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**Multiple-reaction geobarometry for olivine-bearing igneous rocks**

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# Supplementary Material 2

Example of avP calculation and diagnostics

This section describes a step-by-step procedure for the calculation of $\overline{P}$ with avP for an igneous rock that includes spinel, clinopyroxene, olivine and plagioclase in its assemblage. As an example, here we use the olivine-gabbro xenolith DC90 from Dominica, Lesser Antilles (see Supplementary Material 8 for sample description). The mineral compositions used for the calculations refer to the electron microprobe analyses made on the rims of adjacent crystals (Supplementary Material 5 and Fig. 10). Calculations here are performed by running THERMOCALC directly. Note that a GUI (Graphical User Interface) wrapper that calculates the compositional variables and performs calculations for multiple samples at once (so far only available for Mac) will be made available upon request to the authors.

**1) Place the files required for the calculations in the same folder.** These are the executable program THERMOCALC (version 3.47i; "tc347i" for MAC, "tc347.exe" for PC), the dataset (version 6.3, generated 29 March, 2016 as stamped on last line of file; "tc-ds63.txt") and *a-x* model ("tc-ax-SCOlP.txt") files, the preference file ("tc.prefs.txt") and the script file ("tc-script.txt"). These files can be requested from the authors. They will also be made available to download from the reorganised THERMOCALC website, to be hosted by the University of St Andrews. Note that the THERMOCALC website offers general resources on avP calculations and the program itself, and at the time of writing is found at http://www.metamorph.geo.uni-mainz.de/thermocalc. Of the files listed above, the user should only modify the script file.

**2) Calculate mineral formulae and their uncertainties.** Starting from the mineral composition in oxides wt%, calculate the formula in terms of cations expressed as atoms per formula unit (apfu) , with olivine, spinel, clinopyroxene and plagioclase recalculated on a basis of 4, 4, 6 and 8 oxygens respectively. Non-zero values

for $Fe^{3+}$ in clinopyroxene and spinel is required; below these are calculated from stoichiometry following the method of Droop (1987). Uncertainties are propagated from analytical errors in the oxides wt% determined from counting statistics of the electron microprobe (e.g., Supplementary Material 5 for the analyses in this work).

**3) Calculate the activity-composition (*a–x*) model compositional variables and their uncertainties.** Compositional variables in THERMOCALC are written in terms of site fractions, which are derived from the cations expressed as apfu (see below). If a calculated compositional variable is < 0.001, set the value to 0.001. The variables Q(ol) and Q(cpx) express the amount of ordering involved in partitioning $Fe^{2+}$ and Mg over the cation sites. The equilibrium values of these variables at $P_0$, $T_0$, are found automatically by THERMOCALC at the beginning of the avP calculation, and the user has only to provide a standard starting guess, which in general can be 0.05. Uncertainties are propagated from the analytical errors. Uncertainties on x(sp) and f(sp) are then increased by a factor of 4 (see main text for the rationale behind this choice). Compositional variables are defined as follow (resulting values refer to calculations for sample DC90):

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'1-site' Spinel:

$$x(sp) = \frac{x^M_{Fe^{2+}}}{x^M_{Fe^{2+}} + x^M_{Mg}} = \frac{\mathrm{Fe^{2+}}}{\mathrm{Fe^{2+} + Mg}} = 0.823 \pm 0.029$$

$$f(sp) = \frac{3\, x^M_{Fe^{3+}}}{2} = \frac{\mathrm{Fe^{3+}}}{2} = 0.653 \pm 0.041$$

$$ti(sp) = 3\, x^M_{Ti} = \mathrm{Ti} = 0.203 \pm 0.004$$

$$cr(sp) = \frac{3\, x^M_{Cr}}{2} = \frac{\mathrm{Cr}}{2} = 0.001 \pm 0.001$$

Clinopyroxene:

$$x(cpx) = \frac{x^{M1}_{Fe} + x^{M2}_{Fe}}{x^{M1}_{Fe} + x^{M2}_{Fe} + x^{M1}_{Mg} + x^{M2}_{Mg}} = \frac{Fe^{2+}}{Fe^{2+} + \mathrm{Mg}} = 0.181 \pm 0.011$$

$$y(cpx) = 2\, x^T_{Al} = 2 - \mathrm{Si} = 0.117 \pm 0.008$$

$$f(cpx) = x^{M1}_{Fe^{3+}} = \mathrm{Fe^{3+}} = 0.059 \pm 0.013$$
$$z(cpx) = x^{M2}_{Ca} = \mathrm{Ca} = 0.878 \pm 0.006$$

