pyroxene geothermometer is less effective between 900 and 1200°C at high pressure than previously accepted.

7. Some problems in petrologic applications to natural pyroxenes

Applying Figs. 2 and 3, one may in theory estimate both pressure and temperature simultaneously from chemistry of coexisting enstatite and diopside. However, this is impractical as the isochemical contour lines for the two pyroxenes are nearly parallel throughout the P-T field except at temperatures above 1200°C where the two lines cross with a rather high angle between them. Even at high temperature, however, the application of this method to natural pyroxenes requires a full understanding of chemical effects in the multicomponent system. Consequently, the enstatite-diopside solvus can be used as a geothermometer only if the pressure of formation is estimated by another method, except in those cases where temperature is so low that the clinopyroxene limb is independent of pressure.

Application of the present results will necessitate revision of many temperature estimates found in the literature, particularly for assemblages of low-temperature peridotites and granulites and for high-pressure, high-temperature assemblages such as peridotite nodules in kimberlites. For example, estimates of temperature in the range 1200-1400°C at 30 kbars based on Davis and Boyd [4] would be revised upwards by about 100°C based on Fig. 3. An estimate of 1000°C at 30 kbars would be little changed but estimates of 900°C at 30 kbars would be revised downwards by more than 100°C. We emphasize, however, that data on the multi-component pyroxene system are required before unambiguous P-T determinations can be obtained for natural two-pyroxene assemblages.

8. Phase relations of pyroxenes in the system Mg₂Si₂O₆-CaMgSi₂O₆

Not only are enstatite and diopside stable in the system $Mg_2Si_2O_6$ -CaMgSi₂O₆, but at least two more



Fig. 4. An arrangement of the univariant lines around the invariant point where protoenstatite, enstatite, pigeonite and diopside coexist. Each line is identified by the missing phase from the invariant assemblage. Composition-assemblage diagrams are shown in each divariant field with, from left to right: Pr = protoenstatite, En = enstatite, Pi = pigeonite, Di = diopside. Open circle: unstable phase, filled circle: stable phase.

Data: squares [1,18,20], a bracket at 5 kbars [18], triangles: enstatite and diopside assemblage is stable [6], star: either enstatite-diopside, or pigeonite-bearing assemblage is stable [6,18]. See text for discussions.

stable phases exist, protoenstatite and pigeonite^{*}. Protoenstatite is restricted to a low-pressure, high-temperature region [2,16]. Recent work by Smyth [17] reported protoenstatite of the composition $Mg_2Si_2O_6$ is stable up to melting point at 1 atm. Pigeonite appears over a wide P-T range from 1 atm to at least 20 kbars [2,18,19].

Three univariant assemblages known to occur are protoenstatite—enstatite—diopside at 1 atm and about 1400°C [1], enstatite—pigeonite—diopside at 17.5 kbars and 1450°C [18], and protoenstatite—pigeonite diopside at 1 atm and about 1230°C [2]. For conditions for the last assemblage, the temperature, 1276°C [20], was preferred. This choice, in spite of

* This mineral is called iron-free pigeonite in the literature but the term "pigeonite" is used in this paper for convenience.



Fig. 5. A. A schematic phase diagram at about 5 kbars. B. A schematic phase diagram at just above T_0 , based on the assumption that the slope of the univariant line (En) is negative as shown in Fig. 4.

the presence of Al_2O_3 in the system studied by Yang [20] was made because the coexistence of protoenstatite, pigeonite and diopside was confirmed at that temperature, and the Al_2O_3 content of less than 0.5 wt.% in the pyroxenes should have little effect on the temperature of the equilibrium. An invariant assemblage of all the four pyroxenes almost certainly occurs and Warner and Luth [6] estimate this to be at about 2 kbars and 1320°C.

A geometrical arrangement of four univariant lines around the invariant point is obtained following Schreinemakers' method [21]. An assumption here is that the CaMgSi₂O₆ content of pyroxenes at the invariant point increases in the order protoenstatite, enstatite, pigeonite, diopside. The shaded area in Fig. 4 limits the conditions for the invariant point. This area is partly defined by: (1) demands by the arrangement of the univariant lines, (2) three fixed points noted above, (3) a bracket for the univariant line (Pr) at 5 kbars [18], and (4) stability of enstatite and diopside at 10 and 5 kbars and 1300°C [6].

The nature of the stable assemblage at 2 kbars and 1300°C is confusing: it is enstatite and diopside

(homogenization experiment) or pigeonite-bearing assemblage (unmixing experiment) [6,18]. This confusion might imply that a reaction, pigeonite = enstatite + diopside, characteristic of the univariant line (Pr), occurs near 2 kbars and 1300°C. If so, the invariant point will be further restricted to less than 2 kbars.

The deviation of the area thus restricted from Warner and Luth's estimate [6] is small but critical: their value implies that (En) is at a higher temperature than 1320°C at 1 atm [6, Fig. 5]. In fact it is not [2,20]. The conditions of the invariant point are hereafter referred to as P_0 and T_0 .

It is now easy to draw the geometry of phase diagram at any T-P conditions. Fig. 5A, B shows examples at constant pressure and temperature around P_0 and T_0 . They are only schematic, and partly exaggerated. Fig. 5B is drawn on an assumption that the slope of (En) is negative. A positive slope removes the protoenstatite-diopside solvus from the figure. The detail of the phase relations around P_0 , T_0 must be determined by experiments, which should be concentrated in the shaded area (Fig. 4). However, such experiments will be extremely difficult because of

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