12.48 Handout #5

Thermometry-barometry using pyroxenes

Reading

Lindsley et al. (1981) Adv. in Physical Geochem., 149-175

Davidson and Lindsley (1985) Contrib. Min. Pet., 91:383-404.

This endeavor got its start thanks to an elegantly presented paper by Boyd (1973) GCA37 - 2533-2546.

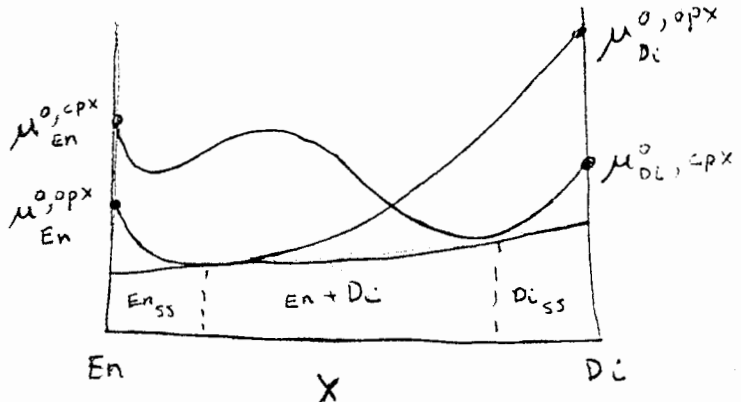
Boyd's suggestion was that two equilibria be used to estimate the T & P of equilibration of garnet lherzolites.

Boyd proposed that coexisting cpx-opx be used to infer temperature and that exchange equilibria involving garnet-opx be used to infer pressure.

We've come a long way from Boyd's initial proposal to the thermometry calcs of today. Today we'll look at progress and pitfalls encounted in this endeavor.

opx-cpx - 2 phases with 2 associated G curves, correct formulation treats each phase as a distinct solution.

G



at equilibrium $\mu^{cpx}_{En} - \mu^{opx}_{En} = \Delta G^{rxn}_{En} = 0$

$\mu^{cpx}_{Di} - \mu^{opx}_{Di} = \Delta G^{rxn}_{Di} = 0$

We could also write an exchange reaction

$$En^{cpx} + Di^{opx} \rightarrow Di^{cpx} + En^{opx}$$

$$\Delta G_{exch} = \Delta G^{Di} - \Delta G^{En}$$

and $= \mu_{Di}^{cpx} + \mu_{En}^{opx} - \mu_{Di}^{opx} - \mu_{En}^{cpx}$

Now we need to develop a realistic & workable soln. model.

We have at equil.

$$\mu_{En}^{o,opx} - \mu_{En}^{o,cpx} = RT\ln \frac{X_{En}^{cpx}}{X_{En}^{opx}} + RT\ln \frac{\gamma_{En}^{cpx}}{\gamma_{En}^{opx}}$$

$$\Delta G_{En}^{o} = RT\ln \frac{X_{En}^{cpx}}{X_{En}^{opx}} + RT\ln \frac{\gamma_{En}^{cpx}}{\gamma_{En}^{opx}}$$

Now we may plug what we know and solve for T.

X_{En}^{cpx}

X_{En}^{opx}

ΔG_{En}^{o} ΔG_{Di}^{o}

γ_{Di}^{cpx} γ_{En}^{cpx} - assymmetric

γ_{Di}^{opx} γ_{En}^{opx} - symmetric

} This is what Lindsley et al. do... using exp+l. data in Di-En

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Note - This is the right way of doing things-other ways

Assumption of Wood & Banno (1973) CMP 42 109-124 was that

activity coefficient ratio $= 1$ $\dfrac{\gamma_{Mg_2Si_2O_6}^{cpx}}{\gamma_{Mg_2Si_2O_6}^{opx}} = 1$ didn't consider constraints from $CaMgSi_2O_6$

Warner & Luth (1973) Am. Min. 58,998-
assume opx-cpx obey single equ. of state and used W_{Gs} as fitting parameters.

