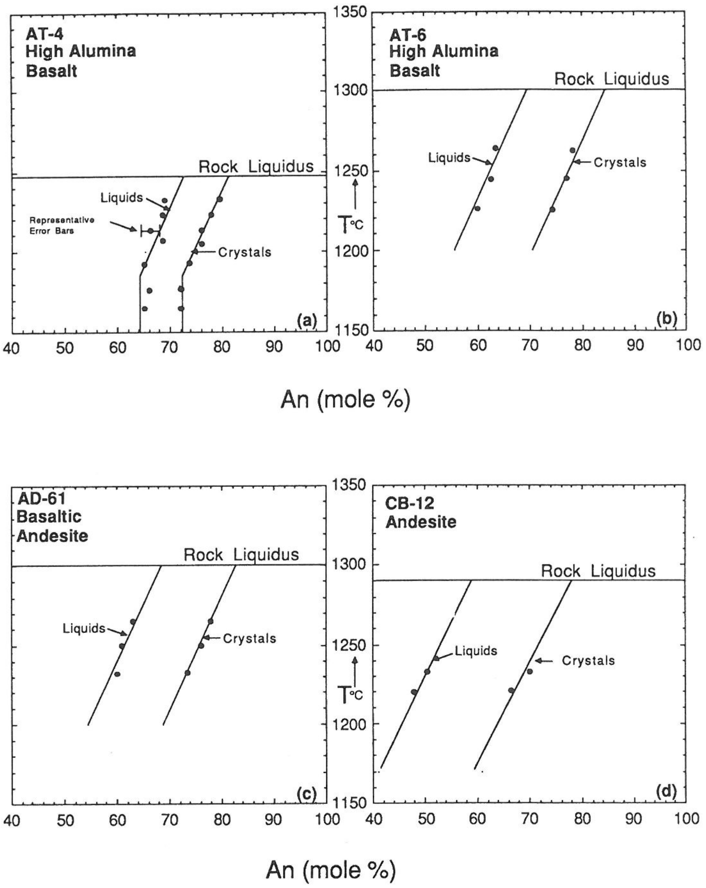

FIG. 1. Binary plots depicting the experimental crystal and liquid compositions found in the experiments. All compositions have been recalculated to an 8-oxygen basis. The liquidi and solidi have been fit by eye using the slope from the AT-4 run results with some compensation for the uncertainty of each analysis.

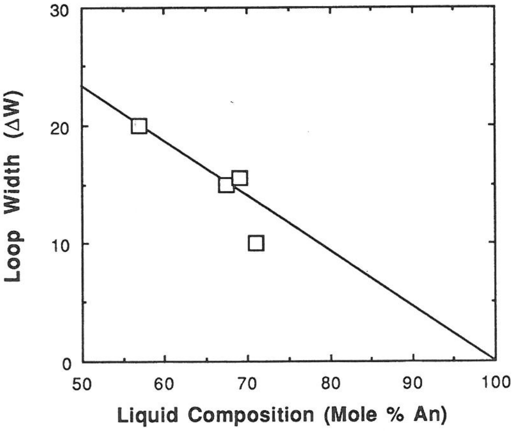

FIG. 2. The apparent liquidus-solidus loop width (ΔW) as measured from Fig. 1 plotted against the liquid composition assuming $\Delta W = 0$ at An_{100}.

anorthite-rich compositions are in part a reflection of the high (1 atm., dry) liquidus temperatures of these rocks, but it is of course both the composition of the melt and its liquidus temperature that decide the composition of the first-formed plagioclase. At a given temperature the chemical component in the melt most critical in controlling plagioclase composition is soda, whereas it is probably alumina that largely decides the liquidus temperature. This is seen by comparing the results for AT-4 and AT-6. Although they contain roughly the same amounts of silica and lime, AT-6 has substantially more alumina and soda than AT-4. At any temperature, the resulting plagioclase is found to be more An-rich in the low soda, low alumina AT-4 melt, but the liquidus temperature for AT-6 (high alumina) is significantly higher (1300°C) than that of AT-4 (1250°C). Comparing all at their respective liquidi,

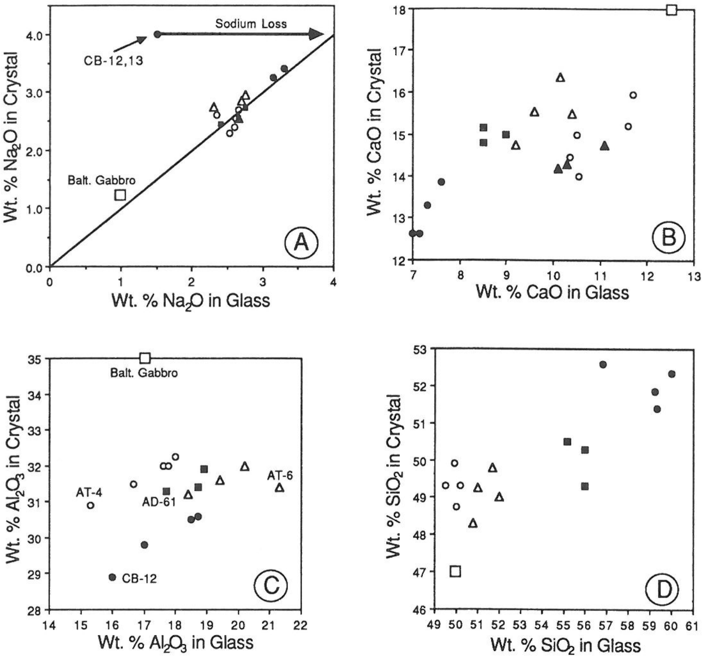

FIG. 3. The concentrations of SiO_2, Al_2O_3, CaO, and Na_2O for liquids and crystals found in these experiments. The symbol designations are given in subfigure C. The arrow in subfigure A indicates the restoration of soda due to probable surface loss.

the plagioclase of AT-6 is significantly more anorthitic. The strong effect of alumina on liquidus temperature in rocks having plagioclase as the liquidus phase has been clearly shown by FRENCH (1971), CAMERON and FRENCH (1977), and FRENCH and CAMERON (1981).

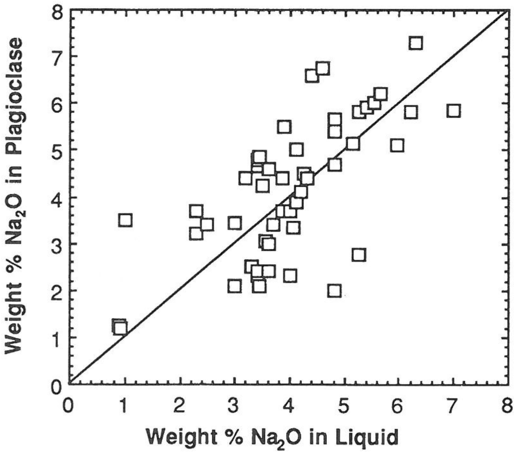

FIG. 4. Soda concentration in crystals and liquids found in Drake's experiments. A distribution coefficient (in wt.%) for soda of unity is indicated by the line.

It should be clear that if a melt were free of soda, the plagioclase would crystallize as anorthite itself. This strong effect of soda in controlling the initial plagioclase composition can be seen more quantitatively by plotting the soda content of the plagioclase against that of the accompanying melt (Fig. 3). In all except one experiment, where the analyzed glass evidently lost soda, there is nearly a one to one (in terms of wt.%, not mole fraction) partitioning of soda between melt and crystal regardless of temperature. Also shown for comparison are data from the Baltimore gabbro (SOUTHWICK, 1969), which is a rock having an unusually low soda content and An-rich plagioclase.

