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Activity–composition relations for the calculation of partial melting equilibria in metabasic rocks.

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ABSTRACT

A set of thermodynamic models is presented that, for the first time, allows partial melting

equilibria to be calculated for metabasic rocks. The models consist of new

activity–composition relations combined with end-member thermodynamic properties from

the Holland & Powell dataset, version 6. They allow for forward modelling in the system

$Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–TiO_2–Fe_2O_3$. In particular, new

activity–composition relations are presented for silicate melt of broadly

trondhjemitic–tonalitic composition, and for augitic clinopyroxene with Si–Al mixing on the

tetrahedral sites, while existing activity–composition relations for hornblende are extended

to include K_2O and TiO_2. Calibration of the activity–composition relations was carried out

with the aim of reproducing major experimental phase-in/phase-out boundaries that define

the amphibolite–granulite transition, across a range of bulk compositions, at ≤ 13 kbar.

Key words: amphibolite; granulite; calibration; pseudosection; Holland & Powell dataset.

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INTRODUCTION

The introduction in recent decades of forward modelling via calculated phase diagrams (e.g. Powell & Holland, 1988; Powell *et al.*, 1998) represents a major development in metamorphic petrology. Suitable phase diagrams, commonly known as pseudosections, map the equilibrium phase assemblages subject to constraints of bulk composition, usually in pressure–temperature (P–T), temperature–bulk composition (T–X) or pressure–bulk composition (P–X) space. To produce such diagrams, the thermodynamics of each of the phases involved must be described by a model. A model consists of one or more end-members, with thermodynamic properties typically taken from an internally-consistent thermodynamic dataset. For multiple-end-member phases, such as solid solutions, the end-member properties must be combined with activity–composition (a–x) relations describing the thermodynamics of mixing of the end-members.

End-member thermodynamic datasets in current use include those of Holland & Powell (most recently Holland & Powell, 2011), Berman (1988), Gottschalk (1996) and Chatterjee *et al.* (1998). The development of model a–x relations for minerals and melts has a long history, with much early work having the purpose of generating thermodynamically-based thermometers and barometers (e.g. Wood & Banno, 1973; Stormer, 1975; Thompson, 1976; Newton & Haselton, 1981). Model a–x relations are almost inevitably under-constrained by the available data, and so, when the aim is to calculate phase diagrams, it is sensible to select a–x relations for the various phases that have been parameterised to work together as a set. In this way, deficiencies in the thermodynamic model for one phase may compensate for those in the model for another phase, producing appropriate stable assemblages overall. Widely used sets of a–x relations include those developed for the modelling of metapelitic or ultramafic rocks based on the Holland & Powell (1998, 2011) datasets (e.g. White *et al.*, 2007, 2014; Chu & Ague, 2013; Holland *et al.*, 2013; Klemme *et al.*, 2009), and those incorporated into the MELTS software and its extensions pMELTS, pHMELTS and

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rhyolite-MELTS, for modelling of partial melting equilibria in ultramafic and felsic systems (Smith & Asimow, 2005; Ghiorso & Sack, 1995; Ghiorso *et al.*, 2002; Asimow *et al.*, 2004; Gualda *et al.*, 2012).

Until now, no set of a–x relations has been available for the modelling of partial melting equilibria in metabasic rocks. The current MELTS, pMELTS and rhyolite-MELTS models are not intended to calculate equilibria between melt and amphibole or biotite. A–x relations by e.g. Coggon & Holland (2002); Diener *et al.* (2007); Green *et al.* (2007); Diener & Powell (2012), founded on the superceded Holland & Powell (1998) dataset, allow modelling of subsolidus metabasic rocks up to amphibolite and eclogite facies. However, there is no corresponding model for the melt phase; the metapelite melt model of Holland & Powell (2001) and White *et al.* (2007, 2014) is not parameterised for any but peraluminous, K_2O-rich, CaO-poor felsic melt compositions. Moreover, the a–x relations for several key solid phases are not appropriate for use at granulite-facies temperatures: the hornblende model of Diener *et al.* (2007) omits K_2O and TiO_2, while the clinopyroxene model of Green *et al.* (2007) does not allow for Al on the tetrahedral site, or for Mg or Fe^{2+} on the M2-site.

Our new work fills these gaps. In this paper we provide a–x relations for broadly tonalitic–trondjhemitic silicate melt, high-temperature augitic clinopyroxene, and K-,Ti-bearing hornblende, representing revision and substantial extension of previous models. Other phases that are required for the modelling also appear in metapelitic equilibria, and we have taken the relevant a–x relations from the set of White *et al.* (2014). The two sets of a–x relations therefore overlap. As a set, the thermodynamic models for metabasite melting equilibria are formally calibrated to 13 kbar, and should be used at higher pressures only with sceptical assessment of the results. The 13 kbar limit was imposed due to the lack of a thermodynamic model for aqueous fluid containing a significant proportion of dissolved silicate material, and was inferred from experimental and modelling work on the solubility of silicate minerals (Manning, 1994; Gerya *et al.*, 2005; Manning, 2007; Newton & Manning, 2008; Dolejš & Manning, 2010; Hunt & Manning, 2012).

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⁸⁰ This paper presents the development and calibration of the new a–x relations, while in

⁸¹ a companion paper (Palin *et al.*, 2016b, this issue), we examine their application to forward

⁸² modelling in a range of basic to intermediate bulk compositions. Calibration of the a–x

⁸³ relations ultimately made use of experiments in natural systems, modelled in the system

⁸⁴ Na$_2$O–CaO–K$_2$O–FeO–MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O–TiO$_2$–Fe$_2$O$_3$ (NCKFMASHTO). A large

⁸⁵ body of experimental work has explored phase relations in partially molten metabasic rocks,

⁸⁶ frequently seeking to determine the origins of tonalite–trondhjemite–granodiorite (TTG)

⁸⁷ magmas (e.g. Beard & Lofgren, 1991; Rapp *et al.*, 1991; Rushmer, 1991; Sen & Dunn, 1994;

⁸⁸ Wolf & Wyllie, 1994; Patiño Douce & Beard, 1995; Rapp & Watson, 1995; Skjerlie & Patiño

⁸⁹ Douce, 1995; Springer & Seck, 1997; López & Castro, 2001; Skjerlie & Patiño Douce, 2002;

⁹⁰ Foley *et al.*, 2003; Auzanneau *et al.*, 2006; Qian & Hermann, 2013; Zhang *et al.*, 2013; Ziaja

⁹¹ *et al.*, 2014). During the calibration process, for a subset of the experimental studies,

⁹² forward calculations of phase relations at the experimental bulk compositions were

⁹³ compared with the observations. The primary goal was to reproduce major

⁹⁴ phase-in/phase-out boundaries, which, it is hoped, ensures that the behaviour of the models

⁹⁵ will be broadly realistic in the forward-modelling context for which they are intended.

