American Mineralogist, Volume 74, pages 31–36, 1989

Effects of pressure on partitioning of trace elements between low-Ca pyroxene and melt

RUSSELL O. COLSON
Department of Earth and Planetary Sciences, Box 1169, Washington University, St. Louis, Missouri 63130, U.S.A.
DAVID GUST
Department of Earth Sciences, University of New Hampshire, Durham, New Hampshire 03824, U.S.A.

ABSTRACT

In order to better understand magma evolution at depth in the Earth, partition coefficients between low-Ca pyroxene and melt have been experimentally determined at 15 and 20 kbar. Results indicate that partitioning of Sc, Yb, and Ca is little affected by pressure but Al partitioning increases significantly. We conclude that the unique dependence of Al partitioning on pressure results from the stabilization of Al on octahedral sites in pyroxene. In contrast to results of previous studies, we further conclude that, in most cases, low-pressure partition coefficients (D = concentration in crystal ÷ concentration in melt) are applicable to high-pressure problems and that the strong dependence of D on cation size observed at low pressure persists at high pressure.

PARTITIONING EXPERIMENTS

A series of partitioning experiments between low-Ca pyroxene and melt has been completed at 15 and 20 kbar. Five-component synthetic starting materials (SiO_2, Al_2O_3, CaO, FeO, MgO) were made in which pyroxene was expected to be the first liquidus phase. All experiments were carried out in a solid-media high-pressure apparatus (Boyd and England, 1960) using the piston-in technique with a 10% friction correction. Temperatures were measured with $Pt\text{-}Pt_{90}Rh_{10}$ thermocouples without pressure correction on emf output. Automatic temperature controllers maintained the temperature within ±10 °C.

Samples were doped with about 1% (Yb + Sc) and loaded in graphite capsules. Duration of the experiments varied between 0.5 and 1.5 h. (Longer experiments were not possible because of equipment limitations at the temperatures of these experiments.) Samples were analyzed using a Cameca Microbeam electron microprobe with ZAF corrections for matrix and background. Compositions of glasses containing quench crystals were determined by averaging the analyses for a linear or rectangular array of 20 to 40 regularly spaced points. Figures 1 and 2 bracket the range of crystal sizes and the extent of quench crystallization for these experiments. The figures also show the points in crystal and glass that were analyzed. Experimental results are reported in Table 1.

The durations of the experiments of this study are short relative to analogous experiments at 1 atm (e.g., Colson et al., 1988). Therefore some consideration of the potential for disequilibrium is necessary. We note that the durations of high-pressure experiments are typically shorter than analogous 1-atm experiments (e.g., Longhi et al., 1978). We also note that equilibrium between pyroxene and melt at high pressure has typically been inferred to occur in experiments lasting 0.5 to 3 h (e.g., Bender et al., 1978; Green et al., 1979), durations similar to those of the present study. More rapid equilibration at high pressure is expected because temperatures (and therefore diffusion rates) are higher than in analogous 1-atm experiments.

Based on diffusion rates in garnet, Harrison (1981) has calculated that equilibrium is reached in 1–2 h in high-pressure garnet/melt partitioning experiments. A similar calculation for Sc and Yb equilibration time in pyroxene cannot be made because diffusion data for Sc and Yb in pyroxene are not available. However, calculations based on the assumption that diffusion of Sc and Yb is similar to Ca and Sr (Freer, 1981; Sneeringer and Hart, 1978) suggest that crystals <50 μm in diameter (all experiments except PR1) will equilibrate in 1.5 h. These calculations indicate that the larger crystals in PR1 will only partially equilibrate. However, because the extent of crystallization in PR1 is low (<5% crystals), zoning arising during the progress of crystallization may be small. Also, other kinetic effects that perturb effective partition coefficients by as much as a factor of 2 (Lindstrom, 1983) are not considered to be significant in this study because of higher temperatures and slower growth rates (slower growth rates are inferred because of controlled cooling rates (1–2 °C/min) and a low degree of undercooling (<20 °C) in this study).