This apparent distribution coefficient for soda of near unity may hold best for this suite or similar suites of rocks, for a similar plot (Fig. 4) using the more varied data of DRAKE (1976) shows less regularity for soda. The lack of coherence for soda in Drake's data may reflect the large range of natural and synthetic bulk compositions used in that study; nevertheless, his data do show a broadly similar correlation. (It should also be readily obvious that this apparent distribution coefficient for soda will not be unity if plotted as mole fraction and not wt.% as in Fig. 3.) The other chemical components in plagioclase show far less coherence when plotted similarly (Fig. 3).

The steep slope of the experimental solidus (~1.4% (mole)/10°C) shows that even rather large changes in temperature (±50°C) will cause only modest (±7%) zoning in the crystal.

PLAGIOCLASE GEOTHERMOMETRY

To fully grasp the significance of these experiments in relation to the commonly used plagioclase thermometers and to further their development using these experiments, some review is necessary. The general procedure in formulating a geothermometer is first to choose an exchange reaction. Any number of reactions can be written, but since the components represented by the reaction must later be represented as activities in a thermodynamic model and these activities must be estimated from the composition of the melt, there are various advantages among the available choices. A group of exceedingly simple components can be chosen that generally lead to complicated models for representing their activities as a function of melt composition. Or a reaction can be sought that yields simple activity models, but more often than not this also calls for a complicated set of components. But if complicated components are used there may not exist the Gibbs free energy data for the standard states, thus crippling the model at its inception. Construction of a useful geothermometer must avoid these difficulties. We thus begin by considering the explicit plagioclase thermometers and then compare them and the experiments to thermometers using full magmatic phase equilibria.

Kudo-Weill model

KUDO and WEILL (1970) chose the simple exchange reaction:

$$\begin{array}{lcc} \text{(phase):} & \text{plagioclase (c)} & \text{melt (m)} \\ & (NaSiO_{2.5})AlSi_2O_{5.5} + & (CaAlSi_{2.5})AlSi_2O_{5.5} \\ \text{(component):} & \text{“albite” (ab)} & \text{“anorthite” (an)} \\ & \text{plagioclase (c)} & \text{melt (m)} \\ = & (CaAlSi_{2.5})AlSi_2O_{5.5} + & (NaSiO_{2.5})AlSi_2O_{5.5}. \qquad (1) \\ & \text{“anorthite” (an)} & \text{“albite” (ab)} \end{array}$$

The exchange reaction written in this way suggests that it is the components $NaSiO_{2.5}$ and $CaAlSi_{2.5}$ that are important in deciding equilibrium. It follows that at equilibrium

$$-\frac{\Delta G^0(T, P)}{RT} = \ln K = \ln\left[\frac{a^{c}_{an}a^{m}_{ab}}{a^{m}_{an}a^{c}_{ab}}\right] \tag{2}$$

where ΔG^0 is the change in Gibbs free energy across the reaction of the components in their standard states, which are the pure components at any temperature and pressure, and the other symbols have their usual meaning.

As this equation stands there are three types of unknowns, namely, the free energy change, temperature (and pressure), and the activities. At the time Kudo and Weill formulated their thermometer free energy data did not exist for the standard state components (*e.g.*, An-glass), and little was known about the partial molar heats and entropies of mixing from which information about the activities could be obtained. They were thus forced to take a nonrigorous thermodynamic treatment and adopt "an empirical approach . . . which, *faute de mieux*, will serve . . . until additional data become available." They therefore replaced (2) with the equation

$$-\frac{\Delta G^0}{RT} = \ln\left(\frac{\lambda}{\sigma}\right) + \ln\left(\frac{\gamma_{Na}\gamma_{Si}}{\gamma_{Ca}\gamma_{Al}}\right) \tag{3}$$

which assumed that the plagioclase solid solution is ideal and where $\lambda = X_{Na}X_{Si}/X_{Ca}X_{Al}$, $\sigma = X_{ab}/X_{an}$, $\Delta G^0 = G^0_{an} - G^0_{ab} + G^0_{Na} + G^0_{Si} - G^0_{Ca} - G^0_{Al}$, the subscripts Na, Ca, Al, and Si refer to, respectively, the oxides $NaO_{0.5}$, CaO, $AlO_{1.5}$, and SiO_2 in the melt and the subscripts an and ab refer to the "anorthite" and "albite" components in the plagioclase. The symbols X and γ, are, respectively, mole fraction and activity coefficient. Strictly speaking, (3) assumes an exchange reaction different from (1).

Because of the lack of fundamental thermodynamic data to substitute into (3), an empirical equation approximating (3) was assumed that could be fitted to data from phase equilibrium studies

$$Y(T) = \ln\left(\frac{\lambda}{\sigma}\right) + \frac{C\phi}{T} \tag{4}$$

where C is a constant and ϕ is some function of composition.

The idea to represent the activity coefficients in (3) by the last term in (4) comes from regular solution theory where $\ln \gamma \approx f(1/T)$. This formulation, however, does not assume a regular solution model and was never intended to (D. WEILL, pers. com., 1981), but is only a formulation "similar to that found for regular solutions". In fact, it can be shown that if a regular solution model itself is rigorously adopted for these multicomponent systems, only in the case where the solution is ideal can the formulation reduce to the last term in (4). The last term in (4) may, nevertheless, empirically adequately represent the data. But on the other hand, a good fit to the data is not evidence that these melts are indeed regular solutions as has sometimes been stated.

The data used by KUDO and WEILL (1970) in the regression of (4) came from experiments on natural granites and from the synthetic systems Ab-An, Ab-An-Sp, Ab-An-Di, and Ab-An-Or. In all systems the relations $X_{Na} + X_{Si} + X_{Ca} + X_{Al} = 1$ and $\phi = X_{Ca} + X_{Al} - X_{Na} - X_{Si} = 1 - 2(X_{Na} + X_{Si})$ were assumed. By working initially with different systems at the same temperature they arrived at a value for C in (4) of 1.29×10^4 (note misprint in original paper) which was subsequently used by them in all succeeding studies in the regression of (4) against temperature. In this regression the function $Y(T)$ was assumed to be of the form $Y(T) = mT + b$, where m and b are constants. Treating each set of experiments under dry conditions and water pressures of 0.5 kb, 1.0 kb, and 5.0 kb as individual sets of data, four sets of the coefficients m and b were found.

Upon application of these results to a diverse group of igneous rocks, KUDO and WEILL (1970) found generally good agreement with other estimates of temperature; the standard deviation in the original regression is 34°C. But occasionally, especially in dealing with basalts, unreasonably high temperatures (~1300°C) were found when this formulation was applied more widely. This led MATHEZ (1973) to use a wide variety of natural and experimental data from mostly basaltic systems to derive a new set of constants (m and b) for (4). (He also introduced a compositional dependence for γ that produces a double or triple-valued function over a narrow temperature interval, suggesting immiscibility in plagioclase.) What is really needed to make a tightly constrained regression over a wide compositional range is actual experimental data over this range. DRAKE (1976) remedied this situation by providing 55 new pairs of experimental liquid (glass) and crystal compositions all at atmospheric pressure. This produced a single, tightly constrained equation with a formal uncertainty of 55°C or about 12% (mole), in solid composition.