⁹⁶ **GENERAL NOTES ON THE THERMODYNAMIC MODELS**

⁹⁷ The set of a–x relations presented here will be referred to as the 'metabasite set'. It is

⁹⁸ suitable for use with versions 6.2 or 6.3 of the Holland & Powell (2011) dataset (ds62, ds63),

⁹⁹ created 6 February 2012 and 15 January 2015 respectively. The figures in this paper were

¹⁰⁰ calculated with version 6.2. The update to version 6.3 includes a key refinement to the

¹⁰¹ thermodynamics of the H$_2$O end-member in the melt, and is expected to give slightly more

¹⁰² realistic results at the wet solidus. In other respects, differences between calculations with

¹⁰³ ds62 and ds63 are believed to be insignificant. The a–x relations should not however be

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104 expected to give meaningful output with the older, widely used version 5.5 (ds55) of the

105 dataset (Holland & Powell, 1998); indeed ds55 lacks one of the necessary melt

106 end-members. Full descriptions of the a–x relations of the metabasite set appear in the

107 Appendix, along with a guide to downloading the files necessary for using them via the

108 software THERMOCALC (Powell & Holland, 1988). Calculations in this paper were carried

109 out with THERMOCALC, version tc340i.

110 This paper will refer to two existing groups of a–x relations used for calculations on

111 metapelitic rocks. The first, the metapelite 'ds55-set', was published by White *et al.* (2007)

112 for use with version 5.5 of the Holland & Powell dataset (created 22 November 2003), and

113 has since been slightly modified. The second, the metapelite 'ds6-set', was a major revision

114 of the same models for version 6.1 of the dataset (created 13 November 2011), by White

115 *et al.* (2014).

116 Abbreviations for the names of end-members are consistent with the Holland & Powell

117 dataset, and are either explained in the text or defined in the Appendix. End-members that

118 are treated as pure phases are quartz (q), albite (ab), sphene (sph), rutile (ru), and

119 lawsonite (law). The following solution phases appear in the text and figures: actinolite

120 (act), glaucophane (gl), hornblende (hb), orthopyroxene (opx), garnet (g), plagioclase (pl,

121 $C\bar{1}$, and pli, $I\bar{1}$, the latter used for comparison with experiments where $x^{an} > 0.8$),

122 potassium feldspar (ksp), biotite (bi), muscovite (mu), chlorite (chl), silicate melt (L),

123 epidote (ep), ilmenite (ilm), magnetite (mt), and olivine (ol). Additionally five

124 clinopyroxene (cpx) phases are referred to, represented with two different sets of a–x

125 relations. Augitic clinopyroxene (aug) and pigeonite (pig) are considered to have the

126 general formula $[\text{Ca, Na, Mg, Fe}^{2+}]^{M2} [\text{Mg, Fe}^{2+}, \text{Al, Fe}^{3+}]^{M1} [\text{Si, Al}]_2^{tet}$, while diopside (di),

127 jadeite (jd) and omphacite (o) have the general formula $[\text{Ca, Na}]^{M2} [\text{Mg, Fe}^{2+}, \text{Al, Fe}^{3+}]^{M1}$

128 Si_2^{tet}, with omphacite forming via order-disorder on the M sites.

129 Among these phases, the a–x relations for metabasite melt (L), augitic clinopyroxene

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130 (aug and pig) and clinoamphibole (hb, gl and act) are newly calibrated to address partial

131 melting of metabasitic rocks. Of the clinoamphiboles, only hornblende is normally relevant

132 to supersolidus amphibolite–granulite facies conditions, but the new amphibole a–x model

133 is also appropriate for actinolite and glaucophane at lower temperatures. The remaining

134 a–x models in the metabasite set, for the phases garnet, orthopyroxene, feldspar,

135 spinel–magnetite and ilmenite, were taken from the metapelite ds6-set.

136   Additionally, the existing a–x model for the potentially ordered sodic–calcic pyroxenes

137 jd, di and o (from Green *et al.*, 2007, for use with ds55), has been updated for use with ds6

138 of the Holland & Powell dataset (Holland & Powell, 2011). This model, the 'omphacite'

139 model, remains the appropriate clinopyroxene model to use under subsolidus conditions

140 where co-existing clinopyroxenes might occur. It should not be used in calculations that

141 also involve the augitic clinopyroxene model.

142 **Form of the a–x relations**

143 Like the metapelite ds55- and ds6-sets, the a–x relations developed in this paper are

144 macroscopic regular solution models, in which non-ideal enthalpic interactions are present

145 between pairs of end-members, expressed as interaction energies $W_{i,j}$. The mixing-on-sites

146 approach is adopted, in order to give an approximately correct form for the ideal entropy of

147 mixing. The regular solution paradigm is modified by allowing the $W_{i,j}$ in principle to be

148 linear functions of P and T, though in practice it is almost never possible to resolve these

149 two dependencies, and the $W_{i,j}$ are usually treated as constant or functions of P only. The

150 formulation is discussed extensively by Powell & Holland (1993) and Holland & Powell

151 (1996a,b), under the name 'symmetric formalism'. A further modification, the asymmetric

152 formalism (Holland & Powell, 2003), introduced asymmetry in the manner of van Laar

153 (1906) via 'volume' parameters, α_i, associated with each end-member i.

154   In the symmetric formalism, non-ideal contributions to the enthalpy of mixing are

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introduced via activity coefficients written as

$$\mathrm{R}T \ln \gamma_{\mathrm{l}} = -\sum_{i}^{n-1}\sum_{j>i}^{n}(p'_{\mathrm{i}} - p_{\mathrm{i}})(p'_{\mathrm{j}} - p_{\mathrm{j}})W_{\mathrm{i,j}}, \tag{1}$$

where γ_{l} is the non-ideal activity coefficient of end-member ℓ, T is the temperature, R is the gas constant, p_{k} is the proportion of end-member k in the phase, p'_{k} is the value of p_{k} in end-member ℓ, such that $p'_{\mathrm{k}} = 1$ where $k = \ell$ and $p'_{\mathrm{k}} = 0$ where $k \neq \ell$, and the n end-members in the phase form an independent set. In the asymmetric formalism, the non-ideal contributions are written

$$\mathrm{R}T \ln \gamma_{\mathrm{l}} = -\sum_{i}^{n-1}\sum_{j>i}^{n}(\phi'_{\mathrm{i}} - \phi_{\mathrm{i}})(\phi'_{\mathrm{j}} - \phi_{\mathrm{j}})W_{\mathrm{i,j}}\Big(\frac{2\alpha_{\mathrm{l}}}{\alpha_{\mathrm{i}} + \alpha_{\mathrm{j}}}\Big), \tag{2}$$

where ϕ_{i} is the proportion of end-member i weighted by the van Laar parameters, $\phi_{\mathrm{i}} = (p_{\mathrm{i}}\alpha_{\mathrm{i}})/(\sum_{k}^{n} p_{\mathrm{k}}\alpha_{\mathrm{k}})$, and ϕ'_{i} is likewise the van Laar-weighted equivalent of p'_{i}.

