THE EFFECT OF KINETICS ON CRYSTAL-LIQUID PARTITIONING IN AUGITE
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The complex chemical trends which have been observed in isochemical suites of mare basalt samples reflect variations in the cooling histories of the rocks. This dependence of pyroxene chemistry on cooling rate has been well documented for quartz-normative basalt 15597 (7). In this study, Grove and Bence found that the partitioning of major elements (Mg, Fe, Ca) between low-Ca clinopyroxene and liquid is rate independent, whereas the partitioning of minor elements (Ti, Al, Cr) is rate dependent. The bulk distribution coefficients ($D = XPX/ XL$) for all elements (as oxides) were shown to be temperature dependent. Data were reported for augite rims on low-Ca clinopyroxene cores which indicate that the partitioning of major elements in augite is also rate independent.

The effects of bulk composition, nature of coexisting phases, and order of appearance of coexisting phases on the rate dependence of partitioning between pyroxene and liquid have not been studied in detail. We have attempted to examine the influence of these parameters by studying pyroxene-liquid partitioning in synthetic analogs of high-Ti mare basalts 10017 and 75055. These compositions were selected because: a) they are compositionally different from 15597 and from the compositions studied isothermally by Duke (4), b) ilmenite (limonite) crystallizes before pyroxene (Fig. 1), c) the order of appearance of plagioclase and pyroxene is different for the two rocks (Fig. 1), and d) the first TiO$_2$ to crystallize is augite and the partitioning of elements between augite and liquid has not been adequately determined.

Isothermal and constant cooling-rate dissection runs were made to determine the phase relations for each composition. The Pt-loop technique was used, and fO$_2$ was maintained at 0.5 log units below I/W.

![Fig. 1a](image_url)
![Fig. 1b](image_url)
Equilibrium phase relations for 10017 (Fig. 1a) are in agreement with the data of O'Hara et al. (10). The order of phase appearance for 75055 (Fig. 1b) is in agreement with the textural interpretation of Dymek et al. (5). Pyroxene-liquid within 10-30 μm of the x1/L interface were analyzed with an EMP. The high temp. augites (Fig. 2a,b) are similar to those reported for the natural samples (3, 5, 6). The pyroxene in 75055 shows a tendency for the formation of both high- and low-Ca (symbol L) populations. The amounts of Ti and Al in the pyroxene increase both with increasing cooling rate and with decreasing temp. The ratio Ti/Al = 1/2 for the pyroxene in both rocks (Fig. 3), as found in the natural rocks (5, 8).

The bulk distribution coefficients for the partitioning of major elements between augite and liquid in 10017 & 75055 (Fig. 4a) are apparently rate independent for cooling rates up to 100°C/hr. This is similar to the x1/L partitioning behavior in augite rims on low-Ca pyroxene cores in 15597 (7). However, the temp. dependence for DFe and DMg is greater than that reported by Grove & Bence (7), and the temp. independent value of DCa is higher. The log KD = log DMg - log DFe calculated from the data obtained in this study appear to be rate independent and temp. dependent. The average log KD ranges from about 0.66 at 1105°C to 0.79 at 1055°C. This is in contrast to the findings of Grove & Bence (7) who report that KD is temp. independent. The results obtained here are in good agreement with KD values calculated from pyroxene/liquid compositional data for other bulk compositions (2, 4, 11).
The bulk distribution coefficients for Ti and Al (Fig. 4b) are significantly different from those reported for low-Ca clinopyroxene in 15597 (7), where the D increased with increasing cooling rate for rates >3°C/hr. In 10017 & 75055, the D appear to be rate independent prior to the appearance of plagioclase, after which the D decrease. Since the temp. of plagioclase nucleation is suppressed with increasing cooling rate, the temp. at which the decrease in D occurs is lowered with increasing cooling rate. This trend is most evident for Ti. The low-Ca (symbol L) populations from 75055 fall below the rate independent trend and may correspond to pyroxene which has co-crystallized with plagioclase. The rate and temp. dependences for D_{Cr} are uncertain, but appear to be about the same as those determined for Ti and Al.

The results of this study indicate that the partitioning of major elements between augite and liquid is rate independent and insensitive to composition and to the nature and order of appearance of coexisting phases. The partitioning behavior of minor elements appears to be complex. The D seem to be cooling-rate dependent, possibly as a result of the suppression of the appearance of phases such as plagioclase. The minor element D seem to depend on the bulk composition, a dependence which may be related to the nature of the first pyroxene to crystallize and the resulting pyroxene evolutionary trend.

References: