EXCHANGE OF Mn, Ca, Mg AND Al BETWEEN SYNTHETIC GARNET, ORTHOPYROXENE, CLINOPYROXENE AND OLIVINE

Tony A. Finnerty (Geophysical Laboratory, 2801 Upton St., N.W., Washington, D.C. 20008)

Fifteen exchange reactions among Fe-free garnet lherzolite minerals have been examined for pressure and temperature effects by experiments in the range 10 to 50 kbar and 1100° to 1400°C. Experiments were conducted on an oxide mixture of composition (wt%): MgO, 34.47; Al_2O_3, 8.80; SiO_2, 48.86; CaO, 7.26; MnO, 0.61, that crystallizes at high pressure and temperature to roughly equal proportions of olivine, ortho- and clinopyroxene, and garnet or spinel. The powder was loaded into graphite capsules, and sealed inside Pt in the presence of a (CO_2 + H_2O) - rich fluid, then run in a 1/2-inch diameter piston-cylinder high-pressure apparatus. Six grains of each mineral from each run were analyzed by electron microprobe. Backgrounds were analyzed at each spot for precise determination of Ca in olivine and Mn in all minerals. Standard deviations were less than 10% for Ca in olivine, less than 5% for all other oxides.

Concentrations of Ca in coexisting minerals at 30 kbar (open circles) and 40 kbar (closed circles) are presented in Fig. A. Components were calculated as $CaMgSi_2O_6$ (Di), $Ca_3Al_2Si_3O_{12}$ (Gr), and Ca_2SiO_4 (La). Al in pyroxene was combined with Mg as $MgAl_2SiO_6$ (Mgts). Pyroxene compositions from 30 kbar runs agree with the 20 kbar data of Lindsley and Dixon (1976) in Fig. A (bars represent their reversal brackets) within analytical uncertainty, suggesting attainment of equilibrium in these runs. The natural logarithms of the concentration ratios for several equilibria calculated as, for example, $K = (X_{Gr}/X_{Py})^{1/3}(X_{En}/X_{Di})$ for garnet-pyroxene Ca-Mg exchange, are plotted against inverse temperature in Fig. B through E (numbers beside data points refer to pressure in kbar).

To account for nonideality in Ca-Mg solid solutions, exchange data were fit by least squares techniques to equations of the form:

$$-RT \ln K = \Delta\overline{H}^\circ - T\Delta\overline{S}^\circ + P\Delta\overline{V}^\circ + \sum_q \nu_q\left(\sum_{i\neq q} X_iW_{iq} - \sum_{j=1}^{n-1}\sum_{k=j+1}^{n} X_jX_kW_{jk}\right) \quad (1)$$

($\Delta\overline{H}^\circ$, $\Delta\overline{S}^\circ$ and $\Delta\overline{V}^\circ$ are changes in molar enthalpy, entropy and volume, respectively, for exchange of one cation, q, i, j, k, and n are indices of components, the ν's are stoichiometric coefficients in the exchange reaction, the X's are mole fractions, and the W's are Margules parameters for symmetric regular solutions). The fits for Ca-Mg and Al exchange were constrained by values (kcal gfw^{-1}) of Ca-Mg Margules parameters of 9.6 (garnet, 12 oxygens), 53.3 (olivine, 4 oxygens), and 5.9 and 25.5 (clino- and orthopyroxene, respectively, 6 oxygens), obtained by fitting data of Newton, et al. (1977), Warner and Luth (1973) and Lindsley and Dixon (1976), respectively, to binary symmetric regular solution models similar to Eqn. 1. Fits to data for exchange of Mn and Mg were unconstrained and, because of low Mn concentrations, an ideal solution model (all W's in Eqn. 1 set equal to zero) was assumed. Results are listed in the table ($\Delta\overline{H}^\circ$ in kcal gfw^{-1}, $\Delta\overline{S}^\circ$ in °K cal gfw^{-1}, $\Delta\overline{V}^\circ$ in cm^3 gfw^{-1}, 1σ standard deviations in brackets).

Exchange reactions for Ca and Mg between garnet and orthopyroxene, between garnet and clinopyroxene, and between clinopyroxene and olivine, and for Mn and Mg between clino- and orthopyroxene and between clinopyroxene and olivine, are as temperature sensitive as the diopside-enstatite equilibrium. These may be useful as geothermometers.

