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## Crystallization of Calc-Alkaline Andesite under Controlled High-Pressure Hydrous Conditions

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*Abstract.* A series of experimental runs has been conducted on a glass prepared from a natural island arc calc-alkaline andesite from Fiji. The crystallization sequence was determined for the pressure interval 9–36 kb under anhydrous conditions and with 2, 5, and 10% by weight of water carefully added.

Addition of water markedly lowers the liquidus, depresses the appearance of quartz and plagioclase in the crystallization sequence, and greatly enlarges the field of garnet-clinopyroxene crystallization above 25 kb. Amphibole crystallizes in hydrous runs up to 25 kb.

Electron microprobe analyses of critical phases allows calculation of controls on crystal fractionation trends. For hydrous conditions at 5–15 kb amphibole-clinopyroxene dominate fractionation and a moderate decrease in Mg/Fe and a slight increase in K/Na occurs. At 15–25 kb garnet also affects the fractionation and a moderate decrease in Mg/Fe and an increase in K/Na results. Above 25 kb garnet-clinopyroxene control the fractionation and there is a slight decrease in Mg/Fe but a significant increase in K/Na and a pronounced silica enrichment.

In terms of major element chemistry, the derivation of the Fijian dacites in the second period of eruption may be satisfactorily explained by the fractionation of hydrous andesite at pressures > 25 kb. Alternatively the dacites may result from lower degrees of melting of the down-going hydrous lithosphere. Similarly other members of this eruptive period may be derived according to a model of eclogite-controlled fractional melting or crystallization. Models involving amphibole fractionation at lower pressures are less satisfactory for explaining compositions in the Fijian second period of eruption, but in other environments models including amphibole-controlled fractionation may form part of a continuum of melting processes in subduction zones.

## Introduction

In recent years the concept of the new global tectonics has focussed attention on orogenic belts and island arc areas as zones of collision and consumption of the lithosphere. These zones are the sites of extensive magmatic activity involving addition of large volumes of material to the crust. In particular the calc-alkaline igneous rock series and the newly defined island arc tholeiitic series constitute the bulk of this activity (Jakes and Gill, 1970; Gill, 1970). Recent syntheses of models linking high pressure experimental results on fractionation of members of the calc-alkaline igneous rock suite (Green and Ringwood, 1968, 1969) with new geochemical results (Taylor, 1969; Taylor *et al.*, 1969) and discussions of subduction zones and island arc tectonics (Raleigh and Lee, 1969) have all concluded that a 2-stage model for the development of calc-alkaline rocks from the mantle is in best accord with the experimental and observational results. In the first stage basalts are erupted at the mid-ocean ridges, then are carried into the subduction zones of the continental margins or island arc areas, and finally undergo melting in the second stage to produce calc-alkaline magmas.

An important corollary of this model is that it provides a mechanism for the transport of water from the hydrosphere into the mantle (Ringwood, 1969). Water plays a significant role in the derivation and crystallization of magmas (Burnham, 1967; Brown and Fyfe, 1970). Hence it is of critical importance to investigate the effect of water on the crystallization and fractionation of calc-alkaline magmas at high pressures. Preliminary reconnaissance hydrous experiments at high pressure on high-alumina quartz tholeiite, basaltic andesite, andesite and dacite have been reported (Green and Ringwood, 1967, 1968). This work demonstrated

- (1) the key role of amphibole at low-moderate pressures,
- (2) a change in liquidus phase in dacite-rhyodacite compositions from quartz (anhydrous) to garnet (hydrous),
- (3) in the presence of water, the andesite liquidus no longer falls in a pronounced thermal valley between more basic and more acid compositions (Green and Ringwood, 1968; Fig. 8).

The present study investigates in detail the crystallization and fractionation of a calc-alkaline andesite under high-pressure hydrous conditions with known quantities of water present. It has the aim of determining the control water exerts on the temperature of melting and the nature of potential magmas produced in the subduction zone.

#### *Choice of Composition*

Recent geochemical work on Fiji (Gill, 1970) has provided the background for the choice of composition. Gill suggested that Fiji represents the development of an island arc passing through several geochemically distinct cycles of igneous activity. These cycles of activity may be summarized as follows—

- (a) island arc tholeiitic series—first period of eruption,
- (b) calc-alkaline series—second period of eruption,
- (c) shoshonitic series—third period of eruption.

A typical calc-alkaline andesite from the second period of eruption was chosen<sup>1</sup>. Slightly more mafic and more silicic members occur in this period of eruption. Thus the experimental work undertaken may be applied to test the possible links, through crystal fractionation processes, between the rock types of this calc-alkaline series, and also to determine the likely depth at which these processes occurred.

#### **Experimental**

The natural andesite was crushed, melted and quenched to a glass. This glass was subsequently checked for homogeneity by optical examination in immersion oils, and by electron microprobe analysis of fragments. The oxidation state, iron content and alkali element content were determined by chemical analysis (E. Kiss, A.N.U. analyst). The resulting composition obtained for the glass is given in Table 1, together with an analysis of the original sample (Gill, 1970). There is excellent agreement between the two analyses.

The high pressure experimental technique using a piston-cylinder apparatus is similar to that described by D. H. Green and Ringwood (1967) for anhydrous runs and by Essene *et al.* (1970) for hydrous runs. In the latter, 2, 5, or 10% by weight of H<sub>2</sub>O was added with

<sup>1</sup> Mr. J. Gill, Australian National University kindly provided a sample of specimen 68-66 (Gill, 1970).

