Notes for Use of the *Cpx-Plag-Ol Thermobar* Workbook
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Cpx-Plag-Ol Thermobar is an Excel workbook that can be used to calculate crystallization pressures and temperatures for clinopyroxene- and plagioclase-liquid composition pairs. For clinopyroxene, the calculations utilize the models of Putirka et al. (1996, 2003) and Putirka (2005). The workbook also allows for calculation of a clinopyroxene saturation surface, using the models of Putirka (1999) (i.e., the worksheet calculates a clinopyroxene saturation temperature, and nominal equilibrium clinopyroxene composition, for a given input liquid composition and input pressure). In addition, the workbook contains several olivine-liquid thermometers.

The workbook is set up so that data entry is performed in the following worksheets Cpx & Liq Input, Plag & Liq Input and Ol & Liq Input. You will need to input clinopyroxene, plagioclase and/or olivine compositions as weight % values. You will also need to input weight % values for nominal equilibrium liquid compositions; for these latter values, whole rock or glass compositions might be used, or perhaps a whole rock composition adjusted for the addition or subtraction of phenocryst phases. Once the appropriate data are entered all results can be viewed in the first few columns of the three worksheets: Cpx P-T Results, Plag P-T Results, and Ol Temp Results. This workbook differs somewhat in format compared to earlier spreadsheets: the various worksheet pairs ("-Input" & "-Results") are linked, hence, there is no longer a need to cut and paste results from one spreadsheet to another. Some notes regarding the application of these models follow.

General Instructions:
1) Input weight % data for nominal liquid and mineral compositions using the "-Input" worksheets, then read the results in the worksheets labeled "- Results". The individual Input worksheets are color-coded:

gray = input, or calculations that are not a function of P and/or T calculations.
colors = results columns.

Cut-and-paste operations will delete these formats, but will not affect *P-T* calculations ("paste special – values only" will preserve the formats).

2) To enter additional data, enter weight %'s in the appropriate columns and then use the fill down command for ALL columns in the "-Results" worksheets.

Caveats:
1) If you receive a 'circular reference' error while using *P-T Calcs*, make sure that in the Tools-Preferences-Calculation window (in Excel) the Iteration box is checked, or that your spreadsheet preferences are otherwise set up to handle iterative calculations.

2) For clinopyroxene P-T calculations, if Excel returns the error: #NUM! one very likely reason is that your clinopyroxene composition was such that a jadeite component could not be calculated (this will happen if either Na or octahedral Al are too low in the analysis/calculation).

Clinopyroxene calculations:
In contrast to the models of Putirka et al. (1996) the model results labeled *Am. Min. 2003* apply to a wider range of liquid compositions (basalt – dacite) as well as hydrous liquid compositions. The 1996 models, though, might be more precise for dry basaltic bulk compositions.

Tests of equilibrium: The predicted clinopyroxene components in Cpx *P-T Results* (columns N – U) and the clinopyroxene saturation temperature, *Cpx sat* in column L are predicted using the models of Putirka (1999) and make use of the input liquid composition, and the estimate of P in column D. These models collectively comprise a saturation surface for clinopyroxene calibrated using experiments performed on a range of silicate liquids. As the Jd component is to a significant extent a function of pressure, prediction of this component is necessarily circular, but most other components, though still P-dependent, should be useful as a test to whether a suitable liquid composition has been selected for a given clinopyroxene. The argument is as follows: If the input liquid composition were at the predicted pressure then (a) at what T would clinopyroxene crystallize (the saturation *T*, in column L)? and (b) what would be the equilibrium composition of the clinopyroxene (the output of columns N – U)? The hope is that if the liquid and clinopyroxene compositions represent an equilibrium pair, then the *T* of saturation should approach that of the crystallization *T* (L compared to C or F). Similarly, clinopyroxene components calculated from the observed phenocryst phases (columns W – AD) should approach values calculated from the assumption of equilibrium (columns N – U). To avoid circularity altogether, one may enter some nominal P value as input into column M (which by default will be the pressure given in column D, from the Am. Min., 2003 paper).