The free parameters available for fitting are therefore the $W_{\mathrm{i,j}}$ and α_{i} values. In addition, it is sometimes necessary to introduce an expression ΔG_{i}, which represents an adjustment to the Gibbs energy of end-member i relative to its function $G_{\mathrm{i}}(P,T)$ in the dataset. The ΔG_{i} take the form a + b T + c P. ΔG_{i} expressions were introduced into the metabasite set for a number of reasons:

- $\Delta G_{\mathrm{i}}^{\mathrm{od}}$ represents the ΔG of ordering. It is applied to an end-member that represents full ordering of cations on sites, at an intermediate composition. It captures the enthalpy change of formation of the ordered intermediate end-member, when it is made by reaction of the end-members at the compositional extremes.

- $\Delta G_{\mathrm{i}}^{\mathrm{mod}}$. This is a modification made to the thermodymamics of a dataset end-member simply in order to improve the behaviour of the a–x relations in phase diagram calculations. A non-zero value may imply that the dataset thermodynamic data for the relevant end-member might be inappropriate, or just that the end-member is accommodating various other deficiencies in the thermodynamic models.

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- $\Delta G_{i}^{\mathrm{make}}$. Certain minor or 'fictive' end-members in the a–x models do not appear in the dataset. To approximate their $G_i(P, T)$ functions, a linear combination of dataset end-members is chosen that produces the right composition. The $G(P, T)$ functions of these end-members are combined likewise, and a $\Delta G_{i}^{\mathrm{make}}$ expression is added that can be calibrated to represent the ΔG between the combination of dataset end-members and the fictive end-member.

- $\Delta G_{i}^{\mathrm{tran}}$. This is a special case of $\Delta G_{i}^{\mathrm{make}}$, in which a first order phase transition separates end-member i from dataset end-member j of the same composition but different symmetry. Then $\Delta G_{i}^{\mathrm{tran}}$ represents ΔG of the i–j transition.

Examples of all of these appear in the a–x relations in the Appendix.

This paper adopts the following notational conventions: (1) as $W_{i,j} \equiv W_{j,i}$, either notation may be used for a given pair of end-members; (2) the interaction energies between an end-member i and multiple, specified end-members $j, k, \ldots$ in the same phase are represented as $W_{i,[j,k,\ldots]}$; (3) the expression $W_{i,n}$, or $W_{iL,nL}$ for the liquid model, represents the set of $W_{i,j}$ parameters between end-member i and all of the other end-members in the same a–x model.

Calibration strategy

The root of the calibration approach was the fitting of key parameters in small, well-constrained chemical subsystems. Thus, each of the new a–x models has a core in a major subsystem that was developed independently of the other new models. The models were then completed sequentially. First the augite model was developed entirely in amphibole-free and melt-free assemblages. Then the clinoamphibole model was completed based on calculations in which the augite model was treated as fixed. Finally, both the augite and clinoamphibole a–x relations were treated as fixed, while the melt model was completed based on observations from a selection of experimental studies on

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₂₀₄ TTG-generation. The choice of TTG-generation studies was limited to those with multiple

₂₀₅ hydrate-breakdown melting runs at ≤ 13 kbar, placing constraints on significant

₂₀₆ phase-in/phase-out boundaries, with bulk compositions that could reasonably be modelled

₂₀₇ in NCKFMASHTO (for example, they should be nominally carbon-free).

₂₀₈ In general (for variance > 2), the calculations performed during the calibration process

₂₀₉ mimicked those performed when the finished models are used; they were forward

₂₁₀ calculations that gave the compositions and modal proportions of phases at equilibrium,

₂₁₁ subject to the constraint of the experimental bulk composition. In some cases the

₂₁₂ calculations took place at the P–T conditions of an experiment, for direct comparison with

₂₁₃ the experimental run products. However, the highest priority for the calibration was to

₂₁₄ make good predictions of the major features of phase relations across P–T space, rather

₂₁₅ than to make accurate predictions of phase compositions. Consequently, the interpolated

₂₁₆ positions of key phase field boundaries (e.g. orthopyroxene-in, hornblende-out) were used

₂₁₇ directly in calibration. The final step in calibration was to calculate full P–T

₂₁₈ pseudosections for key experimental bulk compositions, ensuring that the assemblages

₂₁₉ specified during the calibration were the most stable that could be modelled.

₂₂₀ Calibrations that are new in this work were carried out either by manual trial and error

₂₂₁ or by using a Monte Carlo method, MCTC, within the THERMOCALC software. When MCTC

₂₂₂ is invoked, THERMOCALC calculates a set of phase equilibria repeatedly, using a–x models

₂₂₃ with parameters drawn randomly from within specified distributions. 'Successful' sets of

₂₂₄ model parameters are identified by comparing the resulting calculated phase equilibria with

₂₂₅ the observations, and the distribution of successful model parameters is reviewed, leading to

₂₂₆ refinement of the initial distribution. Over the course of many MCTC runs, the user will first

₂₂₇ widen the initial distributions of model parameters until, for each parameter, a peak is

₂₂₈ visible in the distribution of successful values. Then, certain model parameters may be

₂₂₉ given fixed values, especially those that are weakly constrained (their 'successful'

₂₃₀ distributions are wide), or strongly correlated with other parameters. The distributions of

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₂₃₁ all parameters are narrowed over time, with the aim of deriving quasi-optimised values.

₂₃₂ The MCTC approach is thus a hybrid between manual trial and error and a formal,
₂₃₃ automated technique. It robustly handles two problems: the very high and
₂₃₄ multi-dimensional correlations among successful distributions of model parameters, and the
₂₃₅ presence of parameters that are essentially unconstrained by the data. A fitting method that
₂₃₆ does not take these phenomena into account is at risk of generating physically implausible
₂₃₇ parameter values, leading to a–x relations that do not extrapolate well in P–T–X space.

₂₃₈ In order to use phase equilibrium experiments as constraints, it is necessary to infer
₂₃₉ bulk compositions that represent the experimental run products at equilibrium. Two
₂₄₀ components of bulk composition in particular are hard to estimate: those of fluid content,
₂₄₁ assumed to be all water ('molar bulk H_2O', M_{H_2O}), and of oxygen ('molar bulk O', M_O).
₂₄₂ Experimental studies routinely provide estimates of H_2O content in the starting material,
₂₄₃ though these are uncertain, and unlikely to include H_2O gained by adsorption during the
₂₄₄ pulverisation of the sample, which may be retained even during storage under desiccation
₂₄₅ (London *et al.*, 2012). M_O may be equated directly to molar bulk Fe_2O_3, via the reaction
₂₄₆ $Fe_2O_3 = 2\,FeO + O$, if iron is the only element considered to have variable oxidation state.
₂₄₇ The fraction of iron present as Fe_2O_3 in the starting material is rarely estimated. During
₂₄₈ experimental runs, values of M_{H_2O} and M_O in the capsule are subject to interdependent
₂₄₉ changes. The experiments considered in this work were not formally buffered to specified
₂₅₀ fO_2, but even in such cases, the experimental apparatus has an 'intrinsic fO_2' that
₂₅₁ influences the oxidation state of the starting material during the run; hence M_O is not
₂₅₂ conserved. The process of oxidation or reduction of starting materials primarily involves
₂₅₃ diffusion of H_2, to which experimental capsules are effectively open. If the apparatus
₂₅₄ provides an environment that is reducing with respect to the oxidation state of the starting
₂₅₅ materials, H_2 will enter the capsule and may form H_2O by reduction of iron oxides,
₂₅₆ constituting an increase in M_{H_2O} and decrease in M_O (carbon, derived from graphite
₂₅₇ furnaces, may play a under-acknowledged role in this process; see Brooker *et al.*, 1998;