Table 1. Comparison of analysis of andesite 68-66 (Gill, 1970) with glass prepared for this experimental work

	68-66	Glass	Glass (recalculated to 100%, values based on chemical analyses)
SiO <sub>2</sub>	59.39	60.27 <sup>a</sup>	60.24
TiO <sub>2</sub>	0.68	0.67 <sup>a</sup>	0.69
Al <sub>2</sub> O <sub>3</sub>	16.73	16.95 <sup>a</sup>	16.98
Fe <sub>2</sub> O <sub>3</sub>	3.66	0.87 <sup>b</sup>	0.88
FeO	2.61	5.28 <sup>b</sup>	5.35
MnO	0.13	0.13 <sup>c</sup>	0.13
MgO	3.08	3.30 <sup>a</sup>	3.14
CaO	7.12	7.34 <sup>a</sup>	7.22
Na <sub>2</sub> O	3.97	3.91 <sup>b</sup>	3.91
K <sub>2</sub> O	1.27	1.26 <sup>b</sup>	1.26
P <sub>2</sub> O <sub>5</sub>	0.20	0.20 <sup>c</sup>	0.20
Loss	0.55		
	99.39	100.18	100.00
Norms			
q	13.9	11.4	11.3
or	7.5	7.2	7.5
ab	33.6	33.0	33.1
an	24.1	25.1	25.0
di	7.9	8.2	8.0
hy	4.8	12.0	12.1
mt	5.3	1.3	1.3
il	1.3	1.5	1.3
ap	0.4	0.4	0.4

<sup>a</sup> Denotes content determined by electron microprobe analysis of glass fragments.

<sup>b</sup> Denotes content determined by chemical analysis (E. Kiss, A. N. U. analyst).

<sup>c</sup> Denotes content not determined; presumed same as analyzed in natural rock.

the aid of a microsyringe. A pressure correction of -10% to the nominal pressure was applied (Green *et al.*, 1966). For runs at temperatures less than 1100° C Ag-Pd capsules were used. Generally run times were between 12-24 hours for temperatures less than 950° C and from 6-12 hours at 950-1100° C. For temperatures above 1100° C Pt capsules were used and run times reduced to 1-4 hours (< 1300° C) or to less than 1 hour (> 1300° C).

At the conclusion of a run, the sample was examined optically and by X-ray diffraction. When crystal size was adequate, quantitative analyses of minerals present were obtained using an electron microprobe (A.R.L., EMX model) following the methods outlined by Sweatman and Long (1969) and Lovering and Ware (1970). The principal fractionation trends for differing pressures and water content were then determined, using these analyses.

## Results

The results for the crystallization of the andesite glass from 9-36 kb for anhydrous conditions and 2, 5, and 10% by weight of water added are summarized in Figs. 1-4.

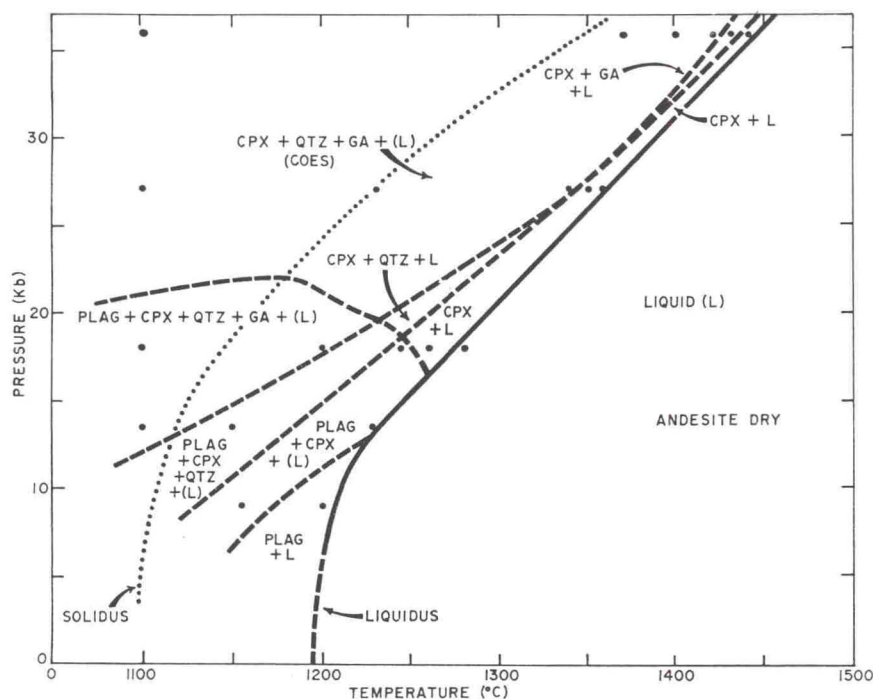


Fig. 1.  $P, T$  diagram for crystallization of andesite under anhydrous conditions (in this and subsequent  $P, T$  diagrams (1-4) solid points represent experimental runs, dashed lines the approximate phase boundaries, solid lines the liquidus and in Fig. 1 the dotted line denotes the approximate solidus. Abbreviations: *L* liquid; *plag* plagioclase; *cpx* clinopyroxene; *qtz* quartz; *coes* coesite; *ga* garnet; *amph* amphibole

Noteworthy features are as follows:

1. There is marked depression of the liquidus with the addition of water. This effect is most pronounced for the first small quantities of water added, e.g. the depression caused by the first 2% of water added is similar to the depression caused by the increase of water present from 5 to 10% by weight. This effect is clearly illustrated in Fig. 5. A separate vapour phase was identified in runs a few degrees below the liquidus at 9 kb with 10% of water present, but the composition was never saturated with water at the liquidus for the pressure range and water contents used in this study.

2. The liquidus phase changes with increasing water content. It is clinopyroxene between 18 and 36 kb (anhydrous), clinopyroxene between 9 and 27 kb (5%  $H_2O$ ) with garnet from 27 to 36 kb (5%  $H_2O$ ), and finally clinopyroxene between 9 and 22 kb (10%  $H_2O$ ) with garnet from 22 to 36 kb (10%  $H_2O$ ).

3. The appearance of quartz (or coesite) in the crystallization interval is markedly depressed below the liquidus at high pressures as water is added to the composition (see Fig. 6), e.g. at 36 kb quartz is present at  $<30^\circ C$  below the liquidus (anhydrous),  $250^\circ C$  below the liquidus (5%  $H_2O$ ) and about  $350^\circ C$  below the liquidus (10%  $H_2O$ ).

