

# THERMOCALC Short Course (São Paulo): 2006

## Day 1 Practical: Recalculating mineral analyses

The purpose of this practical is to do simple garnet-clinopyroxene (g-cpx) thermometry using THERMOCALC using mineral analyses of Proyer *et al.* (2004, *Contributions to Mineralogy and Petrology*, **147**, 305–318) for a Dabie Shan eclogite (SM9) in order to investigate the sensitivity of the calculated temperatures to the recalculation of clinopyroxene. The good thing about their study is that they performed Mössbauer spectroscopy on their omphacite (and garnet) so the amount of ferric iron in the minerals is known.

	Si	Ti	Cr	Al	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mn	Mg	Ca	Na	K
1	2.01554	0.00133	0.00168	0.48883	0	0.11303	0.0012	0.41074	0.44315	0.52342	0.00135
2	2.0154	0.00133	0.00168	0.4888	0.00079	0.11222	0.0012	0.41071	0.44312	0.52338	0.00135
3	1.99866	0.00134	0.00169	0.49282	0.03518	0.07853	0.00121	0.41406	0.44684	0.52832	0.00136
4	1.99866	0.00134	0.00169	0.48034	0.06117	0.05211	0.0012	0.41377	0.44652	0.54184	0.00136
5	1.99867	0.00133	0.00167	0.4944	0.061	0.05196	0.0012	0.41014	0.44255	0.51572	0.00135
4'	1.99866	0.00134	0.00169	0.48302	0.05557	0.05784	0.0012	0.41383	0.44658	0.53891	0.00136

This table is for one clinopyroxene analysis recalculated on 6 oxygens in different ways, using a variety of logic and approaches as outlined below.

In clinopyroxene there are 2 tetrahedral sites that can only be occupied by Si<sup>4+</sup> and Al<sup>3+</sup>, one M1 octahedral site involving the remainder of the Al<sup>3+</sup>, and all of the Ti<sup>4+</sup>, Cr<sup>3+</sup>, and the Fe<sup>3+</sup>, and one M2 octahedral site involving Ca<sup>2+</sup>, Na<sup>1+</sup> and K<sup>1+</sup>. The Fe<sup>2+</sup>, Mg<sup>2+</sup> and Mn<sup>2+</sup> are distributed across the octahedral sites with the assumption that

$$x = \left( \frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg}} \right)_{\text{M1}} = \left( \frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg}} \right)_{\text{M2}} = \left( \frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg}} \right)_{\text{cpx}}$$

This is adopted in the simple parameterisation of cpx used in the THERMOCALC datafile coding we will use below, along with

$$J = \left( \frac{\text{Na}}{\text{Na} + \text{Ca}} \right)_{\text{M2}} = \left( \frac{\text{Na}}{\text{Na} + \text{Ca}} \right)_{\text{cpx}}$$

The cpx datafile coding is actually an order-disorder one appropriate for omphacitic pyroxene, involving an order parameter,  $Q$ . Use the datafile value appropriate for the input  $PT$  for  $a$ - $x$  (see below).

1. Analysis 1 above takes the analysis “as is”, with all Fe as Fe<sup>2+</sup>, as is commonly used in thermometry. As you heard in the lecture, this will commonly introduce a strong upwards *bias* to thermometric results. Use the datafile, **tcdproyer1.txt**, which is set up to do this. Open this datafile: note that all the composition and interaction energy ( $W$ ) uncertainties (sd, followed by a number) are very small. This means that output uncertainties will relate only to dataset uncertainties (not to uncertainties stemming from non-ideality or the mineral analysis—including Fe<sup>2+</sup> → Fe<sup>3+</sup>).

Run THERMOCALC in mode 3 (first prompt on the screen), with **tcdproyer1.txt** (second prompt). For  $PT$  for  $a$ - $x$ , enter 30 and then 700 (the latter because this is the  $T$  of the cpx  $Q$  value you have used). For the  $P$  range of the calculations you could use 20 to 40 kbar,

and hitting return for the  $T$  range will give you the default (which is fine). Note down the  $T$  you get at 30 kbar (we will use this as a reference pressure today for this coesite-bearing eclogite), and also its uncertainty (sdT). (Note that all input and output for  $PT$  is in kbar and  $^{\circ}\text{C}$ ).