Binary system - two phases

equilibrium conditions

$$Mg_2Si_2O_6^{opx} \rightleftharpoons Mg_2Si_2O_6^{cpx}$$

$$CaMgSi_2O_6^{opx} \rightleftharpoons CaMgSi_2O_6^{cpx}$$

$$\mu_{En}^{opx} - \mu_{En}^{cpx} = 0; \quad \mu_{Di}^{opx} - \mu_{Di}^{cpx} = 0$$

$$X_{Di}d\mu_{Di} + X_{En}d\mu_{En} = 0$$

Gibbs-Duhem relates Di & En components at equilibrium

$$\mu_{En}^{cpx} - \mu_{En}^{opx} = \overbrace{\mu_{En}^{o,cpx} - \mu_{En}^{o,opx}}^{\Delta\mu^o} + RT\ln\frac{X_{En}^{cpx}}{X_{En}^{opx}} + RT\ln\frac{\gamma_{En}^{cpx}}{\gamma_{En}^{opx}} = 0$$

$$\mu_{Di}^{cpx} - \mu_{Di}^{opx} = \mu_{Di}^{o,cpx} - \mu_{Di}^{o,opx} + RT\ln\frac{X_{Di}^{cpx}}{X_{Di}^{opx}} + RT\ln\frac{\gamma_{Di}^{cpx}}{\gamma_{Di}^{opx}}$$

Use symmetric soln. model for opx & asymmetric for cpx.

$$\mu_{En}^{o,opx} - \mu_{En}^{o,cpx} = RT\ln\frac{X_{En}^{cpx}}{X_{En}^{opx}} - W_G^{opx}(X_{Di}^{opx})^2 + 2W_{G1}X_{En}^{cpx}(X_{Di}^{cpx})^2 + W_{G2}(1-2X_{En}^{cpx})(X_{Di}^{cpx})^2$$

$$\mu_{Di}^{o,opx} - \mu_{Di}^{o,cpx} = RT\ln\frac{X_{Di}^{cpx}}{X_{Di}^{opx}} - W_G^{opx}(X_{En}^{opx})^2 + W_{G1}(1-2X_{Di}^{cpx})(X_{En}^{cpx})2 + 2W_{G2}X_{Di}^{cpx}(X_{En}^{cpx})^2$$

Lindsley, Grover, Davidson model

$$GXS, opx = W_G^{opx} X_{En}^{opx} X_{Di}^{opx} = 25X_{En}^{opx} X_{Di}^{opx}$$

(KJ)

$$GXS, cpx = W_{G1}X_{En}^{cpx}(X_{Di}^{cpx})^2 + W_{G2}X_{Di}^{cpx}(X_{En}^{cpx})^2$$

W_{G1} W_{G2}

↑ ↑

(25.484 + .0812P) (31.216 - .0061P)

calculation of temperature from
opx - cpx pairs (binary system $CaMgSi_2O_6$-$Mg_2Si_2O_6$)

Note: these two expressions should give you the same T

$$T°K\ (Mg_2Si_2O_6^{opx} \leftrightharpoons Mg_2So_2O_6^{cpx}) =$$

$$3.561 + .0355P + 2W_{G1}X_{En}^{cpx}(X_{Di}^{cpx})2 + W_{G2}(X_{Di}^{cpx})^2(1-2X_{En}^{cpx}) - W_G^{opx}(X_{Di}^{opx})^2$$

$$.0091 - R\ln(X_{En}^{cpx}/X_{en}^{opx})$$

$$T°K(CaMgSi_2O_6^{cpx} \leftrightharpoons CaMgSi_2O_6^{cpx}) =$$

$$-21.178 - .0908P + W_{G1}(X_{En}^{cpx})^2(1-2X_{Di}^{cpx}) + 2W_{G2}X_{Di}^{cpx}(X_{En}^{cpx})2 - W_G^{opx}(X_{En}^{opx})^2$$

$$-.00816 - R\ln(X_{Di}^{cpx}/X_{Di}^{opx})$$

So, we've done the pure system Di-En, but the pyroxenes we want to study are almost always Fe-Ca-Mg solid solns. (at least!) - also Al, Ti, Cr, Na, Fe^{3+}

etc.

How do we generalize to these complex phases?

1st ----- We must generalize activity approx. to multi-site phase where the species can be ordered on sites -

2nd----- We must generalize such an expression for two component systems to complex systems. This has been done by Davidson and Lindsley (1985). There are also several graphical/empirical thermometers for pyx solns. that can be used.