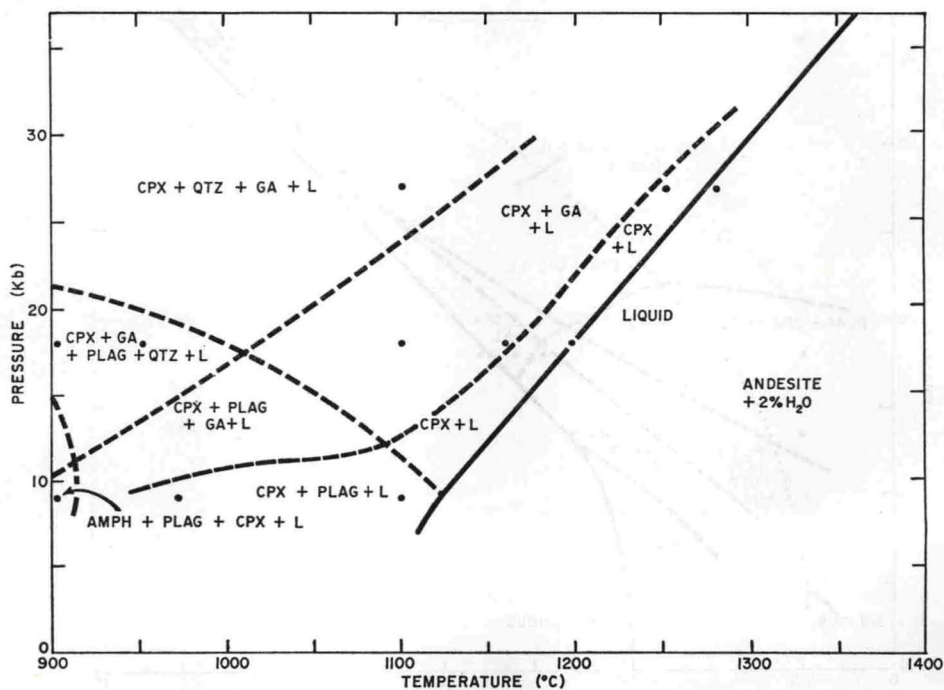


Fig. 2.  $P, T$  diagram for crystallization of andesite + 2% by weight of water

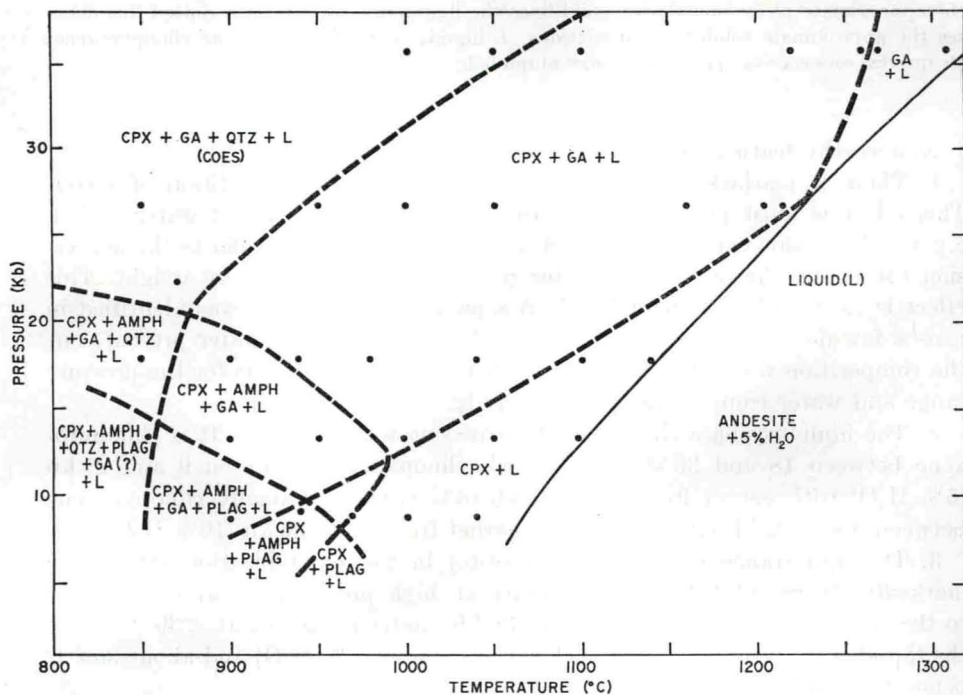


Fig. 3.  $P, T$  diagram for crystallization of andesite + 5% by weight of water

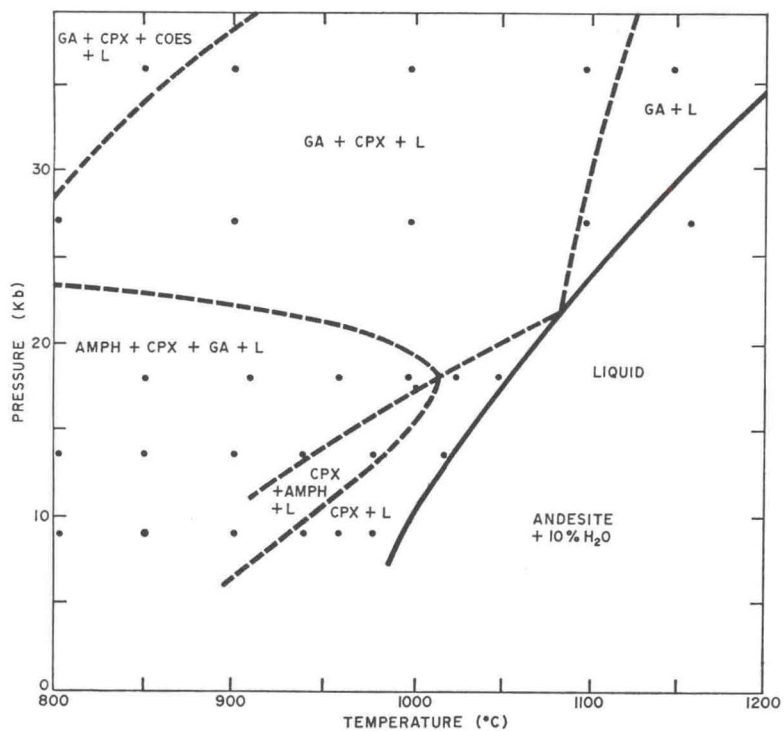


Fig. 4. *P, T* diagram for crystallization of andesite + 10% by weight of water

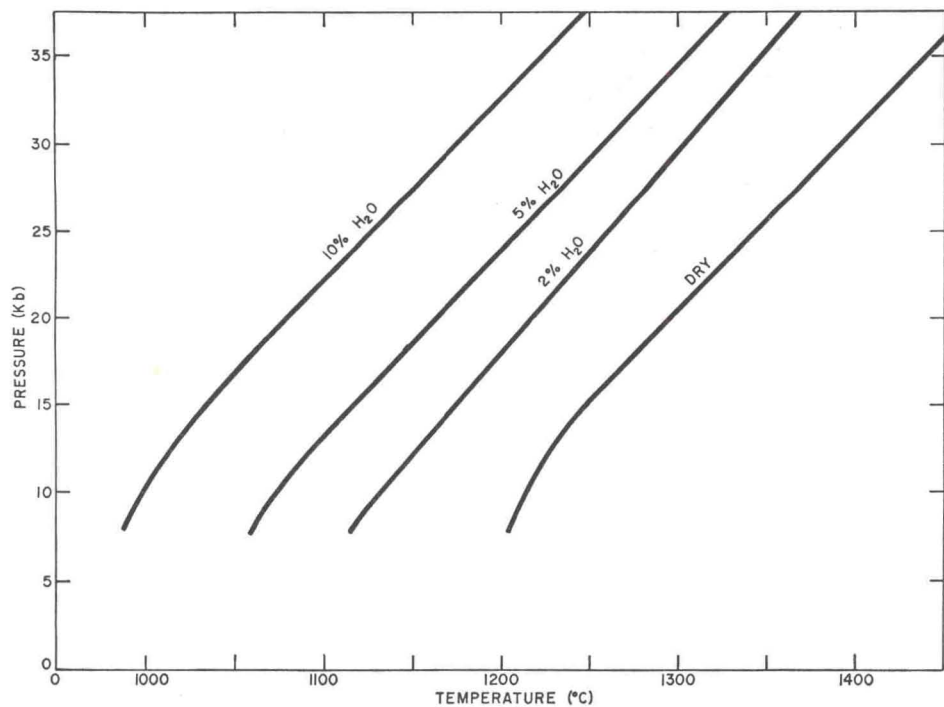


Fig. 5. *P, T* plot showing effect of addition of water on lowering the andesite liquidus

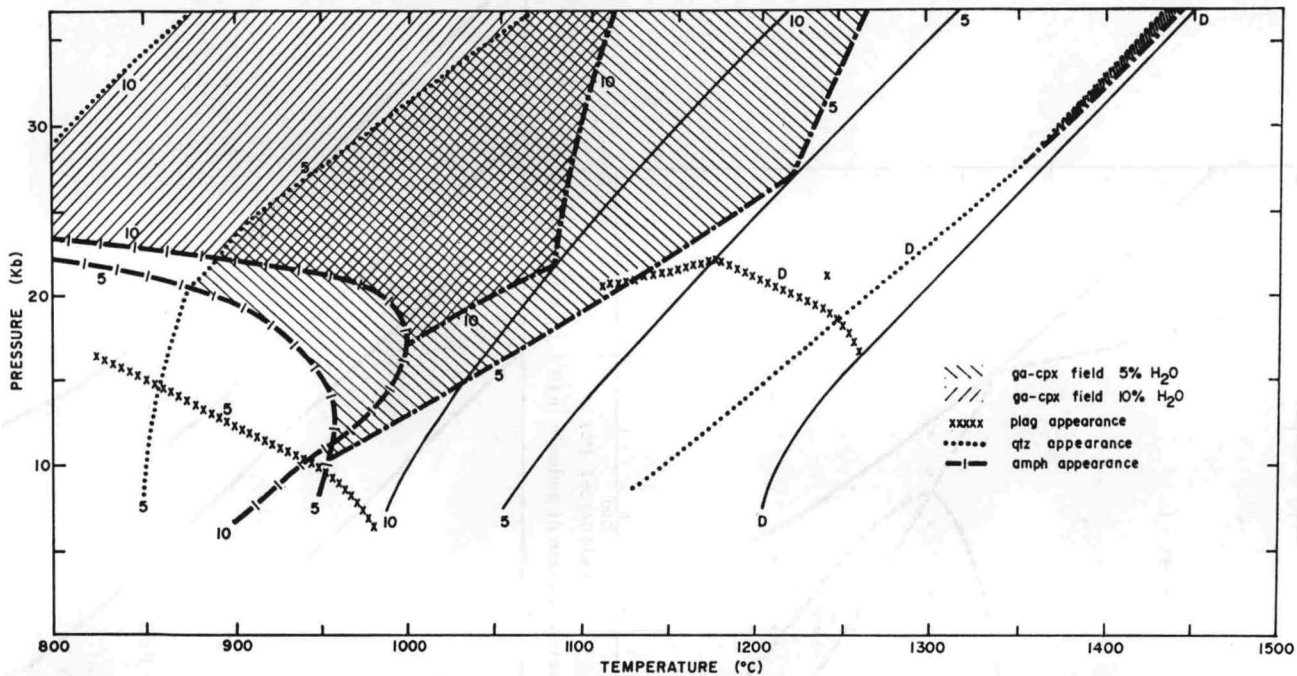


Fig. 6. Combined  $P, T$  plot for the anhydrous and hydrous runs showing effect of water on (a) enlargement of garnet-clinopyroxene crystallization field; (b) suppression of quartz, plagioclase appearance; (c) stability of amphibole. Note: numbers beside curves refer to water content applying to that particular stability curve

4. The depression of the appearance of quartz results in a significantly enlarged field of crystallization of garnet-clinopyroxene with increasing water content at pressures greater than 25 kb. This is clearly illustrated in Fig. 6.



5. In the garnet-clinopyroxene crystallization field the proportion of garnet relative to clinopyroxene increases with increasing pressure and with increasing water content.

6. The appearance of plagioclase in the lower pressure interval is strongly depressed by the addition of water. It is a liquidus or near-liquidus phase to nearly 18 kb (anhydrous) but only appears near the liquidus up to 9 kb (2% H<sub>2</sub>O). It is well below the liquidus at 9 kb (5% H<sub>2</sub>O) and does not appear in the crystallization sequence until 800° C at 9 kb (10% H<sub>2</sub>O) (see Fig. 6).

7. With the addition of >2% H<sub>2</sub>O amphibole becomes a significant phase in the crystallization interval at pressures up to almost 25 kb, particularly at temperatures of <950° C. It is stable to slightly higher temperatures at higher pressures with greater water contents (see Fig. 6).