The effect of pressure on the exchange equilibria is nearly as large for

Al in clinopyroxene coexisting with garnet as is the case for orthopyroxene. The Mn-Mg equilibria display pressure effects up to 15% as strong as for Al in pyroxenes. Simultaneous solution for pressure and temperature using two of these equilibria whose $\Delta\bar{V}°$'s differ in sign may be useful as alternative barometers, about 30% as sensitive as Al in pyroxenes.

The apparent effects of pressure on Ca-Mg equilibria are strongly dependent upon Al content of the pyroxenes. For example, a fit to the data of Lindsley and Dixon (1976) for Al-free diopside-enstatite yielded a value of $\Delta\bar{V}° = -0.43 \pm 0.46$ cm^3 gfw^{-1}. More experiments are required to calibrate this effect.

Di content of orthopyroxene coexisting with clinopyroxene in garnet lherzolite nodules used to construct the Lesotho geotherm of Boyd (1973) is lower than expected from experiments. Temperature estimates from Ca-Mg equilibria involving orthopyroxene are 100°-300°C lower than those of Boyd (1973). Strong preference of Fe for ortho- over clinopyroxene is probably responsible for this discrepancy. Simultaneous solution of equations for Mn-Mg exchange between garnet and olivine and between ortho- and clinopyroxene yields temperature estimates whose means are 60°C lower, and pressure estimates that average 1.9 kbar lower (sheared nodules) and 10.5 kbar higher (granular nodules) than the "Al_2O_3-Na_2O" estimates of Boyd (1973), owing most likely to the effect of Cr solution in garnet and clinopyroxene. Application of these exchange data to thermobarometry must await calibration of the effects of other components.

The concentration of CaO in olivine coexisting with ortho- and clinopyroxene decreases by about 0.002 wt% per kbar at fixed temperature, and may be useful as an empirical geobarometer with resolution of about ± 3 kbar. Pressures of equilibration estimated in this way for 14 garnet lherzolite nodules from the Lesotho geotherm (temperatures estimated from diopside compositions) agreed with the "Al_2O_3-Na_2O" estimates of Boyd (1973) to within 5 kbar.