The absence of any major-element zonation in the pyroxenes further supports the contention that equilibrium is indeed reached in these experiments. For pyroxenes less than about 50 μm in size, no zoning is observed with either SEM backscatter imagery (Fig. 2) or electron-microprobe analyses. Although the larger crystals seen in Figure 1 appear somewhat skeletal, suggesting rapid growth, major-element analyses reveal ≤5% relative zoning. This is less than the 10% relative zoning reported for the pyroxenes in Colson et al., 1988. We do not consider a ≤5%

0003–004X/89/0102–0031$02.00

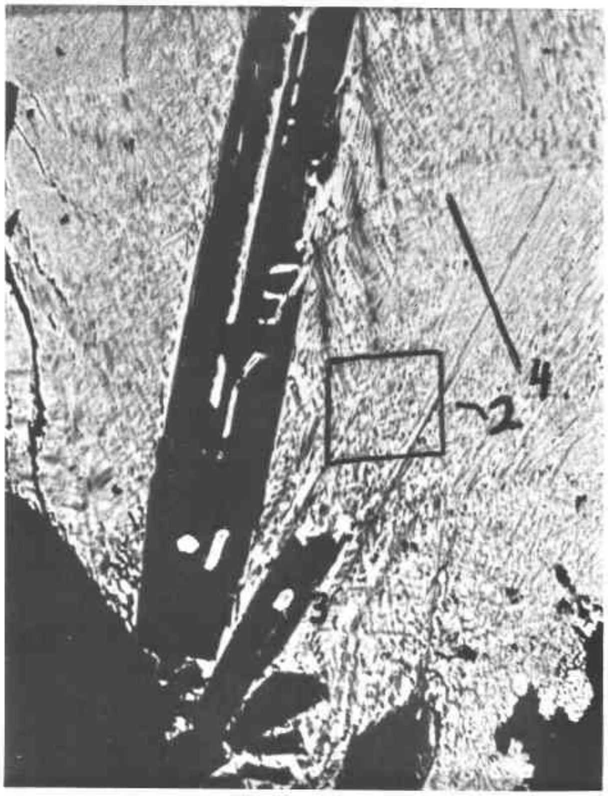

Fig. 1. SEM backscatter image of run PR1 showing large crystals in matrix of radiating quench crystals and glass. Points 1 and 3 are points analyzed in the crystal. Compositions of the glass were determined by averaging analyses for an array of regularly spaced points in the regions numbered 2 and 4. The large central crystal is about 120 μm in width and several hundred micrometers in length.

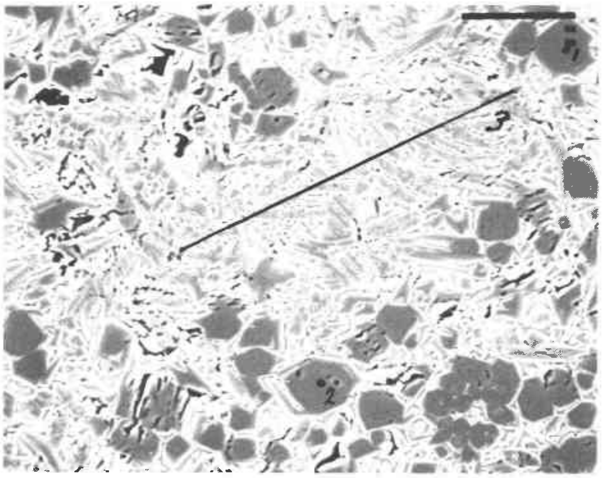

Fig. 2. SEM backscatter image of run PR5 showing medium-sized to small crystals in a "mush" of quench crystals and glass. Points 1 and 2 represent crystal points that were analyzed. Forty equally spaced points along line 3 were averaged to get the glass/quench composition. The black bar in the upper right is about 100 μm in length.

deviation from equilibrium to be significant because it is less than the analytical error we report in Figure 3. We conclude that these experiments represent a reasonable approximation of equilibrium conditions.

DISCUSSION

It is generally not possible to isolate experimentally the effects of pressure from the effects of other variables like temperature and composition. For example, it is impossible to hold temperature and phase composition constant while varying pressure. Changes in partitioning with pressure must be attributed to several covarying parameters of the system. Therefore, we divide partitioning changes with pressure into two categories: (1) the effects of covarying temperature and composition and (2) the remaining pressure effects that must be caused by either the preference of cations for the lower-volume side of a reaction at high pressure or changing activities in the melt or crystal.

