12.480 Handout #6: Thermometry-Barometry Using Pyroxenes

Reading

Supplementary Reading

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 calculations of today. Today we’ll look at progress and pitfalls encountered in this endeavor.

opx-cpx — 2 phases with 2 associated $G$ curves. Correct formulation treats each phase as a distinct solution.

At equilibrium:

$$\mu_{E_{En}}^{cpx} - \mu_{E_{En}}^{opx} = \Delta G_{E{En}}^{En} = 0$$

$$\mu_{D_{Di}}^{cpx} - \mu_{D_{Di}}^{opx} = \Delta G_{D{Di}}^{En} = 0$$
We could also write an exchange reaction:

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

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

$$= \mu^{\text{cpx}}_{Di} + \mu^{\text{opx}}_{En} - \mu^{\text{opx}}_{Di} - \mu^{\text{cpx}}_{En}$$

Now we need to develop a realistic and workable solution model. We have at equilibrium:

$$\mu^{\text{cpx}}_{En} - \mu^{\text{opx}}_{En} = RT \ln \frac{X^{\text{cpx}}_{En}}{X^{\text{opx}}_{En}} + RT \ln \frac{\gamma^{\text{cpx}}_{En}}{\gamma^{\text{opx}}_{En}}$$

$$\Delta G^{\text{c}}_{En} = RT \ln \frac{X^{\text{cpx}}_{En}}{X^{\text{opx}}_{En}} + RT \ln \frac{\gamma^{\text{cpx}}_{En}}{\gamma^{\text{opx}}_{En}}$$

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

$$X^{\text{cpx}}_{En}$$

$$X^{\text{opx}}_{En}$$

$$\Delta G^{\text{c}}_{En} \quad \Delta G^{\text{c}}_{Di}$$

$$\gamma^{\text{cpx}}_{Di} \quad \gamma^{\text{cpx}}_{En} \quad \text{← asymmetric}$$

$$\gamma^{\text{opx}}_{Di} \quad \gamma^{\text{opx}}_{En} \quad \text{← symmetric}$$

This is what Lindsley et al. do, using experimental 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

$$\frac{\gamma^{\text{cpx}}_{Mg_2Si_2O_6}}{\gamma^{\text{opx}}_{Mg_2Si_2O_6}} = 1$$

didn’t consider constraints from $CaMgSi_2O_6$.
Warner & Luth (1973) Am. Min. 58, 998- assume opx-cpx obey single equation of state and used $W_{G_0}$ as fitting parameters.
Binary system - two phases

equilibrium conditions:

$$Mg_2Si_2O_6^{\text{cpx}} = Mg_2Si_2O_6^{\text{opx}}$$

$$CaMgSi_2O_6^{\text{cpx}} = CaMgSi_2O_6^{\text{opx}}$$

$$\mu^{\text{opx}}_{En} - \mu^{\text{cpx}}_{En} = 0; \quad \mu^{\text{opx}}_{Di} - \mu^{\text{cpx}}_{Di} = 0$$

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

Gibbs-Duhem relates Di & En components at equilibrium.

$$\Delta \mu$$

$$\mu^{\text{cpx}}_{En} - \mu^{\text{opx}}_{En} = \mu^{\text{cpx}}_{En} - \mu^{\text{opx}}_{En} + RT \ln \frac{X^{\text{cpx}}_{En}}{X^{\text{opx}}_{En}} + RT \ln \frac{\gamma^{\text{cpx}}_{En}}{\gamma^{\text{opx}}_{En}} = 0$$
\[
\mu_{D_i}^{cpx} - \mu_{D_i}^{opx} = \mu_{D_i}^{o,cpx} - \mu_{D_i}^{o,opx} + RT \ln \frac{X_{D_i}^{cpx}}{X_{D_i}^{opx}} + RT \ln \frac{\gamma_{D_i}^{cpx}}{\gamma_{D_i}^{opx}}
\]

Use symmetric solution model for opx and asymmetric for cpx.

\[
\begin{align*}
\mu_{En}^{o,opx} - \mu_{En}^{o,cpx} &= RT \ln \frac{X_{En}^{cpx}}{X_{En}^{opx}} - W_G^{opx} (X_{D_i}^{opx})^2 + 2W_G^{cpx} (X_{D_i}^{cpx})^2 + W_{G2} (1 - 2X_{En}^{cpx}) (X_{D_i}^{cpx})^2 \\
\mu_{D_i}^{o,opx} - \mu_{D_i}^{o,cpx} &= RT \ln \frac{X_{D_i}^{cpx}}{X_{D_i}^{opx}} - W_G^{opx} (X_{En}^{opx})^2 + W_{G1} (1 - 2X_{D_i}^{opx}) (X_{En}^{opx})^2 + 2W_{G2} X_{D_i}^{cpx} (X_{En}^{cpx})^2
\end{align*}
\]

Lindsley, Grover, Davidson model:

\[
\begin{align*}
GXS, \ opx &= W_G^{opx} X_{En}^{opx} X_{D_i}^{opx} = 25 X_{En}^{opx} X_{D_i}^{opx} \\
GXS, \ cpx &= W_{G1} X_{En}^{cpx} (X_{D_i}^{cpx})^2 + W_{G2} X_{D_i}^{cpx} (X_{En}^{cpx})^2
\end{align*}
\]

\[
\uparrow \quad \uparrow \quad (25.484 + .0812P) \quad (31.216 - .0061P)
\]

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 \(T\).

\[
\begin{align*}
T^\circ K (Mg_2Si_2O_6^{opx} \rightleftharpoons Mg_2Si_2O_6^{cpx}) &= 3.561 + .0355P + 2W_{G1} X_{En}^{cpx} (X_{D_i}^{cpx})^2 \\
+ & W_{G2} (X_{D_i}^{cpx})^2 (1 - 2X_{En}^{opx}) - W_G^{opx} (X_{D_i}^{opx})^2 \Big/ \left[ .0091 - R \ln \frac{X_{D_i}^{cpx}}{X_{D_i}^{opx}} \right] \\
T^\circ K (CaMgSi_2O_6^{cpx} \rightleftharpoons CaMgSi_2O_6^{opx}) &= -21.178 - .0908P + W_{G1} (X_{En}^{cpx})^2 (1 - 2X_{En}^{opx}) \\
+ & 2W_{G2} X_{D_i}^{cpx} (X_{En}^{opx})^2 - W_G^{opx} (X_{En}^{opx})^2 \Big/ \left[ -.00816 - R \ln \frac{X_{D_i}^{cpx}}{X_{D_i}^{opx}} \right]
\end{align*}
\]

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

How do we generalize to these complex phases?

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

2. 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.