$j(cpx) = x_{Na}^{M2} = \mathrm{Na} = 0.016 \pm 0.002$

$Q(cpx) = 2\left(\frac{x_{Fe}^{M2}}{x_{Fe}^{M2}+x_{Mg}^{M2}} - x(cpx)\right) = 0.05$ (order-disorder variable, use 0.05 as a standard starting guess)

Olivine:

$x(ol) = \frac{x_{Fe}^{M1}+x_{Fe}^{M2}}{x_{Fe}^{M1}+x_{Fe}^{M2}+x_{Mg}^{M1}+x_{Mg}^{M2}} = \frac{\mathrm{Fe}}{\mathrm{Fe}+\mathrm{Mg}} = 0.286 \pm 0.001$

$Q(ol) = 2\left(\frac{x_{Fe}^{M2}}{x_{Fe}^{M2}+x_{Mg}^{M2}} - x(ol)\right) = 0.05$ (order-disorder variable, use 0.05 as a standard starting guess)

Plagioclase:

$ca(pl) = \frac{\mathrm{Ca}}{\mathrm{Ca}+\mathrm{Na}+\mathrm{K}} = 0.932 \pm 0.003$

$k(pl) = \frac{\mathrm{K}}{\mathrm{Ca}+\mathrm{Na}+\mathrm{K}} = 0.001 \pm 0.001$

---

**4) Enter the calculated compositional variables and their uncertainties in the THERMOCALC script file.**

The script file below can be used as a guide for the inputs (user inputs that need to be set at each calculation are highlighted in bold). Save the file (don't change the file name).

---

```
% AvP/AvPy geobarometry: software distribution for:
% Ziberna, Green & Blundy (2017) Multiple-reaction
% geobarometry for olivine-bearing igneous rocks
% American Mineralogist xx xx.
%
% This is the "scriptfile" containing details of
% the calculations that Thermocalc should perform.
% N.B. Thermocalc reads in model information from
% an axfile (see below) and from tc-ds63.txt.
%
% If using the avPy GUI wrapper (only available for Mac),
% the user does not need to edit this file.
%
% If running in Thermocalc directly, this file should
% be used to enter compositions and their uncertainties
%
% ================================================
% User-set information

% ------------------------------------

axfile ax-SCOlP               % axfile to read

printcov yes          % print covariance matrices?

printcor yes          % print correlation matrices?


% ------------------------------------
% Compositional variables and their standard
% deviations for spinel (sp), cpx, olivine (ol)
% and plagioclase (pl). Definitions in terms
% of site fractions of cations are found at the
% bottom of this file; see also Ziberna et al 2017.
% N.B. The user does NOT need to give a value for
% Q(cpx), Q(ol).
```

```
xyz  x(sp)     0.823   sd 0.029
xyz  f(sp)     0.653   sd 0.041
xyz  ti(sp)    0.203   sd 0.004
xyz  cr(sp)    0.001   sd 0.001
xyz  x(cpx)    0.181   sd 0.011
xyz  y(cpx)    0.117   sd 0.008
xyz  f(cpx)    0.059   sd 0.013
xyz  z(cpx)    0.878   sd 0.006
xyz  j(cpx)    0.016   sd 0.002
xyz  Qfm(cpx)  0.05    range  0 2  % do not change
xyz  x(ol)     0.286   sd 0.001
xyz  Q(ol)     0.05                % do not change
xyz  ca(pl)    0.932   sd 0.003
xyz  k(pl)     0.001   sd 0.001


% ================================================
% Some standard information: no edits needed
infolevel 1

calctatp ask

setdefTwindow no  500.001 1500.001
setdefPwindow no  0.01 50


negp yes       % minimum for P window is -50.0 kbar

oisr yes       % print independent reactions matrix in the log file


% -----------------------------------
% Matrix of reactions: editing not advised

%              di    cenh     cfs     jd      acm    cats     fo      fa      abh     an      sp     herc      mt
setisr         0      -1       0       0       0      -1       1       0       0       1       0       0       0    % r2
setisr         0       0      -1       0       0      -1       0       1       0       1       0       0       0    % r3
setisr         0      -1       0      -1       0       0       1       0       1       0       0       0       0    % r4
setisr         1      -1       0       0       0      -2       0       0       0       1       1       0       0    % r5
setisr         0      -1       0      -1       0       0       0       1       1       0       2      -2       0    % r6
setisr         0       0      -2       0      -2       0       0       2       2       0       0      -1       1    % r7