If you are concerned that the  $T$  result is much higher than the  $T$  (and  $Q$ ) you input for  $a-x$ , then substitute the  $Q$  for  $1000^{\circ}\text{C}$ , rerun and enter 30 and then 1000 for  $PT$  for  $a-x$ . Is the change of the  $T$  at 30 kbar

2. Analysis 2 is for a simple (i.e. naive) charge balance calculation. It assumes that the extra Si over and above the 2 needed for the tetrahedral site goes on the octahedral sites. We are fairly happy that this does not happen in nature, so this analysis is not much use to us.

But check that the analysis *is* charge-balanced: first distribute the cations across the sites (and for the purpose of this exercise put the excess Si onto M1) using the scheme outlined above. Then, taking a “reference” molecule like  $\text{CaMgSi}_2\text{O}_6$ , count up first the charges that are above those in diopside (i.e. octahedral tri- and quadrivalent cations), then count up those below (tetrahedral trivalent cations and octahedral monovalent cations): these two numbers must be equal for charge balance.

3. Analysis 3 is a “best” analysis, produced by least squares (as outlined in the lecture), that allows Si to just fill the tetrahedral site (with enough Al to balance the octahedral Ti via a molecule like  $\text{NaTiAlSi}_2\text{O}_6$ ), *and* which involves charge balance. This gives a minimum conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

Calculate the  $x(\text{cpx})$  value for this analysis, substitute it into the datafile, `tcdproyer1.txt`, and rerun THERMOCALC. Do you think the change in  $T$  is significant?

4. Analysis 4 uses the Mössbauer value for the ferric iron; this is also a “best” analysis with regards Si and the tetrahedral site (as in 3. above). Calculate the  $x(\text{cpx})$  value for this analysis, substitute it into the datafile, `tcdproyer1.txt`, and rerun THERMOCALC. (Note the sdt value as we shall use it below in assessing uncertainties: let’s call it  $\sigma_T^{\text{ds}}$  as it is the uncertainty stemming from the dataset itself)
5. Analysis 5 uses the Mössbauer value for the ferric iron, and additionally assumes that there is a small proportion (0.04) of eskolaite ( $\text{Ca}_{\frac{1}{2}}\text{v}_{\frac{1}{2}}\text{AlSi}_2\text{O}_6$ , where v is a vacancy), at the upper limit of likely proportion. Calculate the  $x(\text{cpx})$  value for this analysis and rerun THERMOCALC. (This shows that whereas eskolaite is relevant in other contexts, for example regarding quartz exsolution from omphacite, it has a minor effect on thermometry).
6. Analysis 4’ is the same as 4, except that the Mössbauer value for the ferric iron has been decreased by its analytical uncertainty. Calculate the  $x(\text{cpx})$  value for this analysis and rerun THERMOCALC. the difference between this  $T$  result and the one for analysis 4 gives an estimate of the  $T$  uncertainty stemming solely from the uncertainty in the Mössbauer analysis. Let’s call this  $\sigma_T^{\text{mo}}$ .

7. Now run `tcdproyer2.txt`, which has a (minimal) uncertainty of 1 kJ applied to each w, and see what the resulting sdt is (for analysis 4): let’s call it  $\sigma_T^{\text{ds+w}}$  as it stems from dataset and  $w$  uncertainties. We can determine  $\sigma_T^{\text{ds+w}}$  easily from  $(\sigma_T^{\text{ds+w}})^2 = (\sigma_T^{\text{ds}})^2 + (\sigma_T^{\text{w}})^2$ . (So  $\sigma_T^{\text{w}} = \sqrt{(\sigma_T^{\text{ds+w}})^2 - (\sigma_T^{\text{ds}})^2}$ ).
8. For comparison or relative uncertainties the *minimum*  $\pm_T \approx 2\sigma_T^{\text{mo}}$  (but will be larger without Mössbauer), and absolute uncertainties will be, at a minimum, of the order of  $\pm_T \approx 2\sqrt{(\sigma_T^{\text{mo}})^2 + (\sigma_T^{\text{ds}})^2 + (\sigma_T^{\text{w}})^2}$ . What is this value?