# Use of the Holland *et al.* (2018) models

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## 1. Context for the thermodynamic models, and when to use them

The Holland *et al.* (2018) thermodynamic models comprise a collection of activity-composition (*a-x*) relations for key mineral and melt phases, built on the Holland & Powell (2011) internally-consistent dataset of end-member thermodynamic properties. The models facilitate phase equilibrium calculations on fractionation from granitic to basaltic (tholeiitic to mildly alkalic) melt compositions. They are calibrated for use in dry peridotite melting calculations up to 70 kbar, or for wet melting calculations up to 20 kbar, using a model for $H_2O$-fluid containing dissolved silicates.

The solution phases in the *a-x* input files provided are: silicate melt (liq), aqueous fluid (fl), spinel (Al-spinel, spn; Cr-spinel, cm; magnetite, mt), garnet (g), olivine (ol), orthopyroxene (opx), clinopyroxene (augite, cpx; pigeonite, pig), cordierite (cd), ilmenite (ilm), feldspars (Ibar1 plagioclase, pl; Cbar1 plagioclase, plc; Cbar1 potassium feldspar, ksp), muscovite (mu), biotite (bi), clinoamphibole (hb), epidote (ep).

Previously, similar sets of thermodynamic models were developed for calculations on partial melting equilibria in metapelites (White, Powell, Holland, Johnson & Green, 2014, *J. Metam. Geol.* 32, 261-86) and metabasites (Green, White, Diener, Powell, Holland & Palin, 2016, *J. Metam. Geol.* 34, 845-69). For the phases silicate melt, spinel, garnet, olivine, orthopyroxene, clinopyroxene and cordierite, the *a-x* relations in the different model sets are differently structured and parameterised. Additionally, the different model sets are provided with different versions of the underlying Holland & Powell (2011) dataset. *A-x* relations and dataset versions in the various model sets **should not be mixed up**.

For phase equilibrium calculations within the domain of the metapelite or metabasite set of models (see the respective papers as cited above), it is safer to keep using those model sets at present, though we do aim eventually to produce a single library of thermodynamic models with one model per phase. Note in particular that the clinopyroxene model used in the Holland *et al.* (2018) model set has **no capacity for omphacite-like order-disorder**. For calculations involving jadeitic or omphacitic clinopyroxene, the metabasite set of models will be needed, using the models jd, dio, o (only) for clinopyroxene.

## 2. Compatibility with the Holland & Powell dataset and THERMOCALC

The Holland *et al*. (2018) *a-x* relations should be used with **version 6.33** of the Holland & Powell dataset (see Holland & Powell, 2011). This is encoded for THERMOCALC in the file **tc-ds633.txt**, generated at 20:37 on 23 June 2017 (see timestamp at bottom of file). The models can be run in THERMOCALC version 3.47 or later.

## 3. Tips for users

**Using the THERMOCALC software as a calculator**

THERMOCALC finds the compositions and modal proportions of phases at a given pressure and temperature in a specified bulk composition. It does this by solving an independent set of equations for equality of chemical potential and mass balance.

Note that THERMOCALC doesn't look for the most stable assemblage, but simply seeks to calculate an equilibrium among the phases provided by the user. The user is responsible for building a stable phase diagram based on logical steps constrained by the phase rule (see *Where to get help* below).

Currently (July 2018) it is not possible to do automated fractionation calculations in THERMOCALC, though such calculations can be done manually as described in the tutorial on the "rbi" script provided on the THERMOCALC website. The models will soon be available for use with the Gibbs energy minimisation software Perple_X, which already provides a fractionation option.

**Compositional and order parameters in THERMOCALC**

The Holland *et al*. (2018) *a-x* relations are written in terms of compositional variables that are defined in terms of site fractions (for minerals) or end-member proportions (for fluids). Definitions of these variables can be found in the input file of *a-x* relations (e.g. *tc-KNCFMASTOCr.txt*, *tc-KNCFMASHTOCr.txt*), in the header for each model, along with some key thermodynamic variables. Alternatively, compositions are provided in mole% oxides in the output file with the suffix "-ic". In the mole% oxide lists, "FeO" is all-Fe-as-FeO (FeOt), with O indicating the amount of FeO converted to O, such that Fe2O3 = O and $FeO_{true}$ = FeOt – 2*O.