8. The absolute limit of stability of amphibole in this composition, independent of the amount of water present, is not likely to exceed 25 kb. This is consistent with Lambert and Wyllie's results on amphibole stability in a quartz diorite composition with excess water (Lambert and Wyllie, 1970).

Quantitative results from electron microprobe analyses of garnets, clinopyroxenes, and amphiboles are summarized in Figs. 7-9.

#### *Garnet (Fig. 7)*

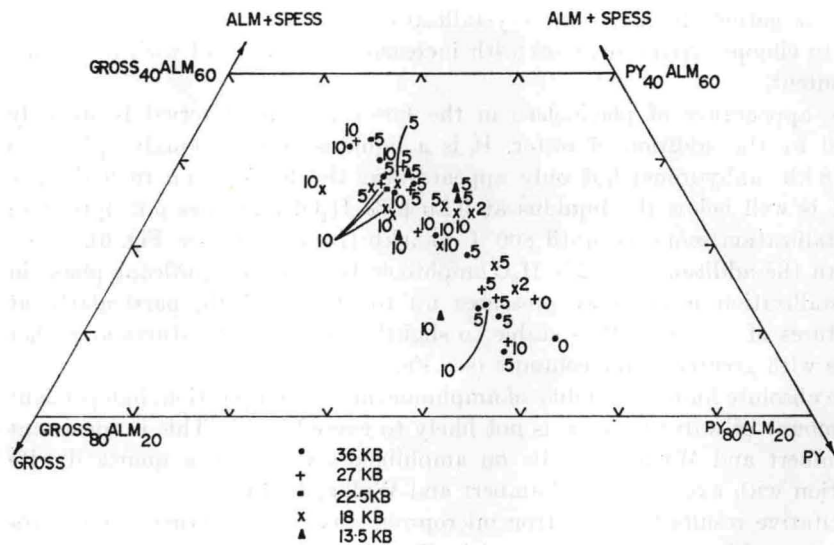
There is only a slight change of garnet composition with change in pressure or water content. This change consists of an increase in Ca and Fe/Mg ratio with increasing water content and an increase in Ca and decrease in Fe/Mg ratio with increasing pressure. With decreasing temperature at all pressures there is a pronounced increase in Fe, a moderate increase in Ca, and a marked decrease in Mg. The Mg/Fe ratio of garnet crystallizing is slightly greater than the Mg/Fe value for the co-existing glass. The partition of Mg between crystals and liquid favours garnet to a markedly smaller extent than clinopyroxene or amphibole. Thus, when garnet is an important crystallizing phase, it will only impose a small iron enrichment on crystal fractionation trends.

#### *Clinopyroxene (Fig. 8)*

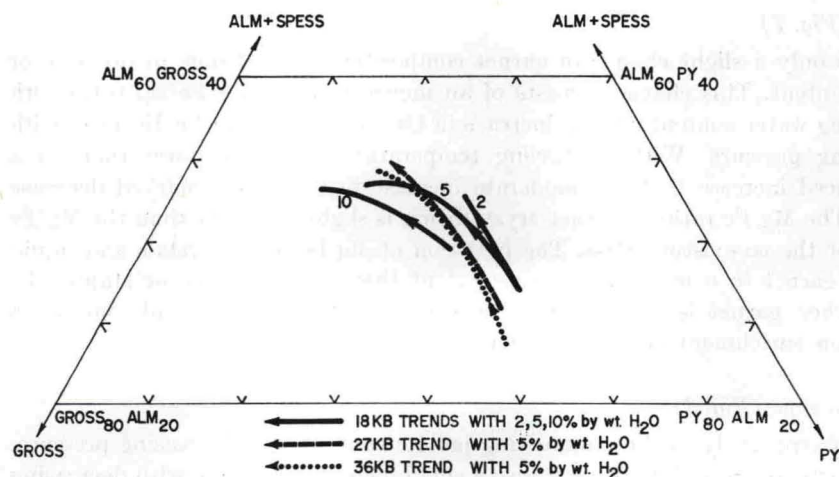
The pyroxene analyses show increasing jadeite content with increasing pressure, particularly above 18 kb. There is also a small increase in jadeite with decreasing temperature. The solubility of Tschermak's molecule in the pyroxene solid solution is strongly dependent on temperature and is indirectly affected by water content and pressure, since these variables dictate the temperature of appearance of pyroxene in the crystallization sequence. Thus, maximum solubility of Tschermak's molecule occurs at 9-18 kb in runs with low water content. The increasing solubility of orthopyroxene in the clinopyroxene solid solution with increasing temperature is illustrated in Fig. 8b. The Mg/Fe ratio of clinopyroxenes analyzed is always greater than the ratio for the andesite starting composition.

#### *Amphibole (Fig. 9)*

The amphibole analyses do not show any significant trends over the *P-T* range where analyses were obtainable. They plot in the field of magnesio-hornblende



a



b

Fig. 7. a Garnet composition diagram showing analyses of garnets from experimental runs. The numbers beside each point refer to the water content of that particular experiment. *Gross* grossularite, *py* pyrope, *alm* almandine, *spess* spessartine. b Garnet composition diagram showing clear trends with decreasing temperature and possible minor trends of increasing grossular content with increasing pressure and water content. The almandine/pyrope ratio increases with increasing water content and decreasing pressure (a reflection of the lower temperature of near-liquidus crystallization accompanying increase in water content and decrease in pressure)

towards the ferro-tschermakitite corner (Leake, 1968). They also have a significant Ti content. The Mg/Fe ratio is slightly greater than that for the andesite starting composition, but is always less than that found in co-existing clin-

