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Coexisting Garnets and Ilmenites Synthesized at High Pressures from Pyrolite and Olivine Basanite and Their Significance for Kimberlitic Assemblages

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Abstract. Coexisting garnets and ilmenites have been synthesized at high pressure (21–40 kb) within the temperature range between 900 and 1100° C from pyrolite-less-40% olivine and olivine basanite with various water contents. The two compositions yield phases with a range in the 100 Mg/Mg+Fe ratio for both garnet (41–76) and ilmenite (15–47). The distribution coefficient for iron and magnesium ($K_{D(\text{Fe}, \text{Mg})}^{\text{ilm-ga}} = 4.0 \pm 0.5$) for coexisting phases does not appear to vary with change in the bulk composition or temperature of synthesis. The synthesized ilmenites are of similar composition to those of kimberlites in 100 Mg/Mg+Fe ratio and Al_2O_3 and Cr_2O_3 solid solution. Cr_2O_3 content in ilmenite is dependent on Cr_2O_3 in the bulk composition and also on Fe_2O_3 content of ilmenite. Fe_2O_3 content of ilmenite is very sensitive to f_{O_2} and natural ilmenites from peridotites have formed under low f_{O_2} . Al_2O_3 solid solution in ilmenite as well as TiO_2 in coexisting garnet tend to be higher with higher temperature. All the variety of compositions of ilmenites from kimberlites may be obtained from rocks rather close in composition to those used in experiments, within the same range of pressure and temperature but at variable oxygen fugacities.

Introduction

Pyrope—almandine garnets and magnesian ilmenites are among the most common minerals found in a majority of kimberlitic pipes. Garnets occur in xenoliths of various peridotites and eclogites and as discrete nodules and isolated grains in the heavy mineral concentrates from kimberlites. In most cases, garnets do not have a paragenetic relation to ilmenites. Ilmenite is mainly found as nodules of varied size and as isolated grains in concentrates, and more rarely as regular intergrowths with pyroxenes (both diopside and enstatite), (Williams, 1932; Sobolev, 1959, 1964; Frantsson, 1970; Mitchell, 1973; Milashev *et al.*, 1963). It also occurs rarely within ilmenite-bearing peridotites. The rare occurrences of ilmenite coexisting with other phases such as olivine, pyroxenes and garnet attract special attention in attempts to clarify possible systematic relationships of its formation in kimberlite. (Ringwood and Lovering, 1970; Dawson and Reid, 1970; Boyd and Nixon, 1973; Ponomarenko *et al.*, 1971, 1972).

In experimental studies of several basaltic and peridotitic compositions, mineral assemblages containing co-existing garnet and ilmenite, had been syn-

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thesized in studies aimed at determining solidus, liquidus and phase relationships as functions of pressure, temperature and water content. The known variations in composition of natural ilmenite and garnet, particularly in Ti-content of garnet, Al-content of ilmenite etc., suggested that useful constraints on P , T conditions of crystallization of the natural minerals might be obtained by analysis of the coexisting mineral pairs synthesized under known P , T conditions. The study was of reconnaissance character seeking to isolate P , T dependent substitutions or partition relationships which would then repay further detailed study in compositions chosen specifically to calibrate the potential P, T indicator (cf. the study by Raheim and Green (1974) of the $K_D^{\text{ga-cpx}}$ partition coefficient for Fe, Mg in garnet and clinopyroxene).

Experimental Methods

Selection of Compositions

For the present study the composition of pyrolite-less-40% olivine (Green and Ringwood, 1970; Green, 1973b) and also olivine basanite (Green, 1973a) were used. These compositions contain garnet and ilmenite in both subsolidus and above-solidus mineral assemblages and phase relationships have been investigated for a wide range of pressure and temperature conditions and for various water contents (Green 1972, 1973a, b, c).

The comparatively low TiO_2 content of the bulk compositions and the appreciable solubility of TiO_2 in pyroxenes, amphibole and garnet, meant that ilmenite was a minor phase and though identifiable in many runs, could only be analyzed with sufficient accuracy when crystals were >3 microns diameter. In several runs (Tables 1 and 2) garnet was analyzable but ilmenite was absent or not confirmed by electron probe (pyrolite composition). These data give information on minimum TiO_2 solubility in garnet at the various temperatures and pressures.

Microprobe Analyses

The analyses of synthesized phases were carried out using the TPD electron probe micro-analyzer with energy-dispersive detection and analysis system (Reed and Ware, 1973; Green, 1973a). This instrument is uniquely suited for complete analyses of very small grains ($>3 \mu$) present in experimental high pressure runs. Some minerals from the kimberlites of Yakutia were analyzed using the MS46 electron probe using the procedure described by Sobolev, Lavrent'iev *et al.* (1969).

The ten to twenty individual analyses of garnet and ilmenite were carried out on each experimental run and the analyses listed in Tables 1 and 2 were selected as having totals between 98% and 102%, acceptable structural formulae and (for ilmenites only) $\text{SiO}_2 < 1\%$.

Analytical Data (Tables 1 and 2)

(a) *Garnet*. At 35 kb, 1500° C in pyrolite composition garnet containing 1.4% TiO_2 may not coexist with ilmenite so that the TiO_2 content of 1.4% is a minimum value for TiO_2 solubility in garnet. Similarly, in the olivine basanite runs at 30 kb, 1280° C and at 25 kb, 1160° C, 1140° C and 1120° C, garnet coexists with liquid and clinopyroxene but not with ilmenite and the TiO_2 contents of these garnets are also minimal values. The increase in TiO_2 at 25 kb from the 1160° C run (1.2% TiO_2), through the 1140° C run (1.6% TiO_2) to the 1120° C run (1.8% TiO_2) is considered to reflect increasing TiO_2 content of the coexisting liquid and possibly changing partition coefficient between liquid and garnet [Mg_{68} to Mg_{55}] as the degree of crystallization increases at lower temperatures. At the same