THERMOCALC requires good guesses to be provided for the phase compositions, in terms of the model variables, in order to solve the equilibria. These compositions should be controlled via the "xyzguess" scripts provided the scriptfile (see *Where to get help* below).

In addition to compositional variables, many of the a-x relations involve order parameters. These are designated with variable starting with Q, or

followed by the script 'isQ'. The Q parameters express the partitioning of cations across different sites, and usually can't be compared with observations.

## 4. Where to get help

This file distribution includes Tim Holland's tutorial for new users of THERMOCALC, *RE46 tutorial.pdf*, which demonstrates calculations on the Icelandic basalt composition RE46.

More information and tutorials can be found on the THERMOCALC website maintained by Richard White. This is currently (as of July 2018) found at http://www.metamorph.geo.uni-mainz.de/THERMOCALC/, but will eventually be migrated to the University of St Andrews domain.

## 5. Citing the a-x relations and ensuring reproducibility

Please cite the relevant *a-x* models, as listed below, and in the headers for each model in the axfile. This identifies the models used in order that the calculations should be reproducible. Also in the interests of reproducibility, please record the following in publications:

- the version of the Holland & Powell internally-consistent dataset: Holland & Powell (2011), dataset version 6.33 (generated at 20:37 on 23 June 2017.
- the version of THERMOCALC, e.g. THERMOCALC 3.47.

The thermodynamic models provided here are built on the work of numerous experimentalists, who have made the quantitative modelling of petrological phase equilibria possible through their painstaking and skilful work. Key studies used in calibration are described in Holland *et al*. (2018). However the internally-consistent dataset of end-members incorporates data from many more sources, as detailed in Holland & Powell (2011).

E.C.R. Green, T.J.B. Holland & R. Powell, July 2018

## References for thermodynamic models

% ----------
% **Dataset version 6**:
% ----------
% Holland, TJB, Powell, R (2011) An improved and extended internally
% consistent thermodynamic dataset for phases of petrological interest,
% involving a new equation of state for solids. *Journal of Metamorphic*
% *Geology*, 29, 333-383.
%

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% ***A-x* models in the Holland *et al*. (2018) file distribution**:
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% ***Silicate melt*, *Aqueous fluid*, *Spinel*, *Garnet*, *Olivine*, *Orthopyroxene*,**
% ***Clinopyroxene, Cordierite***:
% Holland, TJB, Green, ECR & Powell, R (2018). Melting of peridotites
% through to granites: a simple thermodynamic model in the system
% KNCFMASHTOCr. *Journal of Petrology*, egy048, in press.
%
% ----------
% ***Ilmenite***:
% White, RW, Powell, R, Holland, TJB & Worley, BA (2000). The effect of
% TiO2 and Fe2O3 on metapelitic assemblages at greenschist and amphibolite
% facies conditions: mineral equilibria calculations in the system K2O-FeO-
% MgO-Al2O3-SiO2-H2O-TiO2-Fe2O3. *Journal of Metamorphic Geology*, 18,
% 497-511.
%
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% ***Feldspars***:
% Holland, TJB & Powell, R (2003). Activity-composition relations for phases
% in petrological calculations: an asymmetric multicomponent formulation.
% *Contributions to Mineralogy and Petrology*, 145, 492-501.
%
% ----------
% ***Muscovite*, *Biotite***:
% White, RW, Powell, R, Holland, TJB, Johnson, TE & Green, ECR (2014).
% New mineral activity-composition relations for thermodynamic
% calculations in metapelitic systems. *Journal of Metamorphic Geology*, 32,
% 261-286.
%
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% ***Clinoamphibole***:
% Green, ECR, White, RW, Diener, JFA, Powell, R, Holland, TJB & Palin, RM
% (2016). Activity-composition relations for the calculation of partial melting
% equilibria in metabasic rocks. *Journal of Metamorphic Geology*, 34, 845-869.
%
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% ***Epidote***:
% Holland, TJB & Powell, R (2011). An improved and
% extended internally consistent thermodynamic dataset
% for phases of petrological interest, involving a
% new equation of state for solids.
% *Journal of Metamorphic Geology*, 29, 333-383.