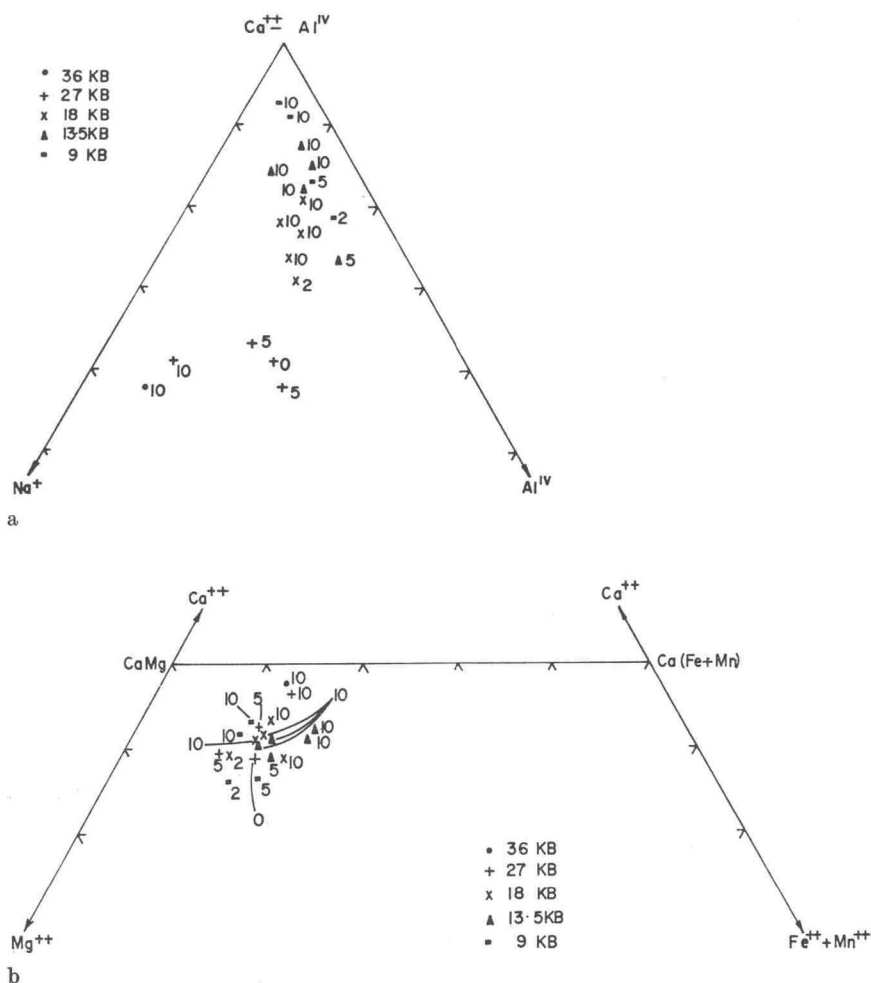


Fig. 8a and b. Pyroxene compositional diagrams (atomic %) showing compositions of pyroxenes analyzed from experimental runs. Numbers beside each point refer to the water content of the charge from which that pyroxene crystallized

pyroxene. The K/Na ratio of the amphibole is slightly less than the same ratio in the starting composition.

#### Discussion of Equilibrium Problems

In runs at temperatures  $<900^{\circ}C$  and at pressures of 9 and 13.5 kb difficulty is experienced in nucleating garnet even over times of 24 hours. Thus with 10%  $H_2O$  garnet is observed in a run at  $940^{\circ}C$ , 13.5 kb but does not crystallize at the same pressure at lower temperature ( $800-900^{\circ}C$ ). A large field of crystallization of amphibole occurs in this temperature range, but only minor amphibole is present with garnet at  $940^{\circ}C$ . This may indicate a reaction relation garnet +

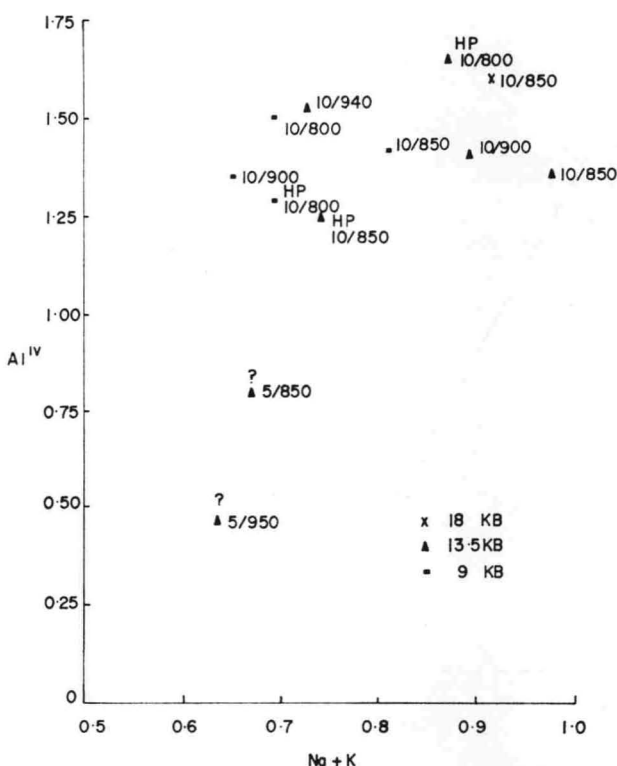


Fig. 9. Plot of atomic % of Al<sup>IV</sup> against Na+K for amphibole crystallizing from experimental runs. Numbers beside each point refer to water content and temperature. *HP* a run seeded with garnet and clinopyroxene

liquid  $\rightleftharpoons$  amphibole with decreasing temperature, or a nucleation problem as suggested above. To investigate this further a mix was prepared, consisting of 70% glass and 30% high pressure assemblage (derived from garnet-clinopyroxene-glass runs at 36 kb, 1000–1100° C, 10% H<sub>2</sub>O). 10% by weight of water was added to this and runs conducted at 9 kb, 800° C, 48 hours; 13.5 kb, 800° C, 71 hours; 13.5 kb, 850° C, 60 hours.

The products of these runs consisted of amphibole, clinopyroxene, garnet and glass. Garnet occurs in both euhedral and fragmental habits. X-ray powder patterns demonstrate it has increased in amount, relative to the proportion present in the starting mix. Analyses of the garnet show that it is zoned, indicating that complete equilibrium has not been attained. However, garnet crystallized at 13.5 kb, 800° C, has a higher average Ca, Fe content than garnet at 13.5 kb, 850° C, consistent with the trend in compositional changes with change in temperature (Fig. 7). This indicates an approach to equilibrium. Similarly, clinopyroxene crystals in the run at 13.5 kb, 800° C, have a lower Mg/Fe ratio and a higher Na content compared with crystals in the run at 13.5 kb, 850° C. This is also consistent with pyroxene trends in composition with changing tem-

perature (Fig. 8). Amphibole results from synthesis in all these garnet-clinopyroxene seeded runs, and does not show any consistent compositional trend. This is similar to amphibole crystallizing in unseeded experiments. One other feature of these seeded runs is the electron microprobe identification of a few crystals of sphene at 13.5 kb, 850° C. Sphene has not been identified in any other charge.

