DAVID H. EGGLER *Geophysical Laboratory, 2801 Upton Street, Washington, D.C. 20008*

C. WAYNE BURNHAM *Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802*

Crystallization and Fractionation Trends in the System Andesite-H_2O-CO_2-O_2 at Pressures to 10 Kb

ABSTRACT

Phase relations of a Mount Hood andesite, which has the composition of an average orogenic andesite, have been determined as a function of O_2 fugacity at 1 atm and of H_2O fugacity to pressures of 10 kb, at O_2 fugacities of the quartz-fayalite-magnetite (QFM) buffer. All runs contained either a H_2O or H_2O–CO_2 fluid phase; melts in runs with a H_2O–CO_2 fluid phase were H_2O undersaturated. The H_2O contents of the melts and H_2O fugacities were calculated from $NaAlSi_3O_8$–H_2O thermodynamic data on the assumption of ideal mixing in the system H_2O–CO_2.

One-atmosphere runs show that melting relations of silicates are little affected by f_{O_2}, but that both ilmenite- and magnetite-out temperatures are raised by higher f_{O_2}. Ilmenite precipitates at higher temperature than magnetite. In these runs and in all runs at high pressure with H_2O and H_2O–CO_2 fluid phases, oxides were not stable at temperatures of the silicate liquidus. Oxides might be stable on the silicate liquidus if f_{O_2} rose two or more log units above the Ni–NiO (NNO) buffer. However, calculations indicate that in natural magmas, those processes which might change f_{O_2}—crystal-liquid equilibria or exchange of H_2, or H_2 and H_2O with the wall rocks—cannot raise f_{O_2} by that magnitude. Because differentiation of basalt melts to andesite must involve iron-rich oxide phase subtraction, such fractionation models appear unreasonable.

For the Mount Hood andesite composition, plagioclase is the liquidus phase under H_2O–saturated conditions to 5 kb and under H_2O–undersaturated conditions at 10 kb when the H_2O content of the melt is less than 4.7 wt percent. For higher H_2O contents, either orthopyroxene or, at H_2O saturation at pressure greater than 8 kb, amphibole assumes the liquidus. In all cases, clinopyroxene crystallizes at lower temperature than orthopyroxene. Melting curves in the H_2O–undersaturated region may be contoured either as percent H_2O in melt or as $P_{e_{H_2O}}$; in either case, the topology of the various silicate melting curves is different from the case of H_2O–saturated melting. Therefore, melting relations determined at H_2O–saturated conditions cannot be used successfully to predict melting relations in the H_2O–undersaturated region.

Amphibole melting relations were studied isobarically at 5 kb as a function of temperature and fluid-phase composition. Amphibole has a maximum stability temperature of 940 $\pm$ 15°C for fluid compositions of 100 to 44 mole percent H_2O; for fluids containing more CO_2 than 56 percent (or, equivalently, less than 4.4 wt percent H_2O in melt), the melting temperature is lower. The same relations would be seen if CO_2 were not present and the melt were H_2O undersaturated. These rather low melting temperatures, relative to other silicate phases, preclude andesite generation by basalt fractionation involving amphibole at pressures less than 10 kb.

INTRODUCTION

Until the last few years, andesites have been regarded as the products of fractional crystallization of basaltic magma at crustal pressures. A particularly elegant model was proposed by Osborn (1959). More recent petrologic research has centered on mechanisms involving partial melting in the mantle, among them hydrous melting of basalt, leaving a residuum mainly of amphibole and aluminous

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pyroxenes (Green and Ringwood, 1968; Holloway and Burnham, 1972), dry melting of quartz eclogite (Green and Ringwood, 1966), and hydrous melting of peridotite (Yoder, 1969; Kushiro, 1972).