*
```

**5) Run THERMOCALC.** Windows users may open THERMOCALC by double-clicking the tc347.exe executable. Mac users should open a Terminal window, set the working directory to be the directory containing the THERMOCALC software and input files, and run THERMOCALC by typing "./tc347i" (for a more detailed explanation see the "Getting started" section of the THERMOCALC website). The log-file below can be used as a guide for the inputs in the calculations (user inputs are highlighted in bold). Select the control code 2 for avP calculations and then type the phases to be used for the calculations (i.e., either "sp cpx ol pl" or "cpx ol pl"). Then enter $P_0$ and $T_0$ (initial estimates of pressure and temperature). For crustal rocks, $P_0$ can be always set to 4 kbar, since it has been noted that variations in the range 1–15 kbar do not cause significant changes in the calculated $\overline{P}$. Set $T_0$ at the temperature of equilibration estimated for the assemblage. THERMOCALC then automatically reads the a–x models and use them to convert the compositional variables to activities. The final

step is to set the T and P window. If temperature is well constrained by some geothermometers (e.g., Putirka 2008; Shejwalkar and Coogan 2013), this can be set a single value for the T window. Alternatively, multiple avP calculations can be performed over a range of temperatures (section "Sensitivity of avP to $P_0$ and $T_0$"). The example here show a calculation for a single temperature value (870 ºC). The pressure window can be set to $P_0$ ± 20 kbar.

```
calculation type :
     0 = table of thermodynamic data of end-members
     1 = phase diagram calculations
     2 = average pressure-temperature calculations
     3 = calculations on all reactions between end-members
     4 = list end-member names and compositions
control code  : 2

THERMOCALC 3.45  running at 12.31 on Fri 30 Jun,2017
the main output is in the file, "tc-script-o.txt"
other (eg drawpd) output is in the file, "tc-script-dr.txt"
additional output is in the file (don't look!), "tc-script-ic.txt"


^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^^

THERMOCALC running at 12.31 on Fri 30 Jun,2017
using tc-ds63.txt produced at 12.44 on Tue 29 Mar,2016 (sigfit =  1.038)
with axfile tc-ax-SCOlP.txt and scriptfile tc-script.txt

cpx  ol  pl  sp

(solid) solutions will be taken apart into their constituent end-members

cpx  ol  pl  sp
which phases :  cpx ol pl sp

activities of end-members in solid solutions are
calculated with input values of compositional variables
(the following PT are the initial values used in a-x calcs)
P for a-x : 4
T for a-x : 870

san excluded
type of rock calculation: average P

             di     cenh      cfs       jd      acm     cats       fo       fa
     a    0.677    0.346   0.0354   0.0111  0.00553   0.0857    0.539    0.108
 sd(a)   0.0127   0.0353  0.00453  0.00295  0.00146   0.0196  0.00700  0.00649

            abh       an       sp     herc       mt
     a    0.206    0.936    0.142   0.0927    0.678
 sd(a)   0.0181  0.00302   0.0854   0.0541   0.0888

these data ok ? yes

specification of PT window:
T range over which average P to be calculated
T window: T low,high : 870
P window within which average P expected to lie
P window: P low,high :  -16 24


%             di cenh  cfs   jd  acm cats   fo   fa  abh   an   sp herc   mt
setisr         0   -1    0    0    0   -1    1    0    0    1    0    0    0
setisr         0    0   -1    0    0   -1    0    1    0    1    0    0    0
setisr         0   -1    0   -1    0    0    1    0    1    0    0    0    0
setisr         1   -1    0    0    0   -2    0    0    0    1    1    0    0
setisr         0   -1    0   -1    0    0    0    1    1    0    2   -2    0
setisr         0    0   -2    0   -2    0    0    2    2    0    0   -1    1


Activities and their uncertainties
```