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258 Jakobsson, 2012; Matjuschkin *et al.*, 2015). Finally, apparent loss or gain of both H_2 and

259 O_2, or possibly molecular H_2O, has has been reported in several piston cylinder studies (e.g.

260 Patiño Douce & Beard, 1994, 1995; Truckenbrodt & Johannes, 1999; Pichavant *et al.*, 2002;

261 Jakobsson, 2012), especially during longer and higher-temperature experiments.

262   There is therefore no satisfactory way to convert the information reported in an

263 experimental study into values of M_O and M_{H_2O} suitable for a representative pseudosection.

264 A crucial part of the model calibration, then, is to analyse the sensitivity of calculations to

265 the assumed values of M_O and M_{H_2O}. This is done most informatively by calculating T–X

266 or P–X pseudosections, in which X is M_O or M_{H_2O}.

267 **CLINOPYROXENE *A*–*X* RELATIONS**

268 **Omphacite model**

269 The 'omphacite model' of Green *et al.* (2007), modified by Diener & Powell (2012), was

270 developed with the aim of modelling coexisting jadeite–omphacite and omphacite–diopside

271 pairs. Previously calibrated with ds55, it was upgraded in this work for use with version 6

272 of the Holland & Powell dataset. It remains the only appropriate choice of *a*–*x* relations

273 wherever diopsidic and sodic clinopyroxenes may stably coexist, since the new augitic

274 clinopyroxene model is intended for use at temperatures higher than the closure of the

275 jadeite–omphacite and omphacite–diopside miscibility gaps, and has no capacity to

276 represent the ordered omphacite structure.

277   The omphacite model allows for cation mixing as $[Mg, Fe^{2+}, Al, Fe^{3+}]^{M1}$ and $[Ca,$

278 $Na]^{M2}$, but in order to represent ordered intermediate end-members such as omphacite

279 $(Ca^{M2}_{\frac{1}{2}}Na^{M2}_{\frac{1}{2}}Mg^{M1}_{\frac{1}{2}}Al^{M1}_{\frac{1}{2}}Si^{tet}_2O_6)$, it treats the M1 and M2 sites as 'split'. That is, Mg, Fe^{2+},

280 Al and Fe^{3+} mix on a M1m and a M1a site, with cations preferentially partitioned onto the

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₂₈₁ M1m site in the order $Fe^{2+}>Mg>Al>Fe^{3+}$, while Ca and Na mix on a M2c and a M2n site,

₂₈₂ with Ca preferentially partitioned onto M2c (Green *et al.*, 2007). The tetrahedral sites

₂₈₃ contain Si only.

₂₈₄ Slight modifications were needed in order to compensate for the change from version 5.5

₂₈₅ to version 6 of the dataset. Following Diener & Powell (2012), modifications were made

₂₈₆ simultaneously for both the omphacite model, and the NCFMASHO core of the ds55

₂₈₇ clinoamphibole model of Diener *et al.* (2007; refined by Diener & Powell, 2012). For the

₂₈₈ omphacite model, the modification amounted to a change in ΔG_{acm}^{mod} on the acmite

₂₈₉ end-member, from -4 to -7 kJ. The change was determined by manually adjusting the

₂₉₀ ΔG_{i}^{mod} values of end-members in both models, until satisfactory calculations were obtained

₂₉₁ for equilibria in a MORB-like composition (composition Mcal, Table 1, H_2O in excess).

₂₉₂ The $W_{i,j}$ parameters were left unchanged from the previous version of the omphacite

₂₉₃ model, since these were relatively well constrained by the observed geometry of the solvi

₂₉₄ between the diopsidic, omphacitic and jadeitic portions of the solid solution. Conversely,

₂₉₅ since the solvi depend solely on the mixing properties of the models, rather than the

₂₉₆ end-member thermodynamics, solvus calculations will be unchanged from the previous

₂₉₇ model.

Augite model

₂₉₉ Prompted by the compositions of clinopyroxene in TTG-genesis experiments (e.g. Patiño

₃₀₀ Douce & Beard, 1995; Skjerlie & Patiño Douce, 2002; Rapp & Watson, 1995), a new 'augite

₃₀₁ model' was developed for calcic clinopyroxene at high temperature, with mixing on sites as

₃₀₂ $[Mg, Fe^{2+}, Al, Fe^{3+}]^{M1}$ $[Ca, Na, Mg, Fe^{2+}]^{M2}$ $[Si, Al]_2^{tet}$. This model is not consistent with

₃₀₃ the omphacite model, even though the models overlap in composition space, and the two

₃₀₄ should not be used in the same calculation. In particular, the simple M1 and M2 sites of

₃₀₅ the augite model do not not allow order-disorder to take place on either of these sites

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³⁰⁶ individually, unlike the split M1 and M2 sites of the omphacite model. In partial

³⁰⁷ compensation for this, different values of ΔG^{mod} are used for some end-members that are

³⁰⁸ common to both models.

³⁰⁹   The heart of the augite model is the pyroxene quadrilateral

³¹⁰ $CaMgSi_2O_6$–$Mg_2Si_2O_6$–$Fe_2Si_2O_6$–$CaFeSi_2O_6$. Figure 1 shows the modelled fit to the

³¹¹ experimental work of Lindsley (1981, 1983) and Turnock & Lindsley (1981) on

³¹² clinopyroxene–orthopyroxene equilibria in this system, including the binary subsystem

³¹³ $CaFeSi_2O_6$–$Fe_2Si_2O_6$. The clinopyroxene a–x relations cover the whole of the quadrilateral

³¹⁴ composition space, with the compositional end-members in appropriate $C2/c$ symmetry

³¹⁵ being diopside (di), clinoenstatite (cenh), clinoferrosilite (cfs) and hedenbergite (hed). The

³¹⁶ clinoenstatite and clinoferrosilite end-members are polymorphs that exist at low-pressure,

³¹⁷ high-temperature in the unary systems, and their stability fields and properties are little

³¹⁸ known. They are generated via ΔG^{tran} expressions from the $Pbca$ end-members en

³¹⁹ (enstatite) and fs (ferrosilite) in the Holland & Powell dataset. An ordered intermediate

³²⁰ end-member, fmc ($Mg^{M1}Fe^{M2}Si_2O_6$), allows non-equal partitioning of [Mg, Fe^{2+}] over the

³²¹ M1 and M2 sites (Holland & Powell, 2006). Since a reaction di + $\frac{1}{2}$ cfs = hed + $\frac{1}{2}$ cenh can

³²² be written among the compositional end-members, the thermodynamic properties of one

³²³ must be treated as dependent, and hedenbergite was chosen for this purpose. Values for

³²⁴ model parameters on the $CaMgSi_2O_6$–$Mg_2Si_2O_6$ join, including $\Delta G^{\text{tran}}_{\text{cenh}}$, were taken from the

³²⁵ CMAS clinopyroxene model of Green *et al.* (2012a), where they were calibrated against the

³²⁶ experimental work of Brey & Huth (1984); Carlson & Lindsley (1988); Lindsley & Dixon

³²⁷ (1976); Mori & Green (1975); Nickel & Brey (1984); Perkins & Newton (1980) and

³²⁸ Schweitzer (1982).

