THE DISTRIBUTION OF Zr AND Nb BETWEEN DIOPSIDE AND COEXISTING SILICATE MELT. J.T. Dunn, Department of Geology, University of Alberta, Edmonton, Alberta T6G2E8 and I.S. McCallum, Department of Geological Sciences, University of Washington, Seattle, Washington 98195

Introduction: Clinopyroxene appears to be the major silicate mineral capable of fractionating Zr from Nb during magmatic differentiation processes (1). We have measured D_i (diopside-liquid), where i = Zr or Nb, in the system Di-Ab-An as a function of liquid composition, temperature and oxygen fugacity. The data, together with data published earlier (1), can be used to refine models for the genesis of mare basalts and KREEP basalts.

Experimental: Six compositions within the crystallization field of diopside in the system Di-Ab-An were prepared from oxide mixes (Fig. 3). Compositions 1 through 4 lie along the 1275°C isotherm; composition 5 has a liquidus T of 1345°C; composition 6 has a liquidus T of 1120°C. Compositions 1-4 were used to evaluate the effect on D_i of changes in liquid composition; all compositions were used to evaluate the effect of temperature. Charges were doped with 0.5, 1.0, 1.5 and 2.0 wt.% ZrO_2 and Nb_2O_5 and runs were carried out ∿5°C below the liquidus temperature using the Pt loop method. Runs were of varied duration and the oxygen fugacity was controlled by gas mixing (CO_2/H_2). For any given composition and temperature, D_i appears to be independent of doping level suggesting that Henry's Law is obeyed. Phase compositions were determined by microprobe analysis. Two different experimental procedures were used. In both, the sample was melted at T∿100°C above the liquidus temperature. In the direct drop (DD) method, the sample was cooled rapidly to the experimental temperature. In the devitrification (DV) method, the sample was quenched, the furnace was reset to the experimental temperature, and the sample was reintroduced into the furnace.

Evaluation of equilibrium: Margaritz and Hoffman (2) have shown that the measured values of $D_i(c/l)$ are functions of crystal growth rate, the diffusion coefficient of element i in the liquid, and the equilibrium value of $D_i(c/l)$. As the crystal growth rate increases, the apparent value of $D_i(c/l)$ tends towards unity. In general, equilibrium will not be achieved in cases of rapid crystal growth or in cases of moderate crystal growth where $D_i(c/l)$ differs greatly from one. To test these predictions, six experiments (DD method) from 2 to 122 hours duration were done on composition 1 (doped with 1% ZrO_2) in which crystal growth rate (V) was measured as a function of time by taking the average of the dimensions of the crystals $\perp c$ and dividing by two times the experimental duration. Growth of diopside crystals occurs in two stages; the first stage involves rapid growth parallel to c at rates up to 2.5×10^{-5} cm sec^{-1}; the second stage involves filling in the interior of the crystal and slow outward growth of the bounding crystal faces. As a result, there is an apparent decrease in linear crystal growth rate (V) with time (Fig. 1). Three DV experiments on composition 1 show much lower crystal growth rates and, as the theory predicts, give a value of $D_{Zr}(c/l)$ that is closer to the equilibrium value and less than the value from the DD experiments. Crystal growth rates on less siliceous composition 2 are approximately the same for both the DD and DV methods. Similar values of D for composition 2 are predicted and observed; $D_{Zr}^{DD}(di/l) = 0.23 = D_{Zr}^{DV}(di/l)$. We have developed the following equation (based on that of Burton *et al.* (3)) to calculate the effects of liquid state diffusion and crystal growth rate on the measured value of $D_i(c/l)$:

$$D_a = D_e(D_e+(1-D_e)\exp(-Vd\bar{A}\eta/2^{\frac{1}{2}}\pi kT\bar{\sigma}^2\rho N))^{-1}$$

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where D_a and D_e are the apparent and equilibrium weight ratio distribution coefficients, respectively, V is the linear crystal growth rate, d is the thickness of the diffusive boundary layer, $\bar{A}$ is the mean atomic number of the melt, η is the vicosity of the melt, k is Boltzmann constant, T is absolute temperature, $\bar{\sigma}$ is the mean ionic diameter in the melt, ρ is the density of the melt and N is Avogadro's number.

Application of this equation requires data relating the crystal growth rate to experimental duration, a value for d (assumed to be 0.1 cm) and an estimated value of D_e. All other parameters are known or can be calculated from the composition of the melt. Appropriate run times can be determined by substitution of values of V (corresponding to experimental durations) into the equation until the difference between D_a and D_e is within limits acceptable to the experimenter. As an example, the results obtained for composition 1 are shown in figure 2. For this case, 100 hours are required to reduce the difference between D_a and D_e to 10% absolute. It is clear that significant errors can result if the effects of liquid state diffusion are ignored. These errors may be avoided by doing long experiments or by correcting the data using the equation listed above. To minimize errors due to slow solid state diffusion, experiments were carried out only a few degrees below the liquidus, thus limiting crystals to a small fraction of the volume of the system.

Results: Distribution coefficients are given in Table 1 and illustrated in Fig. 3. Each D value listed is obtained from the slope of the best fit line through the experimental points (after correction for crystal growth rates); up to 8 experiments at varied doping levels were carried out for each composition. Compositions 1 and 6 (Fig. 3) are viscous, and crystals are difficult to grow; high cooling rates favor crystal growth. Because of the proximity to the Di-An eutectic, composition 4 experiments contained >50% crystals resulting in a value of D_{Zr} that is almost certainly too low.