For low-Ca pyroxene, the relationship between phase composition, temperature, and equilibrium partitioning has been determined previously for 1 atm (Colson et al., 1988). Colson et al. (1988) have modeled the temperature and compositional dependence of trace-element partitioning in bulk compositions similar to those of this study by fitting a large data set to the relationship $\ln K = \Delta S/R - \Delta H/RT$, where the partition coefficient is related to the equilibrium constant, K, by appropriate expressions for activities. In the present study, we isolate the effects of pressure from temperature and compositional effects by a comparison of our data to partitioning values predicted by Colson et al. (1988) for systems of the same composition and temperature but at 1 atm. [We point out the temperatures and compositions in the 1-atm experiments of Colson et al. (1988) are different from the higher-pressure experiments of this study. We use the equilibrium reactions and free energies of reactions determined by Colson et al. (1988) to extrapolate from temperature-composition conditions that exist at 1-atm to those that exist at higher pressures.] Because the bulk compositions in that study and this one are nearly identical, we believe the predicted values accurately model the temperature and compositional dependence of partitioning in the present study. Use of the model in Colson et al. (1988) places better constraints on the effects of covarying temperature and composition than was possible in previous high-pressure partitioning studies (e.g., Green and Pearson, 1983).

Figure 3 illustrates the comparison of high-pressure D values to D values predicted for 1 atm. The line in Figure 3 represents where the value measured at 15 or 20 kbar equals the value predicted for 1 atm. Values for Ca, Yb, and Sc partitioning fall on or near this line, indicating that these partition coefficients are little influenced by the pressure difference. However, Al partition coefficients are increased by an order of magnitude by pressure.

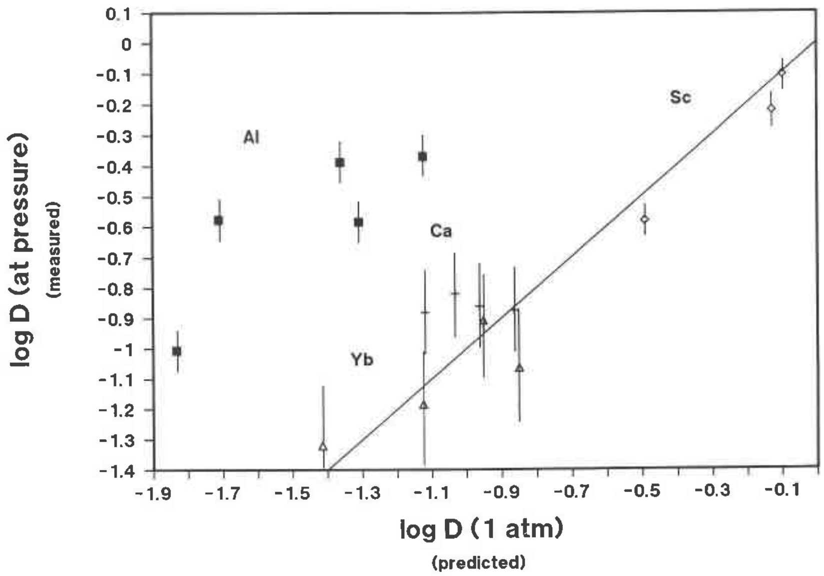

Fig. 3. Plot of the measured partition coefficient against the partition coefficient predicted (Colson et al., 1988) for this same temperature and composition but at 1-atm pressure. Bars equal 1σ errors estimated from counting statistics and the variation in concentrations in the inhomogeneous quench glass. Within error, Ca, Yb, and Sc partition coefficients are unaffected by pressure. Al partition coefficients are significantly increased by pressure.

The increase with pressure of Al concentration in pyroxene is a well-known occurrence (Yoshikawa, 1977). Our goal is not to simply observe that an increase in D_{Al} with pressure occurs, but to explain the cause of the increase. There are three scenarios that might explain the effects of pressure seen in Figure 3.