Applying the basic Kudo-Weill formulation using these various set of constants to the Aleutian experimental results does not show (Fig. 5) particularly close agreement, except possibly for CB-12 (the andesite). Mathez's constants (assuming his $\gamma = 1$ throughout to eliminate the kinked curve) seem to fit best and Drake's constants seem to be almost an average of the other two. For AT-4 the temperature estimates are off by 50°C, or the plagioclase composition by about 10% (mole); for AT-6 the temperature is off by 100°C, or the composition by about 20% (mole); for AD-61 the temperature is off by 10–35°C, or the composition by about 5–15% (mole); and for CB-12 they are all in the same neighborhood, but each thermometer shows a slope distinctly different than that found experimentally. The agreement with Mathez's equation can be made much closer by varying γ until a close fit is found and then holding γ constant for all temperatures (Fig. 6). This method of finding a suitable value of γ and then using this fixed value is hereafter referred to as the Mathez-prime formula.

There seems to be two difficulties with the thermometers, namely, compositional dependence is not adequate and the slope of the solidus is not correct. (The slopes of the solidi found in these experiments are not unusual, for a similar one is shown by the data of BENDER *et al.* (1978) for a tholeiitic basalt.) The (inverse) slopes of the experimental solidi are about 14% An (mole) per 100°C, as compared with the true binary of about 18%/100°C for this region. The slopes of the thermometers are in the range of 20–27%/100°C, and thus they predict less of a temperature decrease than is needed for a corresponding change in crystal composition. The actual slope ($\partial\phi/\partial T$) in these formulations is given by $-\sigma(C\phi/T^2 + m)$, and since $C = 1.29 \times 10^4$ and typically $T \approx 1500°K$, $|\phi| \approx 0.3$, and $m \approx 12 \times 10^{-3}$, m is typically about ten times larger than $C\phi/T^2$. Thus the slope is determined principally by m, and each succeeding formulation after Kudo and Weill has lessened the slope (increased m); to match these experiments the slope must be steepened (decrease m).

All this points to the fact that if a correct slope is initially assigned, the thermometers will be in even stronger disagreement with experiment because their dependence on melt composition is weak

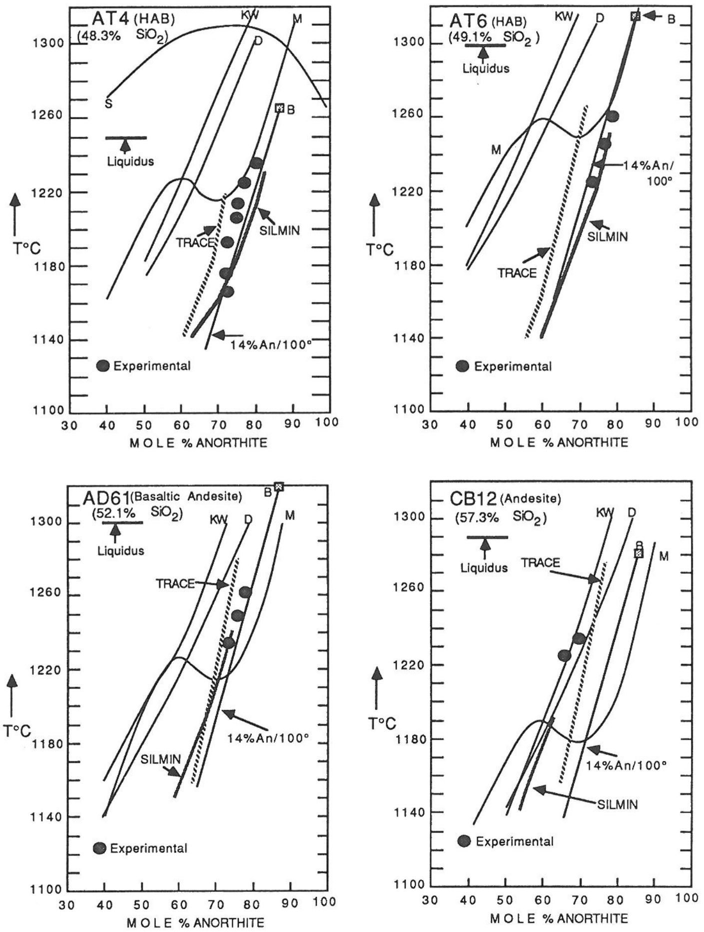

FIG. 5. Plagioclase composition from these experiments in comparison with that derived from various geothermometers. The results of the Kudo-Weill (KW), Drake (D), Mathez (M), Burnham (B), TRACE and SILMIN thermometers are indicated with symbols against each curve. The geothermometer of SMITH (1983; symbol S on AT-4) was considered for the compositions here. Its distinctive parabolic geometry and mismatch (*i.e.,* Fig. 8) led us to not consider it further.

and the thermometer solidi will never cross the now parallel experimental solidi. The slopes found by regression have absorbed some of the inadequacy of the compositional dependence of the activity model. This difficulty reflects our lack of knowledge of how to represent effectively the activities of the components $NaAlSi_3O_8$ ("albite") and $CaAl_2Si_2O_8$ ("anorthite") in the melt. The model used in these geothermometers relies almost solely on silica, alumina, lime, and soda, giving each equal importance and having little dependence on ferromagnesian components. We have, however, seen earlier that the plagioclase composition is strongly dependent on the soda content of the melt and much less so on any other components; alumina is a major influence on the liquidus. It thus seems important to have an activity model that relies heavily on the soda content of the melt, such as in, for example, the model of BURNHAM (*e.g.,* 1979).

Burnham's model

This model rests fundamentally on two premises: (1) that near the liquidus the melt structure mimics the structure, discreteness, and stoichiometry of crystallizing phases, and (2) that properly chosen aluminosilicate components mix ideally with one another (BURNHAM, 1981). When actual magmatic compositions are recast into components based on an 8-oxygen, feldspar-like formula, BURNHAM (1975) has shown that basalts, andesites, and granites have essentially identical equimolal solubilities for water. This solubility is the same as that of water in $NaAlSi_3O_8$ melt. As the phase relations in the plagioclase binary can be adequately calculated assuming both crystals and melt to be ideal solutions (clearly understanding that both solutions are actually non-ideal), and since the solidus-liquidus relations found experimentally for plagioclase in these island arc rocks geometrically mimic those in the binary itself, it seems reasonable that these equilibria might also be calculable assuming a model like Burnham's. No attempt is made here to argue that our assumption is theoretically correct; we simply suggest that it proves to be a sensible and practical way to understand these equilibria.

Burnham's formalism is broadly similar to (1) and (2) except for the fact that separate melting reactions are written for albite and anorthite. This model insists that if the components are chosen on an 8-oxygen, feldspar-like basis, the solution is ideal and $a_i^m = X_i^m$. To calculate the mole fractions X_{ab}^m and X_{an}^m, the CIPW norm is converted to a norm of mineral components each containing 8-oxygens. That is, new (heavier) gram-formula weights based on 8-oxygens (*e.g.*, $SiO_2 = 240$) are used to change the CIPW norm (in wt.%) to moles which, when normalized to unity, give the necessary mole fractions. For the rocks of these experiments both the CIPW and 8-oxygen norms are given by Table 1. It is of interest to recall that, in computing the CIPW norm, soda alone (in common igneous rocks) completely determines the amount of albite component and hence also its activity in the melt. This is decidedly different from the earlier activity model and it is in accordance with the observed strong control of crystal composition by the soda content of the melt.