User input: mineral assemblage

User input: $P_0$ and $T_0$

Activities calculated at $T_0$ and $P_0$

User input: P-T window

Independent set of reactions in matrix form

```
                di      cenh       cfs        jd       acm      cats        fo
a            0.677     0.346    0.0354    0.0111   0.00553    0.0857     0.539
sd(a)/a    0.01869   0.10204   0.12802   0.26514   0.26403   0.22826   0.01299

                fa       abh        an        sp      herc        mt
a            0.108     0.206     0.936     0.142    0.0927     0.678
sd(a)/a    0.06033   0.08754   0.00323   0.60171   0.58313   0.13104

Independent set of reactions
1)  cenh + cats = fo + an
2)  cfs + cats = fa + an
3)  cenh + jd = fo + abh
4)  cenh + 2cats = di + an + sp
5)  cenh + jd + 2herc = fa + abh + 2sp
6)  2cfs + 2acm + herc = 2fa + 2abh + mt

Calculations for the set of reactions at T = 870°C
        P(T)    sd(P)        a    sd(a)         b         c      ln_K sd(ln_K)
1        4.3     1.35   -13.08     0.22   -0.01877     1.767     2.833     0.250
2        4.8     1.61   -20.12     0.20   -0.01820     1.594     3.502     0.269
3        4.0     1.30    14.76     0.24   -0.04845     2.184     3.363     0.298
4        8.1     4.40   -24.01     0.35   -0.02034     1.648     3.565     0.762
5        4.3     7.20     7.25     0.58   -0.03649     2.249     2.603     1.703
6       0.81     2.42   -24.63     3.23   -0.07616     3.651    11.452     0.864

corresponding average P

         avP      sd   fit
lsq     3.58    0.91  0.81

diagnostics on this average P

for 95% confidence, fit (= sd(fit) = sqrt(MSWD)) < 1.49 (but larger may be OK)

column:
1-3: result of doubling the uncertainty on ln a.
4-5: e* and hat for ln(activity) of end-membershat >0.46 influential.
6-7: observed and calculated activities of endmembers.
8-9: e* and hat for enthalpies of end-members

              P     sd    fit     e*   hat    a(obs)    a(calc)     e*   hat
      di   3.58   0.91   0.81    0.0  0.00     0.677      0.677   0.00  0.00
    cenh   3.69   1.02   0.81    0.2  0.18     0.347      0.354   0.01  0.00
     cfs   3.53   0.92   0.80   -0.3  0.03    0.0354     0.0341  -0.02  0.00
      jd   3.32   1.04   0.78   -0.5  0.29    0.0111    0.00984  -0.16  0.00
     acm   3.72   0.92   0.70    0.9  0.03   0.00553    0.00701   0.53  0.01
    cats   3.21   1.04   0.75   -0.7  0.29    0.0858     0.0732  -0.02  0.00
      fo   3.58   0.91   0.81   -0.0  0.00     0.539      0.539  -0.03  0.00
      fa   3.55   0.91   0.81    0.1  0.01     0.108      0.109  -0.01  0.00
     abh   3.65   0.96   0.81   -0.1  0.05     0.206      0.204  -0.15  0.00
      an   3.58   0.91   0.81    0.0  0.00     0.936      0.936   0.05  0.00
      sp   3.71   0.92   0.75    0.8  0.05     0.142      0.232   0.04  0.00
    herc   3.71   0.92   0.75    0.8  0.05    0.0927      0.146   0.04  0.00
      mt   3.60   0.91   0.80   -0.2  0.00     0.678      0.658  -0.07  0.00

|e*| >2.5 suspect?  hat >0.46 influential?

Average pressures  at T = 870°C
For T = 870 °C, av P = 3.6 kbar, sd = 0.91, sigfit = 0.8
```

Activities calculated at $T_0$ and $P_0$

Independent set of reactions

Linearized expressions for the reactions

$a_r + b_r T + c_r P = RT\ln K_r$

avP results: $\bar{P}$, $\sigma_{\bar{P}}$, $\sigma_{fit}$

avP diagnostics

avP results: $\bar{P}$, $\sigma_{\bar{P}}$, $\sigma_{fit}$

**6) Check the results and diagnostics.** The main results are listed at the end of file, where $\bar{P}$, $\sigma_{\bar{P}}$, $\sigma_{fit}$ are given for the temperature specified in the T window. The value of $\sigma_{fit}$, distributed as $\chi^2$, can be compared with the appropriate cut-off value, evaluating the consistency of the input data (Powell and Holland 1994). For an independent set of six reactions, such as our calculations with SCOlP, the cut-off value is 1.49, indicating that in the calculation shown above the $\chi^2$ test is passed and therefore the results are consistent with the input data.

For a set of three reactions (such as COlP), the cut-off value is 1.73. Note that these cut-off values are only indicative and that calculations with higher $\sigma_{fit}$ values (up to ~ 20% of the cut-off value) might still produce acceptable results. If $\chi^2$ test is not passed and $\sigma_{fit}$ >> cut-off value, this may reflect either inaccurate thermodynamic data or incomplete equilibrium of the sample, or both. Other important diagnostics quantify the effect of individual end-members on the results. The first three columns show the result of avP when the uncertainty on ln$a_i$ is doubled. Columns 5 and 9 are the hat values ($h_i$) for end-member activity and enthalpy and are a measure of the degree of influence of the end-member on the least-squares result. Columns 4 and 8 are the activity and enthalpy residuals ($e_i^*$ and $H_i^*$) for the end-member i. $e_i^*$ is defined as

$$e_i^* = \frac{a_i^{obs} - a_i^{calc}}{\sigma_{a_i}}, \qquad (3)$$

where $a_i^{obs}$ (column 6) is the observed activity, $a_i^{calc}$ (column 7) is the calculated activity required for all the equilibria to intersect at $\overline{P}$, and $\sigma_{a_i}$ is the activity uncertainty (Powell and Holland 1994). For an independent set of six reactions and one variable to be solved for (i.e. pressure in our case), the cutoff value for |e*| is 2.5, as printed by THERMOCALC below the diagnostics table.