Thus, from these experiments, it is concluded that garnet is in fact stable in the hydrous andesite composition at 9–13.5 kb at temperatures from 800–900° C. Its absence in some of the synthesis runs is due to nucleation problems in the time interval allowed for these experiments.

#### *Controls on Fractionation Trends*

In island arc areas the Mg/Fe and K/Na ratios are important in characterizing the igneous rock sequences. The analyses of garnet, clinopyroxene, and amphibole in this work enable categorization of 3 main depth intervals of hydrous fractionation, resulting in different trends for these two ratios. These depth intervals correspond broadly to the following pressures:

(a) 5–15 kb. Fractionation involves mainly amphibole with subordinate clinopyroxene. It results in an Mg/Fe decrease and a slight K/Na increase since both phases have an Mg/Fe ratio less than the parent composition and amphibole has a K/Na ratio slightly less than the starting composition<sup>2</sup>.

(b) 15–25 kb. Amphibole, clinopyroxene and garnet all crystallize and influence fractionation trends, resulting in only a slight decrease in the Mg/Fe ratio (because of separation of Fe-rich garnet) and a moderate K/Na increase because of the subordinate role of amphibole containing some K).

(c) >25 kb. Garnet and clinopyroxene only crystallize. There is only a slight decrease in Mg/Fe but a strong increase in K/Na occurs (due to removal of sodic clinopyroxene). Also this "eclogite" controlled fractionation is most efficient for silica enrichment.

#### **Calculated Liquid Fractionation Trends**

Using the analyses of phases crystallizing in the three depth intervals it is possible to calculate compositions of liquids genetically related, through crystal fractionation, to the andesite starting composition. These compositions may then be compared with analyses of other members of the second period of eruption on Fiji (Gill, 1970, and pers. comm.) given in Table 2.

The calculated derivative compositions are given in Table 2 based on the analyses of phases obtained and approximate observed proportions of phases crystallizing in the experimental runs. The results obtained can be directly applied to obtaining the composition of more silicic fractionates (e.g. dacites) as shown in Table 2. This demonstrates that "eclogite" fractionation most satisfactorily explains the major element chemistry of the dacites, and suggests that they are derived through high pressure hydrous fractionation of a parent andesite or through low degrees of melting of hydrous eclogite.

<sup>2</sup> The Mg/Fe decrease may be reduced or eliminated if small amounts of magnetite (2% or less) also crystallize. An opaque phase could not be positively identified in the experimental runs.

Table 2. Typical analyses of rocks from the second period of eruption, Fiji (Gill, 1970 and pers. comm.) compared with calculated compositions derived by addition or subtraction of typical garnet and clinopyroxene crystallizing from andesite 68-66 at 36 kb 1000-1100° C, 10% H<sub>2</sub>O

	Ande- site 68-66	Dacite 874	68-66 less 5% garnet	68-66 less 15% garnet 12% clino- pyroxene	Basal- tic ande- site 876	68-66 + 15% garnet 5% clino- pyroxene	68-66 + 4% garnet 1% clino- pyroxene
SiO <sub>2</sub>	60.24	65.45	61.4	65.0	55.43	57.6	59.4
TiO <sub>2</sub>	0.69	0.52	0.66	0.56	0.82	0.7	0.7
Al <sub>2</sub> O <sub>3</sub>	16.98	16.59	16.7	17.0	18.05	17.4	17.1
FeO <sub>tot</sub>	6.14	3.86	5.6	3.4	8.03	7.5	6.5
MnO	0.13	0.09	0.11	0.08	0.13	0.2	0.14
MgO	3.14	1.59	2.8	1.7	4.26	4.1	3.4
CaO	7.22	5.17	7.0	5.2	8.36	8.1	7.5
Na <sub>2</sub> O	3.91	4.60	4.1	4.5	3.42	3.4	3.8
K <sub>2</sub> O	1.26	1.45	1.3	1.7	1.28	1.0	1.2

N. B. Such calculations can only be approximate, particularly in the case of addition of crystals—this modifies the bulk composition so that the compositions of crystals in equilibrium with this new parent liquid will differ from those in equilibrium with the andesite near its liquidus. Nevertheless these calculations demonstrate the adequacy of the garnet-clinopyroxene model for governing the observed fractionation trends in the second period of eruption.

Lower pressure fractionation models cannot explain the Al content or the Mg/Fe ratio of the dacite, unless plagioclase and magnetite are also removed. Removal of plagioclase and amphibole together in significant quantities is difficult since the water present necessary for the crystallization of amphibole inhibits the appearance of plagioclase (see Figs. 2-4). If essentially dry fractionation conditions are considered then plagioclase, clinopyroxene and magnetite would control the fractionation trends and ~3% magnetite must crystallize with the pyroxene to produce satisfactory Mg/Fe ratios in the derivative liquids. Such a model is not compatible with the work of Taylor *et al.* (1969).

To a limited extent the results can also be applied to determining possible fractionation models linking the andesite composition (68-66) with more mafic compositions in the second eruptive phase on Fiji. In this exercise small proportions of analysed phases are added to the andesite starting composition and the resulting bulk compositions compared with the natural rock compositions (Table 2). It demonstrates that the high pressure regime of fractionation (e.g. "eclogite") gives close compositional trends to the natural rocks.

Difficulties encountered with similar calculations in the lower pressure regime in the case where the water content is too low to stabilize amphibole include values for Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O which are incompatible with the observed content. Thus if plagioclase is added to satisfy the alumina requirements, Na<sub>2</sub>O then becomes too high (unless the plagioclase is more calcic than labradorite; this is unlikely if little water is present). Also magnetite must be added with the clinopyroxene to satisfy the Mg/Fe value. This is limited by the data of Taylor

*et al.* (1969). If water is present and amphibole crystallizes then addition of appropriate amounts of amphibole, pyroxene, calcic plagioclase and minor magnetite could satisfy the composition trends. However this model is not as efficient as the eclogite model and the suppression of crystallization of plagioclase in the presence of water makes it unlikely that sufficient of this phase could be available to satisfy the higher  $Al_2O_3$  content of the basaltic andesite compared with the andesite.