The first check on the thermometer is the agreement of calculated and measured liquidus temperatures (Fig. 5). These are all generally within about 10°C or less. Except for AT-6 which shows near perfect agreement, the calculated plagioclase compositions are generally 2–5% (mole) more anorthitic than what is observed. (The comparison with CB-12 is difficult because of the low temperature of the runs relative to the liquidus, which is where this model pertains.) Since the accuracy of the determination of plagioclase composition is probably no better than about 2 mole%, this disagreement may be somewhat less. Nevertheless, the calculated compositions are generally more anorthitic than observed. If a_{ab}^m is increased slightly, for example, by letting $a_{ab}^m = X_{ab}^m + X_{or}^m$ where the latter term is the very small orthoclase component, which might similarly influence plagioclase composition, the disagreement lessens, but the calculated liquidus temperatures each rise 5–10°C and show less agreement.

The agreement between experiment and Burnham's method is close but not perfect. The calculated plagioclase compositions differ by about 0–5 mole%, or about 5–10°C in liquidus temperatures. More recent versions of this model may more closely fit these data. Burnham's method is sensitive enough such that high requirements are placed on the accuracy of the determination of both plagioclase and melt compositions. The simplest way to employ this method is to use the whole-rock composition to estimate the liquidus composition and then use the measured slope of the solidus ($\approx$14% An(mole) per 100°C) to predict further temperatures and crystal compositions. If some other mineral phase is also crystallizing, its effect on the mass balance of soda must be monitored. For example, in tholeiitic basalts where olivine is the liquidus phase, it is important to know how much the soda concentration has been increased before plagioclase appears. The only way to handle such effects is to use a full solution model.

SILMIN and TRACE

These solution models are due, respectively, to GHIORSO (1985; GHIORSO *et al.*, 1983) and NIELSEN (1988; NIELSEN and DUNGAN, 1983). SILMIN, in its simplest description, uses a broadly regular solution model in concert with experimental phase equilibria. Given an initial liquid composition, SILMIN calculates liquid and mineral compositions as the system cools and crystallizes; either fractional or equilibrium crystallization can be followed. Equilibria at 1 bar and to moderate ($\sim$3 kb) pressures can be investigated with this model (with caveats regarding pyroxenes), which calculates solid and liquid compositions and the relative amounts of each.

TRACE assumes a melt consisting of two independent quasi-lattices, one network-forming and the other network-modifying, with ideal mixing within each. It also has the ability to model trace element behavior. TRACE equilibria was calibrated from 1 bar data but works on dry systems up to pressures of about 2–4 kb (NIELSEN, pers. com., 1989).

The results of using these models to predict plagioclase composition and temperature for these rocks are also shown in Fig. 5. Neither model matches perfectly the experimental data; SILMIN seems to give better agreement. Nevertheless, these two models both give better agreement than either

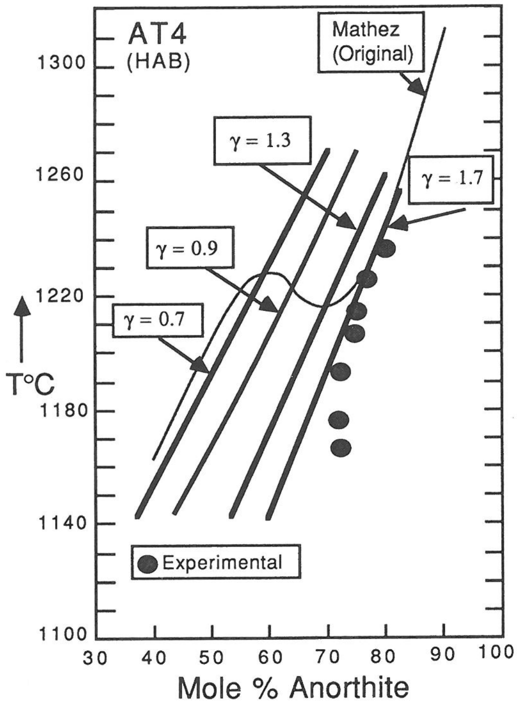

FIG. 6. The effect of varying γ in Mathez's geothermometer.

the Kudo-Weill or Drake models. The solidi slopes predicted by SILMIN and TRACE are generally close to those observed, but at lower temperatures they predict a flattening of the solidus (*e.g.*, see AT-4), which would give a stronger enrichment in the albite component, when in fact the solidus becomes vertical and plagioclase composition invariant with temperature. The liquidi predicted by these models are reasonably close except for CB-12 where SILMIN gives a strikingly low value.

Other compositions

As mentioned earlier, plagioclase-liquid composition data also exist for rocks from the Medicine Lake Highlands (GROVE *et al.*, 1982) and for rocks from the sea floor (MORB; WALKER *et al.*, 1979). Eight of these compositions, ranging from basalt to andesite are shown as Fig. 7. No single method works well for these additional compositions. The Kudo-Weill and Drake models match least well, TRACE and SILMIN overall match best, and Burnham's method gives an overall agreement intermediate to these two groups. The success of TRACE and SILMIN is partly artificial, however, because most of these data were used in calibration of these models (unlike the case of 4 Aleutian compositions). Whereas Kudo-Weill and Drake predict too albitic solid compositions, Burnham's method most often predicts too anorthitic compositions.

Overall ratings

Figure 8 shows an overall rating of each method for each group of rocks, and the following recommendations are made for use of these geothermometers for low pressure, dry conditions.

1. For high alumina basalts, use Burnham, SILMIN, and Mathez-prime (with $\gamma = 1.7$).
2. For basaltic andesites (52–55% SiO_2) use Kudo-Weill, Drake, SILMIN, TRACE, and Mathez-prime ($\gamma = 1.3$).
3. For andesites (>56% SiO_2) use TRACE, Kudo-Weill, Drake, SILMIN and Mathez-prime ($\gamma = 0.7$).
4. For "normal" oceanic tholeiites, use those enumerated in 1 above.
5. For Fe-Ti enriched tholeiites, use SILMIN, TRACE, and Mathez-prime ($\gamma = 1.1$).

Throughout this list, however, the success of Mathez-prime is principally due to a judicious choice of the adjustable parameter (γ) and these values are so mentioned essentially as calibration factors for these compositions. The suggested approach in using these methods is to use the whole rock composition as the initial liquid composition and make a T-X_{An} plot for plagioclase composition from which the observed plagioclase compositions can be used to infer temperature. Those recommended above should, by this means, give temperatures accurate to ±30°C.

EFFECTS OF PRESSURE AND WATER ON PLAGIOCLASE COMPOSITION

The effect of water, and pressure in general, on plagioclase composition is of much concern in light of the frequent appeal to these parameters to explain the mineralogy of arc lavas. This subject is explored here analytically using Burnham's model and numerically using SILMIN.