1. The activity of Al in the melt might be drastically increased while activities of other components are little affected as pressure increases. Changing coordination of melt Al with pressure has been invoked before to explain trace-element partitioning (Mysen and Kushiro, 1979). However, because Sc and Yb are charge-balanced in low-Ca pyroxene by a coupled substitution of Al for Si (Colson et al., 1988; Lindstrom, 1976, by analogy to clinopyroxene), Al will appear in the equilibrium constant for the Sc and Yb partitioning reactions, and any change in Al activity in the melt must affect Yb and Sc partitioning as well. This effect is not seen, suggesting that changes in melt Al activity are not controlling Al partitioning.

2. At high pressures, the lower-volume side of a reaction is preferred due to the effect of the energy term *PdV* (where *P* is pressure and *dV* is the change in volume for the reaction). However, no systematic variation in pressure dependence with cation size for the cations Ca, Yb, Sc, Al (in order of decreasing size) is seen, leading us to conclude that volume changes for the exchange reactions do not cause the pressure dependence of D_{Al}. A small effect of *PdV* is expected since volume changes of metal-metal exchange reactions in silicate systems are typically small (Navrotsky, 1978). We point out that high-pressure stud-

Table 1. Experimental results

Run	*T* (°C)	*P* (kbar)	Phase*	MgO	Al_2O_3	SiO_2	CaO	Sc_2O_3	FeO	Yb_2O_3	D_{Al}	D_{Sc}**	D_{Yb}**	D_{Ca}**
PR1	1473	15	gl	15.2	5.6	48.2	3.1	—	27.6	0.4				
			px	28.5	0.6	55.5	0.4	—	15.9	na	0.10	—	0.048	0.13
PR5	1495	20	gl	10.9	7.9	49.4	4.4	0.3	26.1	0.3				
			px	27.0	2.1	54.3	0.6	na	16.8	na	0.27	0.26	0.066	0.14
PR6†	1344	20	gl	11.4	12.6	49.8	7.8	0.2	18.2	0.1				
			px	22.7	5.2	51.7	2.3	na	18.7	na	0.41	bad	bad	bad
PR7	1318	15	gl	12.2	13.9	47.5	7.5	0.3	18.4	0.2				
			px	26.0	5.7	52.6	1.4	na	14.9	na	0.43	0.79	0.124	0.15
PR8§	1395	15	gl	8.8	12.2	48.9	6.9	0.3	21.8	0.3				
			px	25.1	3.2	53.4	1.1	na	18.1	na	0.26	0.60	0.086	0.13

Note: —indicates that the element was not added to the experimental charge; "bad" indicates that owing to the small size of the crystals grown in the experiment, these partition coefficients could not be determined. CaO in pyroxene was analyzed by both the major-element analysis routine and the trace-element routine (McKay et al., 1986a). The *D* values determined by the trace-element routine are considered the more reliable.

* Phases: gl = glass; px = pyroxene.

** These partition coefficients were determined by techniques outlined in McKay et al. (1986a).

† This run also contains garnet in equilibrium with low-Ca pyroxene.

§ Run contains a grain of hornblende at seam of graphite capsule where H_2O apparently leaked in from the furnace assembly.

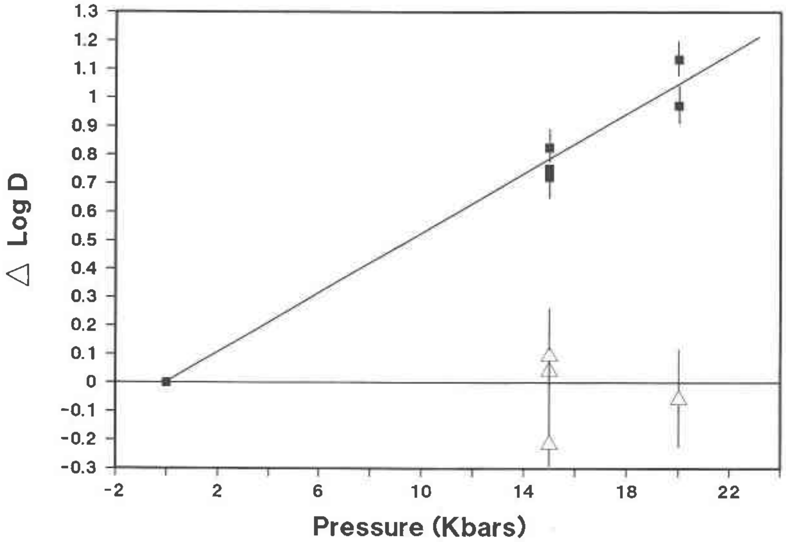

Fig. 4. Plot illustrating the pressure dependence of Al (closed symbols) and Yb (open symbols) partition coefficients. The ordinate plots the difference between the partition coefficient measured in this study and the value predicted at 1-atm pressure for the same temperature and composition. No dependence on pressure of Yb partition coefficients is apparent. Bars equal 1σ errors estimated from counting statistics and the variation in concentrations in the inhomogeneous quench glass.