³²⁹   The MCTC function in THERMOCALC was used to fit the additional CFMS parameters

³³⁰ $W_{\text{di,[cfs,fmc]}}$, $W_{\text{cenh,[cfs,fmc]}}$, $W_{\text{cfs,fmc}}$, $\Delta G^{\text{tran}}_{\text{cfs}}$ and $\Delta G^{\text{od}}_{\text{fmc}}$. The pressure dependence of the

³³¹ inherited CMAS parameter $W_{\text{di,cenh}}$ was applied to $W_{\text{di,[cfs,fmc]}}$. $\Delta G^{\text{tran}}_{\text{cfs}}$ was assumed to have

³³² the same temperature dependence as $\Delta G^{\text{tran}}_{\text{cenh}}$, and was required to give a fs = cfs transition

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curve consistent with the estimation of Lindsley (1981). $\Delta G_{\text{fmc}}^{\text{od}}$ took the mean pressure and

temperature dependencies of $\Delta G_{\text{cenh}}^{\text{tran}}$ and $\Delta G_{\text{cfs}}^{\text{tran}}$, with the constant term fitted such that

the ordered end-member fmc was more stable than its fully disordered equivalent,

$\text{Mg}_{\frac{1}{2}}^{\text{M1}}\text{Fe}_{\frac{1}{2}}^{\text{M1}}\text{Mg}_{\frac{1}{2}}^{\text{M2}}\text{Fe}_{\frac{1}{2}}^{\text{M2}}\text{Si}_2\text{O}_6$, for which G is given by $\frac{1}{2}\left(G_{\text{cenh}} + G_{\text{cfs}}\right)$. At 900°C and 8 kbar,

the dependent value of G_{hed} was constrained to be within 2 kJ/mol of the ds62 dataset

value, with a further constraint of $G_{\text{hed}} < G_{\text{ohed}}$. G_{ohed} is the G function for the

$Pbca$-symmetry orthohedenbergite end-member, derived from the quadrilateral a–x

relations for orthopyroxene in the same way as G_{hed} is derived for the hedenbergite

end-member in clinopyroxene; thus the latter condition specified that the monoclinic

polymorph was the more stable of the two.

The resulting fit successfully reproduces augite–orthopyroxene tielines in the

quadrilateral, and is notably successful at matching the very sensitive divariant

augite–pigeonite–orthopyroxene equilibrium at 15 kbar, 1000°C (Fig. 1). It somewhat

overestimates the width of the augite–pigeonite solvus towards higher FeO/(FeO+MgO)

values.

The quadrilateral model was then combined with the CMAS clinopyroxene model of

Green *et al.* (2012a), introducing the end-member Ca-tschermak's pyroxene (cats;

$\text{CaAl}_2\text{SiO}_6$) and associated parameters, which allowed for the substitution of Al onto the

M1 and tetrahedral sites simultaneously. The cats end-member exhibits internal

order-disorder of Si-Al on the tetrahedral site, with the energy and entropy of disordering

reduced by a factor of 4 (Holland & Powell, 2011). Finally, the end-members jadeite (jd)

and acmite (acm) were added to the model to accommodate Na, Fe^{3+}, and an excess of Al

on the M1 site relative to the tetrahedral site. Values for $W_{\text{di,jd}}$, $W_{\text{di,acm}}$ and $W_{\text{jd,acm}}$ were

adopted from the omphacite model. However, the jd and acm end-members serve a different

role in the augite model from in the omphacite model. In the augite model, they are simply

required to admit minor components, whereas in the omphacite model, they may be present

in substantial proportions, with order–disorder between sodic and calcic end-members

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360 contributing heavily to the thermodynamics of mixing. Consequently it is not very

361 significant that the values of the dependent $W_{\mathrm{hed},n}$ parameters in the augite model differ

362 from their independently-calibrated equivalents in the omphacite model (values are

363 compared in the Appendix). With the same justification a $\Delta G_{\mathrm{jd}}^{\mathrm{mod}}$ term was added to the

364 augite jd end-member, and different $\Delta G_{\mathrm{acm}}^{\mathrm{mod}}$ terms were used in the augite and omphacite

365 models.

366   In addition to $\Delta G_{\mathrm{jd}}^{\mathrm{mod}}$ and $\Delta G_{\mathrm{acm}}^{\mathrm{mod}}$, the free parameters in this second stage of augite

367 model calibration were $W_{\mathrm{cats},[\mathrm{cfs,fmc}]}$, $W_{\mathrm{jd},[\mathrm{cenh,cfs,fmc,cats}]}$ and $W_{\mathrm{acm},[\mathrm{cenh,cfs,fmc,cats}]}$. These

368 interaction energies were not expected to be influential compared with the $\Delta G_{\mathrm{i}}^{\mathrm{mod}}$ terms, so

369 a small number of observed equilibria were carefully chosen to be fitted, primarily with the

370 purpose of finding values for $\Delta G_{\mathrm{jd}}^{\mathrm{mod}}$ and $\Delta G_{\mathrm{acm}}^{\mathrm{mod}}$. The chosen equilibria comprised two

371 natural rock samples, with estimated P and T values, and one experiment; Table 2 shows

372 the equilibria and results. The process of fitting with MCTC revealed very strong

373 multicomponent correlations among the interaction energies. It was not clear *a priori* that

374 these correlations would be relevant for model calculations in general, but in fact, in later

375 calculations on melting equilibria, it was found that violating the correlations for apparently

376 trivial parameters such as $W_{\mathrm{cats,fmc}}$ did indeed have a large and detrimental effect on the

377 calculated compositions of all phases, particularly the anorthite content x^{an} in plagioclase.