To test the fractionation hypothesis and the reasonableness of hydrous conditions postulated by several other hypotheses, phase relations of an andesite from Mount Hood, Oregon, were determined under conditions of controlled temperature, total pressure, and fugacities of the volatile species H_2O, CO_2, H_2, and O_2. Owing to the difficulty of interpreting the results when all the above parameters are varied simultaneously, three separate experimental situations were investigated. First, temperature and f_{O_2} were varied at a total pressure of 1 atm, primarily to examine the stability of oxide phases in andesite melts. Second, phase relations of melts saturated with H_2O were studied from 1 to 10 kb, at f_{O_2}'s defined by the QFM buffer. Finally, melts undersaturated with H_2O were studied at the same total pressures and the same f_{O_2} buffer. H_2O undersaturation was achieved by diluting the fluid phase with CO_2.

WATER-SATURATED AND UNDERSATURATED MELTING

The maximum solubility of H_2O in andesite and basalt melts is a function primarily of pressure (Hamilton and others, 1964), and the amount of H_2O in a melt at any temperature and total pressure is directly related to the fugacity of H_2O in the system (Burnham and Davis, 1971). A melt saturated with H_2O coexists with a fluid phase consisting essentially of H_2O, because the mole fraction of dissolved silicates is negligibly small at crustal pressures. The f_{H_2O} in that melt, $f^m_{H_2O}$, equal to fugacity of H_2O in the fluid, $f^{fl}_{H_2O}$, is therefore only slightly less than the fugacity of pure water ($f^\circ_{H_2O}$) at the same temperature and total pressure. For practical purposes, then, H_2O saturation may be defined by the condition that $f^m_{H_2O} \approx f^\circ_{H_2O}$, whereas H_2O undersaturation is defined by the condition that $f^m_{H_2O} < f^\circ_{H_2O}$ at the same temperature and total pressure.

Although the condition of H_2O undersaturation is defined in terms of $f^m_{H_2O}$, we shall also use the terms $X^{fl}_{H_2O}$, the mole fraction of H_2O in a fluid phase, which is directly related to $f^m_{H_2O}$, and P_{eH_2O}, which by definition

is related to $f^m_{H_2O}$. The condition of H_2O undersaturation is also defined by $X^{fl}_{H_2O} < 1$ and $P_{eH_2O} < P_{total}$.

When H_2O is the only volatile species, no fluid phase coexists with an H_2O–undersaturated melt. When a second volatile species exists which is insoluble in the melt, a fluid phase must *always* be present, and H_2O is partitioned between the melt and fluid, so that $f^m_{H_2O} = f^{fl}_{H_2O} < f^\circ_{H_2O}$.

Such a melt is always H_2O undersaturated by definition. CO_2 is essentially insoluble in granitic melts at low pressure (Wyllie and Tuttle, 1959), in basalt melt to 10 kb (Hill and Boettcher, 1970; Holloway and Burnham, 1972), and in albite melt to 30 kb (Millhollen and others, 1971). The position of a liquidus curve in P–T space, for a specific anhydrous bulk composition and f_{O_2}, depends upon $f^m_{H_2O}$, whether a H_2O CO_2 fluid or no fluid at all is present. Therefore, H_2O-undersaturated liquidus curves for a given amount of H_2O in the melt are the same in the system andesite–H_2O–CO_2 and in the system andesite–H_2O. Experiments by Eggler (1972a) have confirmed this reasoning.

The solidus is a somewhat different case. In the system andesite–H_2O, beginning of melting occurs at one of two univariant reactions (and, isobarically, at one of two temperatures), one in the presence of fluid and one in the fluid-absent region (Robertson and Wyllie, 1971). When CO_2 is added, these reactions become divariant, and melting occurs over a range of temperatures as a function of pressure and composition of the fluid (Holloway and Burnham, 1972).

EXPERIMENTAL TECHNIQUES

Rock Investigated

The rock studied from Mount Hood, Oregon, is a lava erupted in the late Pleistocene, after the bulk of Mount Hood was built (Wise, 1969). William S. Wise donated the sample, which was ground to <200 mesh in a mixer mill. Its analysis appears in Table 1.

A thin section of the rock contained plagioclase phenocrysts, one of which was analyzed (analysis 3, Table 1), and microphenocrysts of orthopyroxene and plagioclase set in a trachytic groundmass of plagioclase, orthopyroxene, clinopyroxene, glass, ilmenite, and magnetite. One glomerophenocryst (or xenocryst) of