ies of trace-element partitioning that express partitioning by a crystallization reaction (or simple Nernst distribution coefficients), rather than as an exchange reaction as in the present study, may observe real *PdV* effects that are normalized out by our expression of partitioning in terms of exchange reactions.

It is possible that Al activity and *PdV* effects for the Sc and Yb exchanges are changing in such a way as to cancel each other out. However, the Ca exchange, which does not involve Al, is also unaffected by pressure, suggesting that this is not the case. Also, although there is a systematic increase in Al partitioning with pressure, there is no systematic variation of partitioning for the other elements (e.g., Yb, Fig. 4). It must be concluded that both the effects of *PdV* and the effects of Al activities in the melt are insignificant.

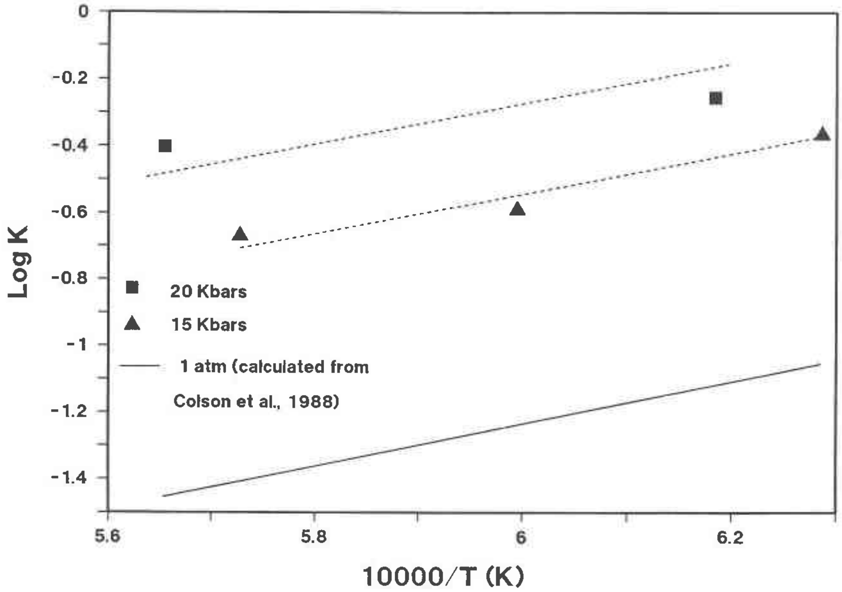

Fig. 5. Temperature and pressure dependence of the equilibrium constant (*K*) for the Al partitioning reaction. For compatibility, the value for *K* is calculated using the same activity expressions and exchange reaction as used in Colson et al. (1988). Lines for 15 and 20 kbar are drawn parallel to the 1-atm line because the data are not sufficient to confirm or disprove any change in slope with increasing pressure.