The eclogite model proposed satisfactorily explains the major element chemistry of the second period of eruption on Fiji. It remains to be seen whether the trace element distributions, in particular the rare earth elements, are also satisfied by the eclogite model. Thus because garnet readily accommodates the heavier rare earth elements, any fractionation process involving extraction of significant proportions of garnet to produce dacite from andesite, should result in a more fractionated rare earth pattern (enriched in light rare earth elements) in the dacite, when compared with the andesite pattern. Investigations are under way to determine if this is the case (Gill, 1971, pers. comm.).

### Conclusions

This experimental study illustrates the significant effect of the presence of water on the crystallization of a typical calc-alkaline andesite at high pressures. It is relevant to models for the derivation of andesite magma from partial melting of the downgoing hydrous lithosphere, an essential tectonic component in the concept of the new global tectonics. The study is based on a natural calc-alkaline andesite composition from the second period of eruption on Fiji (Gill, 1970) and may be applied directly to the interpretation of genetic links between rock types of differing chemistry occurring in this eruptive cycle.

The presence of increasing amounts of water (from 0–10% by weight) has a large effect on lowering the liquidus. This effect is most marked for the first few percent of water added. Thus the liquidus with 2% water present is about 100° C below the anhydrous value while with 10% water it is only lowered a further 150° C. In the present study from 9–36 kb, the water saturated state was not reached on the liquidus. However a separate vapour phase was observed a few degrees below the liquidus at 9 kb with 10%  $H_2O$  added.

This demonstrates the quite modest temperatures of 1200–1300° C at which an andesite magma may be obtained by melting in the presence of minor water at depths up to 120 km. When allied with the thermal models and associated melting postulated in a downgoing slab (Fitton, 1971) it is apparent that andesite magmas may only be derived in the upper kilometre of the slab, at greater than 60 km depth, unless magmas are derived with >10% water by weight. Fitton (1971) emphasized that such conclusions are based on several assumptions which may need refinement as more data become available. In particular, the rate of movement of the downgoing slab is critical.

Variation in fractionation controls with depth and water content are caused by the changing nature of the major crystallizing phases. Under dry conditions clinopyroxene and plagioclase dominate at low to intermediate pressures, changing to garnet, clinopyroxene and quartz at higher pressures. The early appearance

of quartz under anhydrous conditions at high pressure supports the conclusion of Green and Ringwood (1968) that the andesite liquidus occurs in a low temperature trough between more basic and more acid compositions at  $>25$  kb. Thus for these conditions it is impossible to obtain a liquid with more than about 62%  $\text{SiO}_2$  by partial melting of an eclogite parent. With the addition of water, the crystallization sequence changes markedly. At low pressure amphibole-clinopyroxene control the fractionation trends (plagioclase is depressed to near the solidus) giving some decrease in Mg/Fe (unless minor magnetite also crystallizes) and in K/Na. At intermediate pressures garnet, clinopyroxene and amphibole govern the fractionation trends and result in minor Mg/Fe decrease and moderate K/Na increase. At high pressure ( $>25$  kb) garnet and clinopyroxene control fractionation trends (quartz appearance depressed to near the solidus) producing marked increase in Si, K/Na but very little Mg/Fe decrease.

The latter fractionation model explains most satisfactorily the major element chemistry of rock types of the second period of eruption on Fiji. The major magma to be erupted is andesite. This may be derived by dry or near-dry melting of the under-thrust lithosphere (now eclogite) at depths of  $\sim 100$  km. The more acid fractionates may result from minor hydrous melting, or by hydrous fractional crystallization of an earlier derived andesite. The requisite hydrous conditions may well be obtained near the roof of some very deep-level andesite magma chamber, where water and other volatiles become concentrated. The eclogite model provides the most efficient mechanism for Si enrichment and can explain the Al and Mg/Fe values more satisfactorily than any model of fractionation at shallower levels.

When the results are viewed in terms of a coherent picture of magma genesis from the down-thrust lithosphere the following points may be made:

(1) The first stage of melting at depths of  $<80$  km involves hydrous melting of the upper part of the lithosphere; subsequent rise of this magma into the overlying pyrolite wedge instigates melting in this wedge, followed by deep-level mixing of magmas, producing members of the island arc tholeiitic series (Jakš and Gill, 1970). Simple melting of the pyrolite wedge cannot explain the trace element distribution in this series (Gill, 1970; Jakš and Gill, 1970). Fitton (1971) proposed that the breakdown and melting of amphibole in a hydrous amphibolitic lithosphere produced the island arc tholeiitic series. Analyses of amphibole in the present work and in Green and Ringwood (1968) indicate that the K/Na ratio for the amphibole is appropriate for this process. The difficulty with this proposal is that it would involve near complete melting of the lithosphere to produce the island arc tholeiitic series, where the most abundant rock type has a silica mode of 53% (Jakš and Gill, 1970).

(2) The second stage of melting of the now near-anhydrous lithosphere at  $>80$  km depth produces a typical calc-alkaline andesite, or, in local areas of hydrous melting (or crystallization), a dacite. Temperatures of  $>1300^\circ\text{C}$  are required to produce andesite under these conditions. This is high when compared with thermal models for the underthrust lithosphere (Oxburgh and Turcotte, 1969; Fitton, 1971).

(3) The final stage of melting occurs at  $>150$  km depth. This stage is still governed by eclogite fractionation, producing silica enrichment in this third



period of eruption (Gill, 1970). However, in rising from great depths and passing through maximum thickness of mantle [compared with stages (1) and (2)], there is greater scope for modification in the incompatible element composition (especially K) through processes involving wall-rock reaction, breakdown of phlogopite and the possible presence of an aqueous vapour phase (D.H. Green and Ringwood, 1967; Jakš and White, 1969; Lambert and Wyllie, 1970). This stage of melting may produce the high K-calc-alkaline series (e.g. Jakš and White, 1969; Jakš and Smith, 1970).

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