Anhydrous melts

The liquidi for AT-4 (basalt) and CB-12 (andesite) were calculated using Burnham's method and they are shown by Fig. 9. This gives a liquidus, which may not be the true rock liquidus, of constant plagioclase composition. At lower temperatures a slope of 14% (mole) decrease in An-content per 100°C

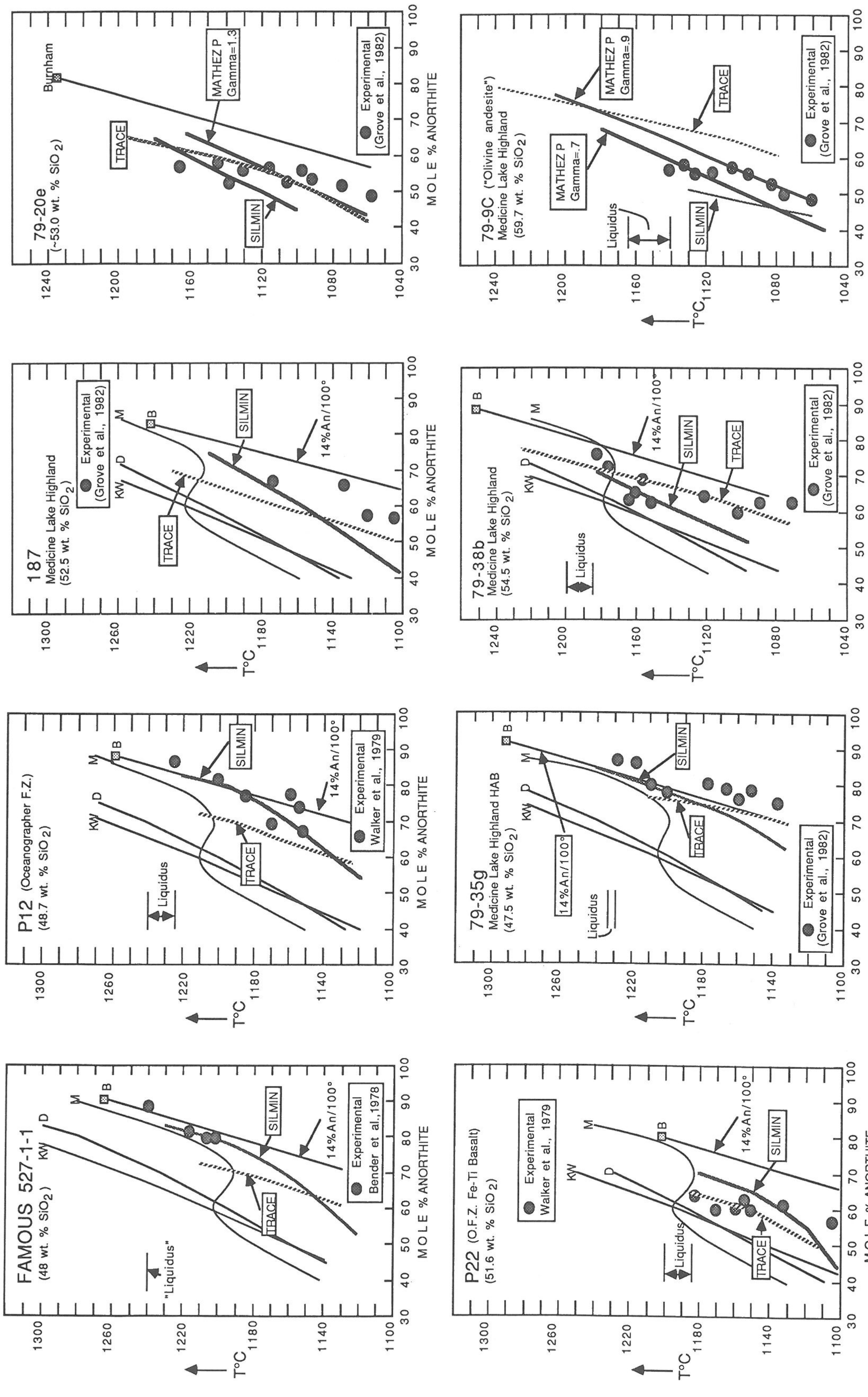

FIG. 7. Comparison of geothermometers with experimental data for rocks from other experimental studies as noted on each subfigure. The liquidus is indicated as an interval, between the lowest temperature with no reported crystals, and the temperature of first reported/analyzed plagioclase crystals.

	Kudo-Weill	Drake	Mathez	Mathez Prime	Smith	Burnham	Ghiorso	Nielsen
High Al Basalt								
High T	▬	○	◒	●	▬	●	●	⊙
Low T	▬	▬	▬	⊙	▬	●	◒	◒
Basaltic Andesite								
High T	⊙	◒	◒	●	▬	●	●	●
Low T	▬	○	▬	⊙	▬	●	⊙	◒
Andesite								
High T	●	●	○	●	⊙	⊙	●	●
Low T	⊙	⊙	○	⊙	▬	⊙	⊙	●
MORB								
Normal	▬	▬	◒	◒	○	●	●	⊙
FeTi	⊙	⊙	⊙	●	▬	○	●	●
Medicine Lake								
High Al Basalt	▬	▬		◒		◒	◒	○
Basaltic Andesite	⊙	⊙		◒		⊙	◒	●
Andesite	●	●		●		▬	○	○

RATING
● ± 20°C
◒ ± 40°C
⊙ ± 60°C
○ ± 80°C
▬ > 80°C

FIG. 8. Rating chart of performance of various geothermometers (across the top) when applied to experimental results for various melt compositions (left column). The various symbols indicate the closeness of fit to the experiments (*e.g.*, ±20°C).

was assumed for all pressures. The compositional contours thus necessarily assume equilibrium crystallization. SILMIN for this same calculation gives a slightly less steep liquidus slope and the liquidus plagioclase with increasing pressure decreases in An-content by about 15% (mole) per 10 kb increase in pressure. The decrease in An-content with temperature is essentially the same as given by Burnham's method, which is no surprise considering the agreement in slope with that found experimentally (*e.g.*, Fig. 5).

A comparison of experimentally determined liquidi slopes (*e.g.*, Mt. Hood andesite, EGGLER and BURNHAM, 1973) with those calculated here shows them to be close to that given by SILMIN. Adopting the SILMIN *P-T* liquidus slope throughout shows that the constant composition liquidi calculated using Burnham's method cut across the SILMIN liquidus and thus suggest a liquidus plagioclase composition that decreases in An-content by ~5% (mole) per 10 kb increase in pressure. On this account, the constant composition liquidi of Fig. 9 are probably only a close approximation to the true liquidus plagioclase composition (*i.e.*, within ~ ±2.5% An).

As seen earlier in the experiments on AT-4, however, if plagioclase crystallizes to a low enough temperature, it will exhaust the melt of one or more components critical to forming plagioclase and plagioclase crystallization will cease. Below this temperature crystal composition becomes invariant with decreasing temperature. The point below the liquidus at which this happens is given by the width of the solidus-liquidus loop in the pseudo-binary for the melt composition in question. As might be expected, the loop width increases (at 1 atm) in direct proportion to the increase of ab-component in the melt. That is, as $X_{ab}^{m} \rightarrow 0$, the loop width $\Delta W \rightarrow 0$. This variation in ΔW with melt composition for these experiments is shown by Fig. 2, and the approximate *P-T* boundary below which the plagioclase composition becomes invariant is indicated on the *P-T* diagrams of Fig. 9. The stability fields of other phases (*e.g* olivine and clinopyroxene in AT-4 and ortho- and clinopyroxene in CB-12) must be calculated independently.