Calculations with the augite versus omphacite models

379 Figure 2 shows pseudosections calculated for an oxidised MORB composition, based on that

380 of Sun & McDonough (1989; SM89, Table 1), in the range 450–700°C and 4–20 kbar. The

381 figure is contoured for $x_{\mathrm{Na}}^{\mathrm{M2}}$ in clinopyroxene. Calculations were carried out with first the

382 augite model (Fig. 2a,b) and then the omphacite model (Fig. 2c,d), in order to compare the

383 two. The comparison demonstrates, firstly, that the omphacite model is the appropriate

384 choice for the relatively low temperatures shown. When modelling is done correctly using

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385 the omphacite model (Fig. 2c,d), $x_{\mathrm{Na}}^{\mathrm{M2}}$ in clinopyroxene rises to > 0.4 towards higher

386 pressures, and the diopside–omphacite solvus is visible at several pressures with closure at

387 $\sim 600°$C. Meanwhile the augite model has no capacity to model omphacite-like Na contents

388 or coexistence between omphacitic and diopsidic compositions, so no solvus appears in Figs

389 2a and b. Secondly, it can be seen that the two models give substantially consistent results

390 for $P < 13$ kbar and $T > 600°$C, where the omphacite model takes on an augitic

391 composition. Phase field boundaries in this region in Figs 2a and c show agreement within

392 20°C, while the augite model gives values of $x_{\mathrm{Na}}^{\mathrm{M2}}$ that are consistently lower than the

393 omphacite model by ~ 0.05, within the likely uncertainty in the modelling.

394   The nature of phase relations in Fig. 2c are discussed in a later section. Subsequent

395 figures will demonstrate the behaviour of the augite model in the $P < 13$ kbar, $T > 600°$C

396 regime for which it was calibrated.

397 CLINOAMPHIBOLE A–X RELATIONS

398 The clinoamphibole model of Diener *et al.* (2007) and Diener & Powell (2012), in

399 NCFMASHO, is suitable for calculations on metabasic rocks under subsolidus conditions,

400 using version 5.5 of the dataset (Holland & Powell, 1998). As described above, it was

401 updated for use with version 6.2 in conjunction with the omphacite model, by adjustments

402 to the end-member thermodynamics. The resulting modifications affected the following

403 end-members: pargasite ($\Delta G_{\mathrm{parg}}^{\mathrm{mod}}$ changed from 15 kJ to -10 kJ), glaucophane ($\Delta G_{\mathrm{gl}}^{\mathrm{mod}}$

404 changed from 3 kJ to -3 kJ), cummingtonite ($\Delta G_{\mathrm{cumm}}^{\mathrm{mod}}$ changed from -6.4 kJ to 0 kJ),

405 grunerite ($\Delta G_{\mathrm{grun}}^{\mathrm{mod}}$ changed from -5 kJ to -3 kJ) and magnesioriebekite ($\Delta G_{\mathrm{mrb}}^{\mathrm{make}}$ changed

406 from 8 kJ to 0 kJ). These were pleasing in that generally the absolute values of the $\Delta G_{\mathrm{i}}^{\mathrm{mod}}$

407 terms decreased, making the end-member G curves more similar to the dataset functions.

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₄₀₈ By granulite facies temperatures, the components K_2O and TiO_2 are significant in

₄₀₉ hornblende (e.g. Robinson *et al.*, 1982). The core model was therefore expanded to include

₄₁₀ the components K_2O and TiO_2, with the intention that the full model in NCKFMASHTO

₄₁₁ would be applicable both above and below the solidus. K_2O was introduced via a

₄₁₂ potassium-pargasite end-member (kprg, $KCa_2Mg_4Al_3Si_6O_{22}(OH)_2$), such that K^+ mixes

₄₁₃ with Na^+ on the partially filled model A site. A deprotonation-style substitution was

₄₁₄ adopted to introduce TiO_2 via an end-member Ti-tschermakite (tts, $Ca_2Mg_3Ti_2Al_2Si_6O_{22}$),

₄₁₅ allowing hornblende to persist to higher temperatures in equilibrium with melt by lowering

₄₁₆ its water activity $a(H_2O)$, although in reality the substitution whereby TiO_2 enters

₄₁₇ metamorphic hornblende is more likely to be a tschermakite-like and/or glaucophane-like

₄₁₈ substitution (Schumacher, 2007). The new end-members tts and kprg are not present in the

₄₁₉ Holland & Powell dataset, but are made via the reactions kprg = mu − pa + parg +

₄₂₀ $\Delta G_{\mathrm{kprg}}^{\mathrm{make}}$ and tts = dsp − 2 ru + ts + $\Delta G_{\mathrm{tts}}^{\mathrm{make}}$ (mu: muscovite; pa: paragonite; ru: rutile;

₄₂₁ dsp: diaspore).

₄₂₂ A key equilibrium is the first introduction of hornblende and glaucophane to the

₄₂₃ assemblage act + chl + ep + ab + sph + q + H_2O ± bi, i.e. the junction of the greenschist,

₄₂₄ blueschist and amphibolite facies. This occurs at around 8–10 kbar and 450–500°C on most

₄₂₅ metamorphic facies diagrams. The presence of three coexisting amphiboles in this

₄₂₆ equilibrium make the calculated values of P, T and compositional variables extremely

₄₂₇ sensitive to the parameterisation of the amphibole a–x relations. It was required that

₄₂₈ minimal amounts of K_2O and TiO_2 should be taken into the amphiboles at this

₄₂₉ temperature, but the prejudice was nevertheless imposed that the amphibole phases would

₄₃₀ incorporate K_2O in the order hb > gl ≈ act, and TiO_2 in the order hb ≈ gl > act. The full

₄₃₁ list of P–T and compositional constraints placed on this equilibrium during fitting, and the

₄₃₂ results obtained, are given in Table 3. The table also compares calculations and

₄₃₃ observations for several upper-amphibolite facies rocks, for which likely values of P, T and

₄₃₄ M_O have been established by previous calculations with older versions of the models. Since

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some of these equilibria contain clinopyroxene, this was also an opportunity to check the behaviour of the ds6-omphacite and augite models.

Fitting was carried out in MCTC, to find values for $\Delta G_{\mathrm{kprg}}^{\mathrm{make}}$, $\Delta G_{\mathrm{tts}}^{\mathrm{make}}$, and the new interaction energies $W_{\mathrm{kprg},n}$ and $W_{\mathrm{tts},n}$. Because the number of interaction energies to be fitted was large, and they were expected to be poorly constrained due to the small amounts of the K_2O and TiO_2 end-members present, the fitting problem was initially reduced by assuming that K^+ and Na^+ would mix with similar energetic consequences on the A-site, and therefore fixing values of $W_{\mathrm{parg},\mathrm{kprg}} = 0$ and $W_{\mathrm{kprg},n} = W_{\mathrm{parg},n}$. The possibility of allowing other, less well constrained parameters to vary in order to improve the fit was also explored. Ultimately however, better results were obtained by allowing the $W_{\mathrm{kprg},n}$ parameters to diverge from the equivalent $W_{\mathrm{parg},n}$ values by up to 5 kJ, while the parameters from the core NCFMASHO model could not convincingly be improved upon. The asymmetry of interactions was inherited from the Diener *et al.* (2007) model, with the addition of the terms $\alpha_{\mathrm{kprg}} = \alpha_{\mathrm{parg}}$ and $\alpha_{\mathrm{tts}} = \alpha_{\mathrm{ts}}$. As in the Diener *et al.* (2007) model and the new augite model, the entropy of Si–Al mixing on the tetrahedral sites was reduced by a factor of 4.

