Crystallization of Calc-Alkaline Andesite

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_2O). It is well below the liquidus at 9 kb (5% H_2O) and does not appear in the crystallization sequence until 800° C at 9 kb (10% H_2O) (see Fig. 6).

7. With the addition of >2% H₂O amphibole becomes a significant phase in the crystallization interval at pressures up to almost 25 kb, particularly at temperatures of $<950^{\circ}$ 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

T. H. Green:



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-tschermakitic 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 clino-

158