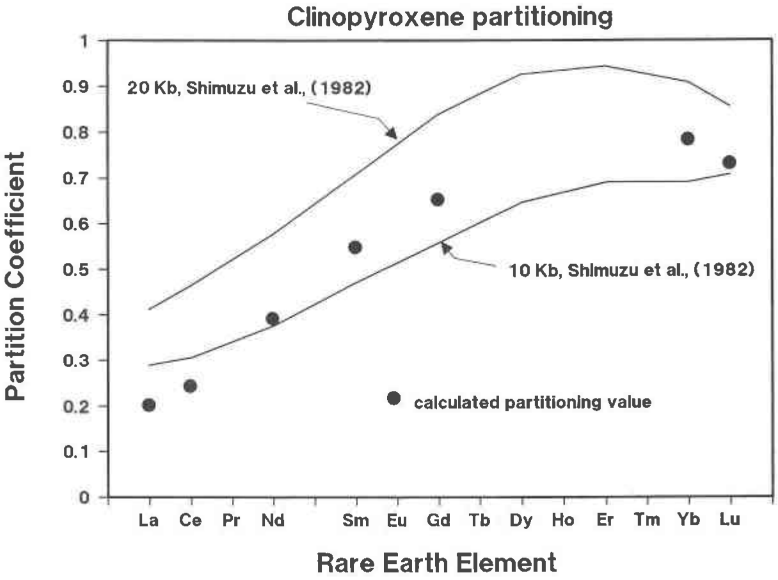

Fig. 6. Partitioning values for the REE between clinopyroxene and melt are plotted for 20 and 10 kbar (data are from Shimuzu et al., 1982). Also plotted are partitioning values calculated as equal to the partition coefficient at 20 kbar + correction for difference in pyroxene composition between the 10- and 20-kbar experiments. The correction for phase composition is after McKay et al. (1986b). Although the fit of the calculated values to the values measured for 10 kbar is not perfect, the closeness suggests that a large part of the pressure dependence of these partition coefficients is related to covarying phase composition.

3. We conclude that the change in D_{Al} with pressure indicates that the activity of Al in low-Ca pyroxene is uniquely sensitive to pressure. We interpret this sensitivity to be due to an energy arising from the high-pressure stabilization of Al in octahedral coordination in pyroxene. The tendency for Al to assume octahedral coordination at high pressure is well documented. This tendency can be understood as resulting from the space-saving qualities of higher coordination (Mason, 1966). The stabilization of small cations on large sites at high pressure is not limited to Al on octahedral sites but also is known for Si on octahedral sites (Chao et al., 1962) and Mg on dodecahedral sites in garnet (Schreyer and Seifert, 1969).

SUMMARY

Not unexpectedly, the partition coefficient for Al in orthopyroxene increases systematically with pressure. The dependence of log *D* on pressure can be approximated by $\log D_P \approx \log D_{1\ \mathrm{atm}} + 0.053P$ (kbar). A more rigorous expression of this relationship is illustrated in Figure 5, where the temperature and pressure dependence of the equilibrium constant for the Al-partitioning reaction is shown.

Furthermore, the Al partition coefficients are shown to increase with pressure owing to changes in Al activity in pyroxene and not to changes in melt structure of *dV*. Suggestions from previous studies that propose that variations in melt activities dominate partitioning changes with pressure (e.g., Mysen and Kushiro, 1979) may be premature.

Except for special cases where a cation is "too small" for a particular lattice site (such as Al in octahedral sites), partitioning is demonstrated to be little affected by pressure. This is in contrast to results of some previous studies (e.g., Mysen and Kushiro, 1979; Harrison, 1981; Shimuzu et al., 1982; Green and Pearson, 1983) but compatible with others (e.g., Irving and Frey, 1984). We interpret differences with previous studies to be due either to the use in previous studies of expressions for the partitioning reaction that are more sensitive to pressure than the exchange expressions we adopt or to the uncompensated effects of covarying temperature and composition in previous studies. For example, the pressure dependence of REE partitioning in clinopyroxene reported by Shimuzu et al. (1982) can be explained (at least partially) by differences in phase composition between higher- and lower-pressure experiments (Fig. 6).

We conclude that these data suggest that 1-atm pyroxene partition coefficients are applicable to high-pressure problems and that the strong dependence of partitioning on cation size previously found at low pressure persists at 15 and 20 kbar. Furthermore, similarity of 1-atm partitioning behavior for orthopyroxene and olivine suggests that partitioning of large cations into olivine will be little affected by pressure but Al partitioning will increase about an order of magnitude.

These conclusions provide important constraints on trace-element partitioning between phases at high-pressure, for the purpose of improving modeling of magma evolution at depth in the Earth. They are also important in achieving a more fundamental understanding of the effects of pressure on component activities in silicate melts and crystals. This understanding is important if geobarometers and geothermometers are to be defined on the basis of trace-element partitioning reactions.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support of the National Research Council Associateship program which made this research possible and the technical staff at JSC where this work was done.