Hydrous melts

Phase diagrams for compositions AT-4 and CB-12 containing various amounts of water are also shown by Fig. 9 as calculated using Burnham's method. It is interesting to note in these *P-T* diagrams that the plagioclase composition is constant along each solubility isopleth. Notice also that at constant pressure, as the water content is increased the composition of plagioclase on the liquidus (the temperature of which decreases with increasing X_{w}^{m}) gets *slightly* more anorthitic. The liquidus pla-

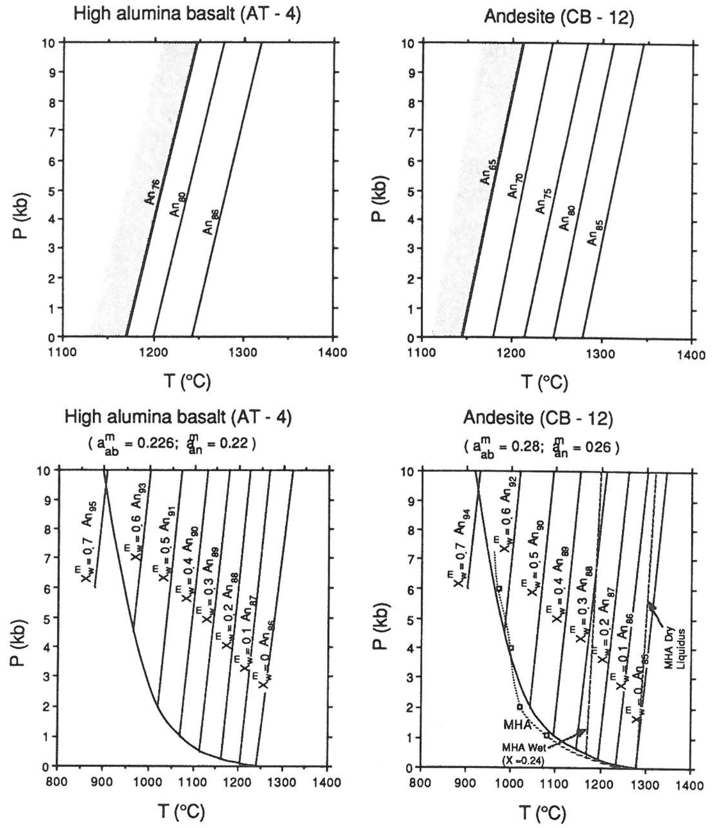

FIG. 9. The *upper* diagrams show the variation with pressure and temperature of the composition of plagioclase for rock compositions AT-4 (basalt) and andesite (CB-12) free of water as calculated using Burnham's method. The shading indicates the point at which the melt is exhausted of plagioclase component, provided that no other solid phases exist, and within which plagioclase composition is invariant with further decreases in temperature. The *lower* diagrams illustrate the same calculation involving the liquidus only and showing the effect of increasing amounts of water. The mole fraction of water in the melt and the composition of the plagioclase in equilibrium with this melt is shown against each line. The experimentally determined liquidus for the Mt. Hood andesite (MHA; EGGLER and BURNHAM, 1973) is also shown (normalized to the CB-12 liquidus). Notice that the plagioclase composition increases in anorthite component at about 1 mole% per 10% (mole) increase in melt water content.

gioclase composition becomes about 1% (mole) more anorthitic per 10% (mole) increase in water content (*i.e.*, $\partial X^{c}_{an}/\partial X^{m}_{w} \approx 0.1$). To increase the liquidus composition from, say, An_{80} to An_{85}, 50% (mole) water must be added to the original melt.

The Mt. Hood andesite studied by EGGLER and BURNHAM (1973) is similar overall to CB-12 and two of these liquidi at $X^{m}_{w} = 0$ and 0.24 are also plotted on the *P-T* diagram for CB-12. For the purpose of comparison, the dry liquidus at $P = 1$ atm for the Mt. Hood andesite has been set equal to that of CB-12, and the values of X^{m}_{w} for the Mt. Hood andesite have been calculated with a mean molecular weight of the melt of 279 grams for $X^{m}_{w} < 0.5$ (BURNHAM, 1975).

It is clear from this comparison that, although the measured liquidus is not of constant plagioclase composition, to pressures of 10 kb it is within about 5% An(mole) of being so. It is also clear that although a relatively small amount of water ($\approx$10% (mole)) significantly lowers the liquidus temperature, the initial plagioclase composition is only slightly increased (1% An). The saturated liquidus of MHA agrees well with that calculated and, considering the uncertainty of the experimental liquidus at $X^{m}_{w} = 0.24$, so does this liquidus. Considering the difference in composition between CB-12 and the Mt. Hood andesite, this agreement is good.

Similar modeling using SILMIN shows that at any pressure adding 1.0% (wt) water to AT-4 depresses the plagioclase liquidus by 100°C and *decreases* the liquidus An-content by about 3% (mole). The possible increase in An-content by adding water is evidently almost equally offset by the strong lowering of the liquidus itself.

Although the two methods of calculating plagioclase composition disagree as to the direction of shift, there is good agreement that the influence of water on plagioclase composition is small. For the amounts of water considered reasonable in most arc magmatic systems, water should have little if any effect on plagioclase composition.

COOLING HISTORY OF THE LAVAS

At the onset of this study we mentioned as a motivating factor the need to explain the plagioclase compositions of basaltic to andesitic lavas of island arcs, such as those of the Aleutians used in this study. It is therefore of some importance to present the actual compositions of plagioclase found in these rocks and understand them in light of the foregoing presentation. Representative profiles of compositional zoning of plagioclase phenocrysts in these lavas (Fig. 10) show that all phenocrysts in each lava are not identical. The phenocrysts do show however some common characteristics both within a single lava and among the suite itself. For example, the often strong change toward a more albitic composition near the rim most probably reflects the rapid cooling upon eruption. But overall it is the range of average compositions that requires explanation.

High An content

At their respective liquidi, either dry or with a reasonable amount of water (*i.e.*, < ~1 wt%), the experimental (and calculated) plagioclase compositions fall among those observed in the rocks. They are, however, generally less anorthitic than the most-anorthitic phenocryst composition observed. Generally this difference is about 5% (An) or less, but lava AT-4, for example, shows an experimental liquidus composition of about An_{80} whereas the observed compositions can reach about An_{90}. The experimental An-content can be increased in several ways: (1) water can be added to the melt; (2) the rock's liquidus can be raised by adding alumina; or (3) the soda content of the rock can be reduced. (Note that loss of soda in any experiment only increases the difference.)

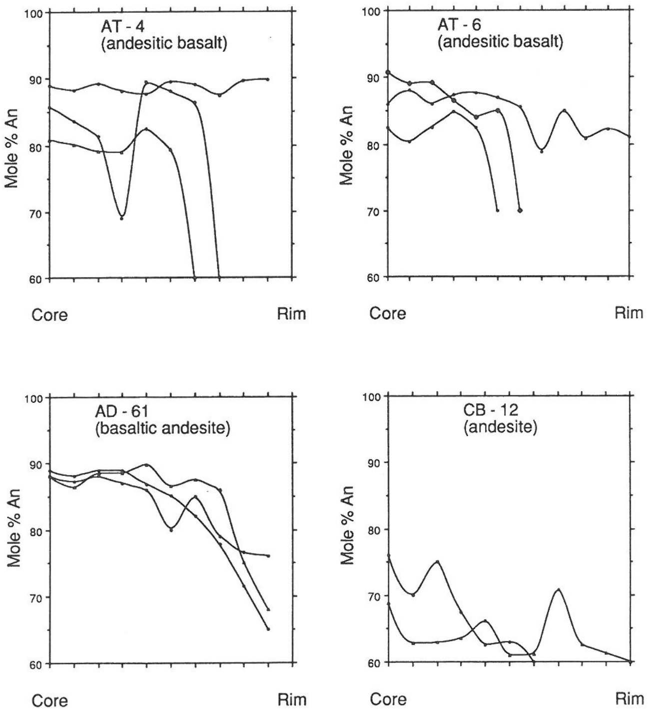

FIG. 10. Observed plagioclase phenocryst compositions found in the starting material lavas. The horizontal scale generally represents an actual distance of 1–2 mm.