Olivine and cpx crystallization temperatures need not match, but the Fe-Mg exchange model of Putirka et al. (1996), and olivine (see below) can be used to compare olivine crystallization conditions to those calculated from cpx. Some whole rock liquid compositions that appear not to be liquids (due to cumulus olivine) can still sometimes be used by adding or subtracting an appropriate amount of olivine to bring Fe-Mg exchange ratios to anticipated equilibrium values. One can then, for example, check whether the amount of olivine removed matches modal proportions (although there are some obvious complications to this approach). In summary, adjusting cumulate whole rock compositions until either (a) olivine-liquid K_D(Fe-Mg) exchange values approach 0.3 (Roeder and Emslie, 1971), or (b) cpx K_D(Fe-Mg) approaches 0.27 (or values predicted from

equation 3.3 in Table 3 of Putirka (1999); see also column *T* of <u>Cpx *P-T* Results</u>), might at times be useful.

<u>The clinopyroxene component</u> calculation scheme follows a normative procedure adapted from Lindsley (1983); cations are calculated on the basis of 6 oxygens (see Klein, 2002). Fe^{3+} is calculated using models of Lindsley (1983) and Droop (1987) (see columns AH – AI in <u>Cpx P-T Results</u>) but Fe^{3+} measurements by McGuire et al (1989) indicate that such values are of limited usefulness. A check of clinopyroxene cation sums (column AF), and a check that K in clinopyroxene is very close to zero, are probably the best means to evaluate the quality of clinopyroxene analyses.

Plagioclase Thermobarometers
These calculations are based on the models of Putirka (2005). Be aware that plag-liquid hygrometers are not very effective at predicting H_2O for samples not used for calibration.

Olivine Temperatures:
An new olivine-melt thermometer is provided (in column D of <u>Ol Temp Results)</u>; it was calibrated in an attempt to provide a single olivine + liquid thermometer that could be applied to both hydrous and anhydrous bulk compositions. I have also added several other olivine theremometers, some of which will yield a single T for a given bulk composition (e.g., Beattie, 1993). Olivine temperature estimates are sensitive to f(O2), and so using cells D5 and J5 in the Ol Temp Results spreadsheet, it is possible to adjust f(O2) conditions. Since the calculations are iterative, please note that adjusting "log units" in cell J5 will not yield a precisely a whole number log unit difference in calculated $f(O_2)$.

Olivine temperatures for the various models in this spreadsheet are compared using 635 experimental data whose experimental conditions range from 950-1950 ^{o}C, and 0-70 kbar. In these experiments, liquid (glass) compositions range from 38-73 wt. % SiO_2, and 107 of these experiments were performed on hydrous bulk compositions. All models predict *T*'s that are too high for the 1600 – 1950 ^{o}C range, hence statistics for all models are compared for the 614 experimental data conducted between in the 940 – 1600 ^{o}C (Tables 1, 2). For anhydrous data, the models of Beattie (1993) and Model 3 are the most precise, though Model 3 yields much better slope and intercept values for the regression line (*T*-predicted *vs.* *T*-measured). The Beattie (1993) model over-predicts *T* for 96% of the 107 hydrous experiments (by a coincidental average of 107 ^{o}C), as can be seen below in Table 2 (Difference of Means = Mean of predicted values – Mean of observed values). The Langmuir et al. (1992) model provides the least systematic offset for the hydrous data, but with a 25% cost in SEE compared to Model 3.

Table 1   *T*(C) Calculated *vs. T*(C) Measured

	Anhydrous and Hydrous data	Anhydrous data only

	T(C) = 940 - 1600; n = 614				T(C) = 945 - 1600; n = 507				
	R^2	SEE	Slope	Intercept	R^2	SEE	Slope	Intercept	Difference of Means
Beattie (1993)	0.77	39	0.63	485	0.87	29	0.68	408	26
Langmuir et al. (1992)	0.72	74	1.04	-83	0.78	65	1.11	-179	-40
Ford et al. (1983) (Mg-model)	0.42	104	0.78	328	0.41	109	0.82	263	51
Model 3	0.77	50	0.80	216	0.83	42	0.86	148	-27

Table 2 T(C) Calculated *vs.* T(C) Measured

Hydrous data only

	T(C) = 940 - 1390; n = 107				
	R^2	SEE	Slope	Intercept	Difference of Means
Beattie (1993)	0.79	38	0.6	567	107
Langmuir et al. (1992)	0.80	64	1.05	-18	46
Ford et al. (1983) (Mg-model)	0.77	54	0.81	354	130
Model 3	0.80	51	0.82	255	48

Some References

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Please note that these Excel worksheets were not originally designed for distribution, but having received a large number of requests, I have tried to put together something useful. I would still greatly appreciate any feedback from you if you have suggestions for improvement or added clarity. Thank you for your interest in this work.

Cheers,

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