CALCULATIONS ON SUBSOLIDUS PHASE RELATIONS

We now return to Fig. 2c, a pseudosection calculated between greenschist–blueschist facies conditions and the solidus using the metabasite set of a–x relations, with the omphacite model representing clinopyroxene. The bulk composition (SM89, Table 1) is based on the MORB composition of Sun & McDonough (1989), but considerably oxidised, with $X_{\mathrm{Fe}^{3+}} = \mathrm{Fe}^{3+}/(\mathrm{Fe}^{2+}+\mathrm{Fe}^{3+}) = 0.36$. The same bulk composition was previously used by Diener & Powell (2012), fig. 1c, allowing the ds55 and ds6x generations of a–x relations to be

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⁴⁵⁸ compared.

⁴⁵⁹ Subsolidus phase relations in the greenschist and amphibolite facies remain similar, with
⁴⁶⁰ hornblende replacing actinolite and chlorite at $\sim 480°$C as in the older calculations, and
⁴⁶¹ diopside now joining the assemblage at $\sim 550°$C rather than $600°$C. Calculations at 12–20
⁴⁶² kbar and $< 550°$C now generate gl + act + chl + ep $\pm$ law $\pm$ o assemblages that resemble
⁴⁶³ natural blueschists, whereas the ds55 generation of a–x relations found omphacite stable
⁴⁶⁴ rather than glaucophane. At 16–20 kbar, between 530 and $580°$C, the blueschist
⁴⁶⁵ assemblages give way to higher-temperature eclogite assemblages containing garnet,
⁴⁶⁶ omphacite and hornblende.

⁴⁶⁷ Phase relations below $650°$C are negligibly affected if the K_2O and TiO_2 components
⁴⁶⁸ are excluded from amphibole. The Diener & Powell (2012) figure was calculated without a
⁴⁶⁹ melt phase, since no suitable melt a–x relations existed at that time; the new figure, using
⁴⁷⁰ the metabasite melt model described in the next section, shows the start of H_2O-saturated
⁴⁷¹ melting at 615–$700°$C.

⁴⁷² **MELT A–X RELATIONS**

⁴⁷³ Existing silicate melt a–x relations for use with the Holland & Powell dataset include the
⁴⁷⁴ ds5 haplogranitic model of Holland & Powell (2001), its expansion into NCKFMASH for
⁴⁷⁵ use in metapelite melting calculations (White *et al.*, 2001, 2007), the ds6 equivalent of the
⁴⁷⁶ metapelite melt model (White *et al.*, 2014), and the mafic melt model of Jennings &
⁴⁷⁷ Holland (2015). These models are exceedingly simple, reproducing the macroscopic mixing
⁴⁷⁸ properties of melt over a limited compositional range while making no attempt to capture
⁴⁷⁹ melt speciation, or otherwise to separate the enthalpic and entropic contributions in the
⁴⁸⁰ models in a way that resembles reality. Like the a–x relations for solid solutions, the melt is

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481 treated as a regular solution with the non-ideal enthalpy of mixing expressed using the

482 symmetric formalism. The end-members are mineral-like compounds that mix as molecules.

483   The metapelite melt model has proved very successful in calculations (e.g. White *et al.*,

484 2001, 2007; Grant, 2009; Johnson *et al.*, 2008; White *et al.*, 2011). It is desirable that the

485 new metabasite melt model and the metapelite melt model should share a core in NKASH,

486 defined by the end-members qL–abL–kspL–h2oL (see Appendix for end-member

487 definitions). However, with respect to the CaO, FeO and MgO components, the metabasite

488 melt model requires a different parameterisation and structure from the metapelite model,

489 in order to allow the melt composition to become sufficiently calcic, and to become

490 metaluminous if required.

491   The qL–abL–kspL subsystem of the White *et al.* (2014) metapelite melt model was

492 strongly constrained by the experiments of Boyd & England (1963); Lindsley (1966);

493 Ostrovsky (1966) and Jackson (1976), and could be retained without change to form the

494 core of the metabasite melt model. In the qL–abL–kspL–h2oL subsystem, a number of

495 changes are planned for a forthcoming revision of the White *et al.* (2014) metapelite melt

496 model, and these have been incorporated directly into the metabasite melt model as

497 presented in this study. The changes to the qL–abL–kspL–h2oL core, relative to the White

498 *et al.* (2014) version of the metapelite melt model, are as follows. (1) The interaction

499 energies $W_{\text{h2oL,[qL,abL,kspL]}}$ have been refined by comparison with the subsystem experiments

500 of Behrens (1995); Kennedy *et al.* (1962); Stewart (1967); Goldsmith & Peterson (1990) and

501 Goldsmith & Jenkins (1985). (2) In ds63, the constant-pressure heat capacity of the h2oL

502 end-member has been lowered to improve the calculated H_2O isopleths for melts. In fig. 9 of

503 Holland & Powell (2001) the H_2O isopleths in granitic liquid are spuriously concave

504 downwards in pressure, as a result of too high a heat capacity for h2oL; this heat capacity

505 has now been optimised such that the isopleths become approximately straight lines, as

506 required by the experimental data of Holtz *et al.* (1995). (3) The formula of the

507 end-member silL has been changed from $\frac{8}{5}Al_2SiO_5$ to Al_2SiO_5.

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508 In the metapelite model, the Ca-rich vertex of composition space is represented by the

509 anorthite-liquid end-member, anL, but the metabasite model has been extended as far as a

510 wollastonite-liquid end-member, woL, in order to encompass metaluminous compositions.

511 However, the woL end-member is compositionally distant from the melts of metabasic

512 rocks, and its thermodynamics are poorly constrained. To compensate for this, an

513 anL-composition end-member was restored to the metabasite melt model in the form of an

514 ordered intermediate, made via the reaction anL = woL + silL with a $\Delta G_{\mathrm{anL}}^{\mathrm{od}}$ term applied.

515 The thermodynamic properties of $CaAl_2Si_2O_8$-composition liquid were approximated by

516 fitting to the anorthite melting curve. This aspect of the model structure follows e.g. Hastie

517 (1983); Hastie & Bonnell (1985); Bonnell & Hastie (1985); Besmann & Spear (2002) and

518 Green *et al.* (2012b), in which the ordered intermediate end-members are termed 'associate

519 species'. The inclusion of an ordered intermediate end-member, intL, in the melt *a–x*

520 relations adds flexibility in fitting the available constraints, since the $\Delta G_{\mathrm{intL}}^{\mathrm{od}}$ term provides a

521 free parameter and the presence of the intL compound contributes to model entropy.

522 However it should be stressed that speciation is not represented in any meaningful way in

523 the metabasite melt model, either by the choice of end-member mixing units or by the

524 ordering taking place among them.