(1) *Water.* To increase the crystal composition by 10% (mole) An, over 80% (mole), equivalent to $\approx$25 wt.%, water must be added to the melt. The addition of a more sensible amount of, say, 2 wt.% ($\approx$8% (mole)) water increases the An-content by only 2% and this is clearly inadequate. (For conversion of wt.% to mole% water use BURNHAM's (1979) Equations (16-5; 16-6) or his Fig. 16-4.)

(2) *Alumina* and (3) *soda.* On the other hand, to raise the An-content by 10%, either about 1 wt.% soda must be removed from the melt or its liquidus temperature (*i.e.* alumina content) must be raised by about 75°C ($\approx$4 wt.% Al_2O_3). The most reasonable solution is to lower the soda content by, say 0.5 wt.% and raise the alumina content by about 2 wt.%, which can be accomplished by replenishing the magma with plagioclase lost through crystal fractionation. Introduction of a realistic amount of water (*i.e.* 1–2 wt.%) adds another 1–2% An to the liquidus phase. This strongly suggests that AT-4 has suffered a loss of plagioclase that has increased the original soda content and decreased the original alumina content. (In fact, among this suite of lavas AT-4 is unusually low in alumina.)

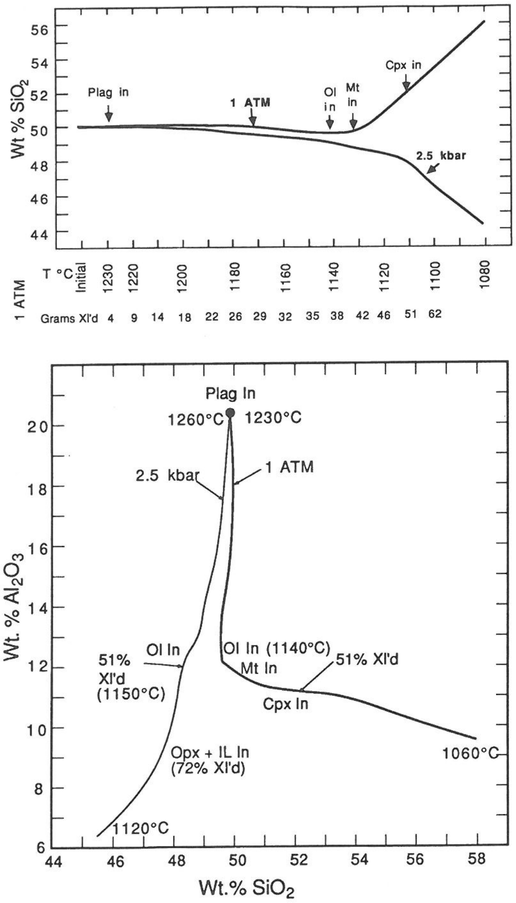

FIG. 11. *upper figure:* The change in silica content of the melt as a function of temperature and fractionation of plagioclase at pressures of 1 atmosphere (upper curve) and 2.5 kb (lower curve). *lower figure:* The variation of alumina with silica content for plagioclase fractionation. Notice that, depending on the exact plagioclase composition, the melt may become either richer or poorer in silica. All calculations were made using SILMIN (GHIORSO *et al.*, 1985).

Upon closer inspection, this result for AT-4 may be a rather general conclusion. That is, a rock whose experimental (or calculated) plagioclase composition is *less* anorthitic than that of the actual phenocrysts has probably suffered plagioclase loss. On the other hand, if a rock represents an accumulation of plagioclase from more primitive melts (as is often suspected), the liquidus temperature will be high, the soda content low (relative to that of the closed system) and more important, the experimental (or calculated) plagioclase composition will be *more* anorthitic than that of the actual phenocrysts themselves. This assumes that the phenocryst composition records both the present and earlier melt compositions. The earlier history can only be recorded if the phenocrysts are slow to re-equilibrate with the changing composition of the melt.

Zoning

The ability of a zoned crystal to homogenize itself or equilibriate with surrounding melt depends critically on the rate of intra-crystalline diffusion. If charge balance is to be maintained, plagioclase homogenization is by coupled diffusion involving Na-Si and Ca-Al (GROVE *et al.*, 1984). The rate of diffusion may therefore depend on the rate of the slowest moving element, which is presumably Al. The diffusivity of Na, for example, in plagioclase is about 10^{-9} cm^2/s at 1000°C (FOLAND, 1974). If diffusion and homogenization are controlled by this element, a crystal with zones 10^{-2} mm thick will homogenize in a few days. This is probably the case for alkali feldspars (involving only Na-K exchange) that are commonly unzoned in lavas with coexisting zoned plagioclase. Even in slow cooling plutons, plagioclase often shows zoning (VANCE, 1962). This feature can be used to infer that the diffusivity (*D*) of Al in plagioclase must be extremely small. It is straightforward to calculate that for a pluton taking 10^6 years to cool, $D < \sim 10^{-16}$ cm^2/sec. By similar reasoning MORSE (1984) has also suggested a very small diffusivity of Al in plagioclase. It is therefore reasonable that plagioclase in lavas may record its previous history of contact with melts of a variety of compositions.

With the experimental determination of the plagioclase binary by BOWEN (1913) came many schemes to explain the zoning patterns in plagioclase. Nearly every scheme discussed today can be traced to early works by BOWEN (1928), HARLOFF (1927), HILL (1936), and PHEMISTER (1934). These have been critically discussed by VANCE (1962) and PRINGLE *et al.* (1974) and recently more quantitatively by SIBLEY *et al.* (1976) and HAASE *et al.* (1980), among others. The aim of these workers has been the explanation of oscillatory and normal zoning. We can add little new to these general schemes, but from the computed phase diagrams we can however quantitatively examine zoning of plagioclase in arc rocks as influenced by changes in (1) temperature, (2) pressure, and (3) water saturation.

(1) *Temperature.* The effect of cooling or heating at constant composition, regardless of water content, is to increase the albite content by $\approx 14\%$ (mole) per 100°C drop in temperature. If equilibrium is not maintained and the early-formed crystals do not react with the melt, the increase in albite content will be greater. Large variations in composition ($\approx 40\%$ An) as observed in some ash flows (MOROHASHI *et al.*, 1974) and non-arc lavas (*e.g.*, LARSEN *et al.*, 1938; MYERS and MARSH, 1981) can hardly be produced by temperature variations alone. The thin albitic rims of Fig. 10 might reflect a severe drop in temperature upon eruption or, perhaps more likely, the onset of vigorous vesiculation and degassing during eruption (GHIORSO and CARMICHAEL, 1987).

(2) *Pressure.* In an anhydrous melt (Fig. 9), it is clear that a magma suddenly moving nearer to the earth's surface (on its way perhaps to eruption) will cool only adiabatically ($\approx 10°$C/5 kb) and thus remain essentially isothermal. But if the pressure is isothermally reduced by, say, 5 kb the crystal will become about 5% (mole) more anorthitic. Under disequilibrium conditions this will produce a reversely zoned crystal, which if repeatedly compressed and decompressed (perhaps due to convection) may become oscillatory zoned. Because the effect is not large, this adiabatic pressure shift will cause only moderate ($\approx 3\%$) reversed zoning and this cannot be a general explanation of oscillatory zoning. This effect may be evident in some of the profiles of Fig. 10. Similar results are found for periodic isobaric and isochoric (constant volume) crystallization by GHIORSO and CARMICHAEL (1987).

(3) *Water saturation.* Consider a magma initially undersaturated with water, say AT-4 of Fig. 9 where $X_w^m = 0.5$ and the liquidus plagioclase composition at 6 kb is An_{91}. As the magma moves along this liquidus to lower pressure, it will become saturated with water at 2 kb and with further decompression water will exsolve, X_w^m must decrease. With reduction of water in the melt (it must go to zero as pressure goes to 1 bar), the liquidus shifts to higher temperatures. If the temperature is maintained, the plagioclase becomes normally zoned. In fact, the heat of crystallization will raise the temperature somewhat but it will not reach the new liquidus. Once water saturation has occurred, the magma cannot again become undersaturated unless dry wall rock or drier magma is assimilated or the magma is carried deeper into the earth. Therefore, subsequent to saturation with water only normal zoning patterns can be produced. This feature has been well recognized before by VANCE (1962) among others and the point at which zoning changes from oscillatory or reversed to strongly normal may represent the onset of water-saturation in the melt. In practice, because lavas commonly contain an assortment of zoning patterns, with some crystals apparently from earlier melts, it is essential to identify those that belong to the present magma. The zoning patterns shown by these Aleutian lavas (Fig. 10) apparently represent crystallization during water-undersaturation.

SILICA VARIATION WITH PLAGIOCLASE FRACTIONATION

Because plagioclase composition is largely controlled by the soda content of the melt, crystals can form that contain more silica than their host magma. That is, if composition AT-4 contained, say, 3.0 wt.% or more soda instead of 2.42, its liquidus plagioclase would have a composition of about An_{75}, which contains about 50 wt.% SiO_2. Fractionation of this plagioclase would drive the magma to more silica-undersaturated compositions. Because with fractionation the soda content increases, the effect with time is amplified by the ever increasing difference between the silica content of the crystal and melt. A tholeiitic melt with plagioclase on the liquidus can thus be driven toward the composition of an alkali basalt. This process is in essence, akin to the "plagioclase effect" that promotes the peralkaline condition in salic lavas (*e.g.*, CARMICHAEL *et al.*, 1974). This silica condition has been apparently overlooked as it is found both in nature (MYERS and MARSH, 1981) and in the experimental products listed by WALKER *et al.* (1979) and BENDER *et al.* (1978). In each of these examples plagioclase crystallizes early and it is more siliceous than the melt. If this plagioclase is able to fractionate from the melt, the melt composition will become *less* siliceous. The condition, however, will reverse upon precipitation of olivine, which overrides the effect of plagioclase and increases the silica content of the melt. The important feature of this effect is that it is not safe to assume that calcalkaline magmas always fractionate towards increasing silica. Lavas placed in progression of ever-increasing silica (*i.e.* Harker variation diagrams) may not necessarily represent monotonically-increasing temporal samples of a fractionating magma.

This effect can be quantitatively investigated using SILMIN to follow the liquid composition during fractional crystallization of a high-alumina basalt. We have chosen a starting composition, (SH5; FOURNELLE, 1988) very similar to AT-6 where at 1-atm. the plagioclase ($\sim AN_{70}$) has a silica content ($\sim$50% wt.) almost equal to that of the rock itself. At a pressure of 2.5 kb the plagioclase is slightly less anorthitic and consequently has a silica content greater than the rock. The change in liquid composition with fractional crystallization at these pressures is shown by Fig. 11. Whereas at 1-atm. silica content increases with fractionation, at 2.5 kb the liquid composition decreases in both alumina and silica. In terms of silica alone, there is little overall change until about 50% fractionation, which reflects the initial compositional similarity. This need not generally be the case, because when the initial plagioclase is significantly more (less) silicious than the melt, strong changes in the melt composition will occur much earlier in the fractionation process.

CONCLUSIONS

Perhaps the most surprising result of these experiments is the finding that the plagioclase pseudobinary exists in these melts in close geometrical similarity to that of Bowen's true plagioclase binary. The slope of the experimental solidus in the pseudobinary is about 14% (mole) An per 100°C. The width of the liquidus-solidus loop varies (to a point) in direct proportion of the "albite" concentration of the melt. The position of the solidus is largely controlled by the soda (or normative albite) content of the melt, and the liquidus temperature varies directly (for the most part) with the alumina content of the melt. The plagioclase composition is well *approximated* by an apparent distribution coefficient (wt.%) of unity. The Kudo-Weill type plagioclase thermometer, which assumes essentially an equal influence of silica, alumina, lime, and soda on "plagioclase" activity in the melt, is insensitive in these rocks to the strong control of soda on plagioclase composition.

Because of this compositional dependence on normative albite (which is of course dictated by soda content) and the geometric similarity of the pseudobinary to the binary itself, the ideal solution model due to BURNHAM (*e.g.*, 1979) is well-posed to describe this equilibria. In this model the activity of "plagioclase" in the melt depends directly on the normative amount of albite (*i.e.* soda content) and agrees fairly well with the experiments. Additional advantages of the Burnham model are that it predicts both plagioclase composition and liquidus temperature at any water content at pressures to 10 kb. Ghiorso's SILMIN model is similarly useful and together the variation in plagioclase composition with temperature, pressure, and water content can be studied.

The liquidus of these rocks is within 5% (mole) An of being of constant composition to 10 kb. With increasing water the liquidus plagioclase becomes slightly more anorthitic at the rate of about 1% mole An per 10% (mole) increase in water. The often observed An-rich plagioclase of island arc rocks can not be explained simply by the addition of water to the melt because excessive amounts of water ($\approx$20 wt.%) are needed. Instead these anorthitic compositions probably reflect earlier equilibria in a low soda, high alumina melt. Because both the experimental and calculated plagioclase compositions for many arc lavas are less anorthitic than the observed phenocrysts themselves, these lavas must have experienced plagioclase *loss*. Their relatively high alumina and low soda contents must have been, respectively, slightly higher and lower in the more primitive parent. This strongly suggests that the high alumina character of arc rocks is a primitive feature of these melts. For if it were not, and the lavas represent plagioclase cumulates, the experimental and calculated plagioclase composition (in the basalts) should be more anorthitic than the actual phenocrysts themselves. The temperature associated with these anorthitic phenocrysts need not have been excessively high (*i.e.*, $\approx$1300°C), for addition of a sensible amount (1–2 wt.%) of water to the melt lowers the liquidus to 1200–1250°C, but hardly changes the liquidus plagioclase composition.

In terms of potential accuracy, because plagioclase composition is rather insensitive to temperature changes (*i.e.,* 14% mole per 100°C) it is not as useful a thermometer as might be expected.

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