Table 1: Distribution coefficients for Zr and Nb between diopside and liquid in the Di-Ab-An system.

	1	2	3	4	5	6
D_{Zr}(di/l)	0.047	0.22	0.39	>0.31	0.038	0.35
D_{Nb}(di/l)	-	0.015	-	-	<0.01	-
T (°C)	1270	1270	1270	1270	1345	1120

It can be shown theoretically that the Zr content of diopside should be proportional to the Al content of the melt. From compositions 1 to 4 there is an increase in the activity of Al_2O_3 in the liquid. Both Zr(M1) and Al(T) increase from compositions 1 to 4 supporting the contention that Zr enters the M1 site in diopside in coupled substitution with tetrahedral Al. However, the 8-fold increase in D_{Zr} (Table 1) is greater than predicted. Attempts to model Zr partitioning thermodynamically were unsuccessful, largely as a result of our inability to model adequately the activity of Al_2O_3 in the liquid phase. The runs on composition 5 and 6 (Table 1) indicate that D_{Zr} (diop-liq) is inversely proportional to temperature although a compositional effect is occult in these data. Nb is effectively excluded from the diopside structure (Table 1) confirming earlier results obtained at low oxygen fugacities (1).

It is of interest to calculate an equilibrium constant for the diopside forming reaction:

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$$CaO(1) + MgO(1) + 2SiO_2 = CaMgSi_2O_6(c)$$

$$K_{Di} = a^{px}_{Di}/a^{1}_{CaO}a^{1}_{MgO}(a^{1}_{SiO_2})^2 = X^{M2}_{Ca}X^{M1}_{Mg}(X^{T}_{Si})^2/a^{1}_{CaO}a^{1}_{MgO}(a^{1}_{SiO_2})^2 \quad .$$

The value of K_{Di} has been calculated from the present data (38 points) along with data from Lindstrom (4) - 6 points, and Weill *et al.* (5) - 21 points. Results are shown in Fig. 4. This reaction has a significant temperature dependence: $\Delta H° = -267$ joules mol^{-1} and $\Delta S° = 0.034$ joules $mol^{-1}deg^{-1}$. The a-x model for diopside is based on the Kerrick and Darken (6) model and that for the liquid on a modification of the Bottinga and Weill (7) model.

Fig. 3 may be used to determine the approximate value of D_{Zr}(cpx-liq) for natural systems by projecting melt compositions on to the Di-Ab-An plane using methods described in (5).

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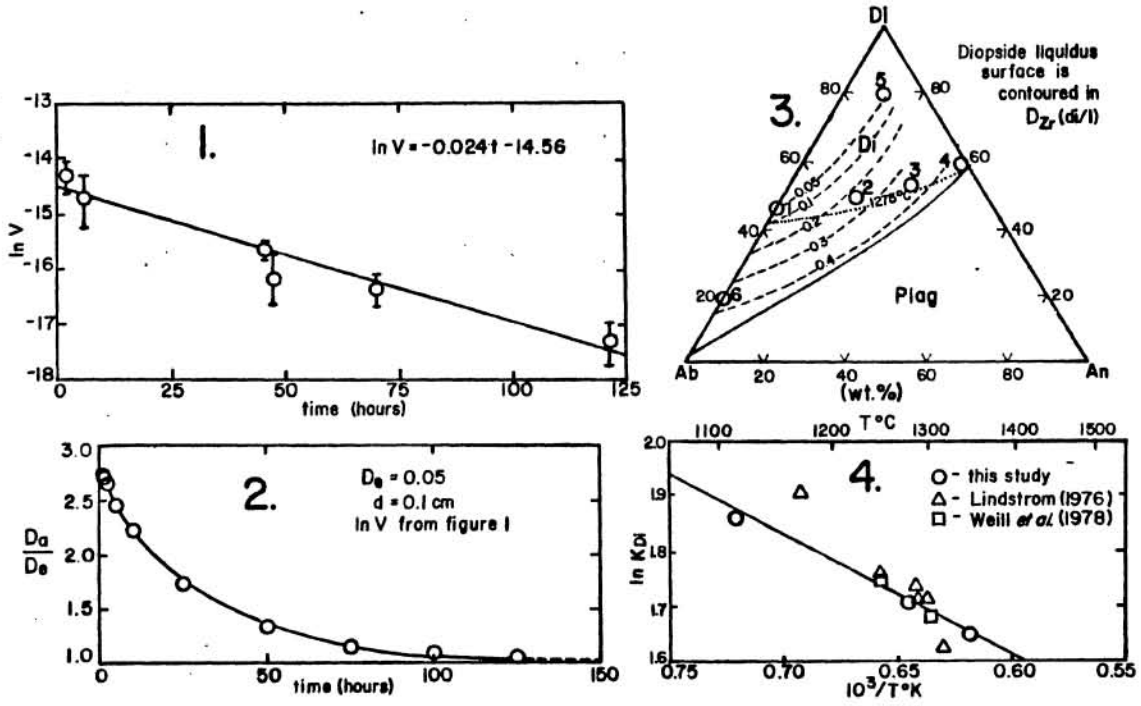

Fig. 1. Linear crystal growth rate as a function of experiment duration for composition 1.
Fig. 2. Apparent distribution coefficient as a function of experiment duration
Fig. 3. Phase diagram for Di-Ab-An system. Starting compositions shown by numbered circles. Diopside liquidus is contoured in D_{Zr}(di/l).
Fig. 4. Ln K versus $10^3/T$ for the diopside forming reaction.

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