REFERENCES CITED

Bender, J.F., Hodges, F.N., and Bence, A.E. (1978) Petrogenesis of basalts from the project FAMOUS area: Experimental study from 0 to 15 kbars. Earth and Planetary Science Letters, 41, 277–302.

Boyd, F.R., and England, J.L. (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750 °C. Journal of Geophysical Research, 65, 741–748.

Chao, E.C.T., Fahey, J.J., Littler, J., and Milton, D.J. (1962) Stishovite, SiO_2, a very high pressure new mineral from Meteor Crater, Arizona. Journal of Geophysical Research, 67, 419–421.

Colson, R.O., McKay, G.A., and Taylor, L.A. (1988) Temperature and composition dependencies of trace element partitioning: Olivine/melt and orthopyroxene/melt. Geochimica et Cosmochimica Acta, 52, 539–553.

Freer, R. (1981) Diffusion in silicate minerals and glasses: A data digest and guide to the literature. Contributions to Mineralogy and Petrology, 76, 440–454.

Green, D.H., Hibberson, W.O., and Jaques, A.L. (1979) Petrogenesis of mid-ocean ridge basalts. In M.W. McElhinny, Ed., The Earth: Its origin, structure and evolution, p. 265–299. Academic Press, London.

Green, T.H., and Pearson, N.J. (1983) Effect of pressure on rare earth element partition coefficients in common magmas. Nature, 305, 414–416.

Harrison, W.J. (1981) Partitioning of REE between minerals and coexisting melts during partial melting of garnet lherzolite. American Mineralogist, 66, 242–259.

Irving, A.J., and Frey, F.A. (1984) Trace element abundances in megacrysts and their host basalts: Constraints on partition coefficients and megacryst genesis. Geochimica et Cosmochimica Acta, 48, 1201–1221.

Lindstrom, D.J. (1976) Experimental study of the partitioning of transition metals between clinopyroxene and coexisting silicate liquids. Ph.D. thesis, University of Oregon, Eugene, Oregon.

——— (1983) Kinetic effects on trace element partitioning. Geochimica et Cosmochimica Acta, 47, 617–622.

Longhi, J., Walker, D., and Hays, J.F. (1978) The distribution of Fe and Mg between olivine and lunar basaltic liquids. Geochimica et Cosmochimica Acta, 42, 1545–1558.

Mason, B. (1966) Principles of geochemistry, 255 p. Wiley, New York.

McKay, G., Wagstaff, J., and Yang, S.-R. (1986a) Zirconium, hafnium, and rare earth element partition coefficients for ilmenite and other minerals in high-Ti lunar mare basalts. Proceedings of the 16th Lunar and Planetary Science Conference, Part 2. Journal of Geophysical Research, 91, D229–D237.

——— (1986b) Clinopyroxene REE distribution coefficients for shergottites: The REE content of the Shergotty melt. Geochimica et Cosmochimica Acta, 50, 927–937.

Mysen, B.O., and Kushiro, I. (1979) Pressure dependence of nickel partitioning between forsterite and aluminous silicate melts. Earth and Planetary Science Letters, 42, 383–388.

Navrotsky, A. (1978) Thermodynamics of element partitioning: (1) systematics of transition metals in crystalline and molten silicates and (2) defect chemistry and "The Henry's Law problem." Geochimica et Cosmochimica Acta, 42, 887–902.

Schreyer, W., and Seifert, F. (1969) High pressure phases in the system MgO-Al_2O_3-SiO_2-H_2O. American Journal of Science, 267-A, 407.

Shimuzu, H., Kazuyoshi, S., and Masuda, A. (1982) Experimental study on rare-earth element partitioning in olivine and clinopyroxene formed at 10 and 20 kb for basaltic systems. Geochemical Journal, 16, 107–117.

Sneeringer, M., and Hart, S. (1978) Sr diffusion in diopside (abs.). EOS, 59, 402.

Yoshikawa, K.J. (1977) Phase relations and the nature of clinopyroxene solid solution in the system $NaFe^{3+}$ Si_2O_6-$CaAl_2SiO_6$. Journal of the Faculty of Science, Hokkaido University, 17, 451–485.

MANUSCRIPT RECEIVED MARCH 18, 1988
MANUSCRIPT ACCEPTED SEPTEMBER 26, 1988