References Cited

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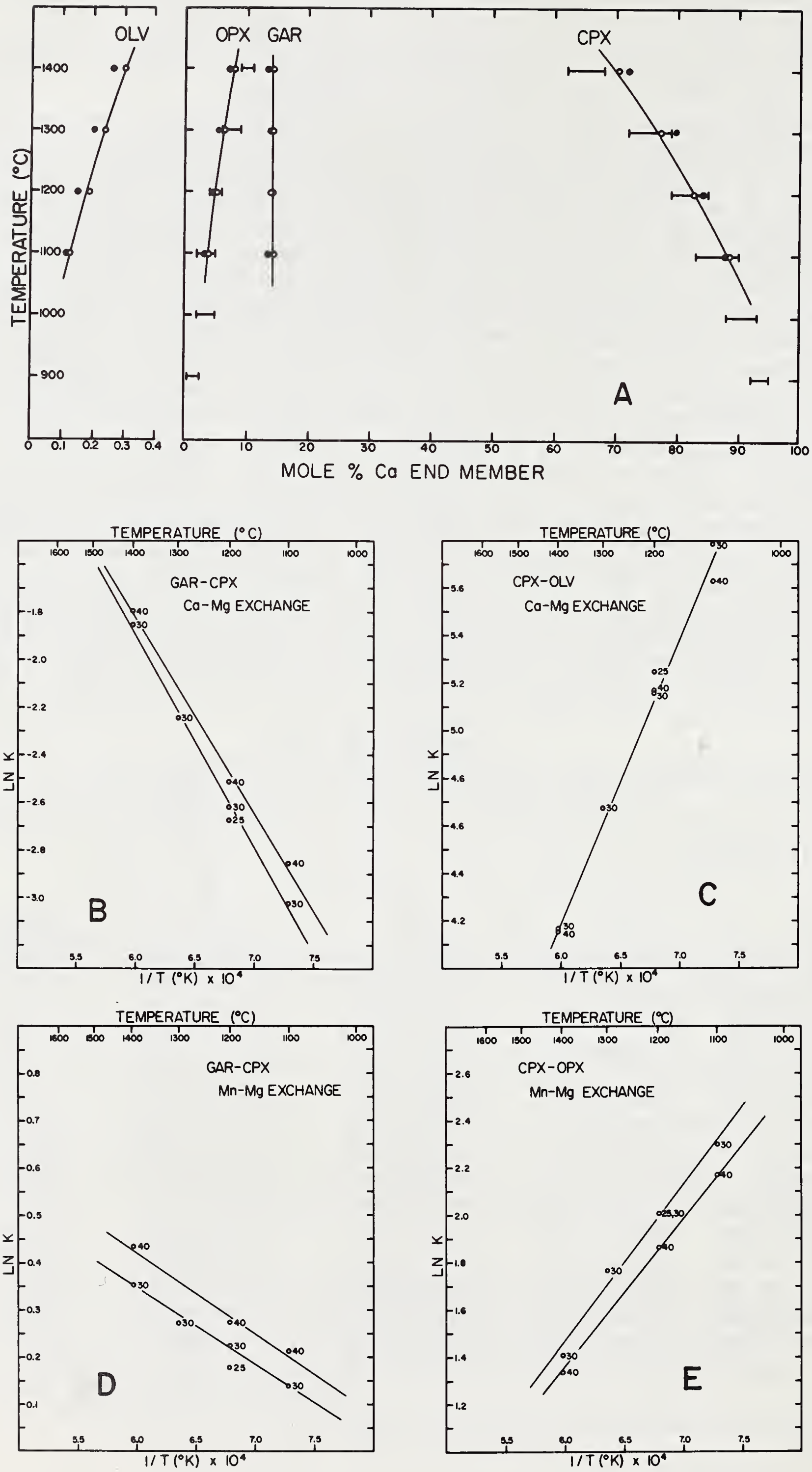
	$\Delta\bar{H}°$	$\Delta\bar{S}°$	$\Delta\bar{V}°$	σ(fit)
Gar/Cpx Ca-Mg	3.37(0.24)	0.82(0.14)	-1.36(0.12)	4.22%
Gar/Opx Ca-Mg	10.02(0.76)	5.72(0.46)	2.24(0.34)	1.20%
Gar/Olv Ca-Mg	19.00(0.30)	1.22(0.18)	-0.74(0.15)	0.34%
Cpx/Opx Ca-Mg	15.66(0.57)	4.91(0.34)	3.59(0.29)	0.75%
Cpx/Olv Ca-Mg	15.64(0.45)	0.40(0.28)	0.61(0.23)	0.56%
Opx/Olv Ca-Mg	-0.02(0.96)	-4.50(0.58)	-2.98(0.49)	4.14%
Gar/Cpx Al	10.0(1.6)	1.90(0.99)	5.28(0.83)	2.76%
Gar/Opx Al	1.95(0.90)	-2.01(0.55)	5.90(0.46)	1.79%
Cpx/Opx Al	-12.8(1.1)	-4.29(0.67)	1.26(0.56)	3.92%
Gar/Cpx Mn-Mg	4.09(0.22)	2.75(0.14)	-0.93(0.11)	5.26%
Gar/Opx Mn-Mg	-3.01(0.31)	0.25(0.18)	-0.21(0.15)	1.63%
Gar/Olv Mn-Mg	-3.26(0.31)	0.49(0.19)	-0.40(0.16)	1.36%
Cpx/Opx Mn-Mg	-7.25(0.29)	-2.52(0.18)	0.86(0.15)	2.01%
Cpx/Olv Mn-Mg	-7.35(0.32)	-2.25(0.20)	0.54(0.17)	1.76%
Opx/Olv Mn-Mg	-0.09(0.42)	0.27(0.25)	-0.32(0.21)	10.5%


OLV
OPX
GAR
CPX
TEMPERATURE (°C)
MOLE % Ca END MEMBER
A
GAR-CPX
Ca-Mg EXCHANGE
B
CPX-OLV
Ca-Mg EXCHANGE
C
GAR-CPX
Mn-Mg EXCHANGE
D
CPX-OPX
Mn-Mg EXCHANGE
E
LN K
1/T (°K) x 10^4