525 To complete the calibration of the metabasite melt model, values had to be found for

526 $\Delta G_{\mathrm{anL}}^{\mathrm{od}}$ and the new interaction energies $W_{\mathrm{woL},n\mathrm{L}}$ and $W_{\mathrm{anL},n\mathrm{L}}$. Parameters such as $W_{\mathrm{anL,qL}}$

527 are not strictly the same as the equivalently-named parameter in the metapelite melt

528 model, because the anL end-member in the metabasite melt model is not the dataset

529 end-member but an 'ordered' end-member that coexists with a 1:1 mixture of woL + silL

530 'molecules', even at the anorthite composition. Due to the significant difference in

531 composition range between the metapelite and metabasite melt models, the non-core

532 parameters from the metapelite melt model were considered to be potentially subject to

533 variation in MCTC, namely the interaction energies $W_{[\mathrm{silL,foL,faL}],n\mathrm{L}}$ and the $\Delta G_{[\mathrm{silL,foL,faL}]}^{\mathrm{mod}}$. A

534 finite $\Delta G_{\mathrm{woL}}^{\mathrm{mod}}$ was also explored.

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535 Calibration in MCTC was carried out simultaneously on (a) the wet and dry melting

536 curves of anorthite (the experiments of Goldsmith (1980); Yoder (1976) and Stewart (1967),

537 constraining the woL–silL and woL–silL–h2oL compositional joins of the melt model), (b)

538 the inferred position of the hb + di + opx + an + q + L + H_2O invariant point in the

539 CMASH system, from Ellis & Thompson (1986), (c) two reported melt compositions at

540 large melt fraction, from the TTG-genesis studies of Patiño Douce & Beard (1995, SQA

541 composition) and Beard & Lofgren (1991, Sample 478), and (d) nine estimates of phase

542 boundary positions (H_2O-out, orthopyroxene-out, hornblende-out, melt-out, quartz-out,

543 plagioclase-out) in the same two experimental bulk compositions. The studies of Patiño

544 Douce & Beard (1995) and Beard & Lofgren (1991) were chosen because the experiments

545 represent a comprehensive P–T grid for $P \leq 12.5$ kbar. The results of the calibration are

546 shown below.

547 **CALCULATIONS ON EXPERIMENTAL COMPOSITIONS**

548 Figures 3 and 4 present pseudosections calculated for hydrate-breakdown melting using bulk

549 compositions SQA (Patiño Douce & Beard, 1995) and Sample 478 (Beard & Lofgren, 1991,

550 hereafter BL478). Bulk composition is treated as constant for experiments on one starting

551 material in one type of apparatus.

552 **Experiments of Patiño Douce & Beard (1995)**

553 The experiments of Patiño Douce & Beard (1995) on SQA, a synthetic quartz amphibolite,

554 yielded assemblages of q + pl + ilm/ru ± hb ± opx ± g ± cpx. Experiments at > 6 kbar

555 were performed in a piston cylinder and experiments at < 6 kbar in an internally heated

556 pressure vessel (IHPV). In Fig. 3a, calculations at > 6 kbar used a value of M_O that gave

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557 $X_{Fe^{3+}} = 0.1$, while calculations < 6 kbar took place with $X_{Fe^{3+}} = 0.25$. These values reflect

558 the more oxidising environment of the IHPV relative to the piston cylinder, and were

559 chosen because they span a range of $X_{Fe^{3+}}$ values inferred from modelling of natural

560 amphibolites and granulites (see Table 1), although they may not correspond closely to the

561 unknown $X_{Fe^{3+}}$ values developed in the experimental apparatus. For each of the two bulk

562 compositions, calculated values of fO_2 fall within the ranges estimated in the experiments,

563 but this does not sensitively constrain appropriate values for M_O. A single estimate for

564 M_{H_2O} was applied to both high- and low-pressure calculations, obtained by Patiño Douce &

565 Beard (1995) through electron probe analysis of the melted starting mixture. In reality, the

566 starting material likely underwent substantial reduction or oxidation in each of the two

567 assemblies, mediated by infiltration or loss of hydrogen and associated with changes in M_O

568 and M_{H_2O}. However, we did not attempt to simulate the relationship between M_{H_2O} in the

569 high-pressure, low-M_O experiments versus the low-pressure, high-M_O experiments, given

570 that the initial value of $X_{Fe^{3+}}$ in the starting material is unknown.

571 The calculations successfully reproduce the major assemblage changes of the

572 amphibolite–granulite transition as characterised by the experiments, specifically through

573 the up-temperature appearance of orthopyroxene and exhaustion of hornblende

574 (summarised in Fig. 3b). The hornblende-out boundary is well defined by the experiments,

575 and the calculations match this constraint reasonably well, although they predict a

576 shallower dP/dT slope for the boundary than the experiments suggest. For the chosen

577 values of M_O and M_{H_2O}, the calculations progressively underestimate the temperature of

578 hornblende exhaustion towards lower pressure. Garnet appears up to 0.6 kbar below the

579 minimum pressure permitted by the experiments, and at the highest pressures the

580 orthopyroxene-in boundary moves rapidly towards excessive temperatures. In the

581 experiments at 840°C and at 875°C, 10 kbar, the experimental assemblage is hb + pl + q +

582 Fe-Ti oxides, while the calculations additionally contain aug + L ± opx ± g. The

583 experimental assemblage is unchanged from that of the starting materials, so an approach

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584 to the stable equilibrium assemblage cannot be demonstrated. Despite the moderate

585 temperatures and very long run durations of 1–2 weeks, the shortage of vapour or a

586 detectable volume of melt may inhibit equilibration, and it is likely that stable assemblages

587 at these conditions do indeed include clinopyroxene ± orthopyroxene ± melt.

588   Figure 3c shows the effect of oxidation state on the calculated assemblages at $P = 7$

589 kbar, over a range of $0 < M_O < 1.62$ mole% ($0 < X_{Fe^{3+}} < 0.50$). Under the relatively

590 reduced conditions assumed for the piston cylinder assembly, the temperature of the

591 hornblende-out boundary in particular is a strong function of M_O, rising from 830°C to

592 905°C over the range $0 < M_O < 0.5$ mole% ($0 < X_{Fe^{3+}} < 0.15$), although further increase in

593 M_O to 1.62 mole% raises the hornblende-out temperature by only 40°C. The sensitivity of

594 the boundary under low-M_O conditions demonstrates the difficulties of extracting

595 calibration information from even the best devised and most careful experimental study,

596 and also highlights the sensitivity of future forward-modelling results to the assumed bulk

597 O content. This sensitivity should always be quantitatively investigated via T–M_O and

598 P–M_O plots (e.g. White *et al.*, 2000; Diener & Powell, 2010; Korhonen *et al.*, 2012).

599   The equivalent analysis for M_{H_2O} at 7 kbar is shown in Fig. 3d. At $M_{H_2O} = 4.6$ mol%,

600 the value used in Fig. 3a, the calculations predict a H_2O-present solidus at 665°C, leading

601 to a volumetric melt fraction of 0.33 at 900°C (Fig. 3e). By contrast, the experiments are

602 thought to represent hydrate-breakdown melting and produce only modest melt fractions at

603 900°C. However, by reducing the estimate of M_{H_2O} in Fig. 3a from 4.6 mole% to 3.0 mole%,

604 a fluid-absent solidus could be calculated at 800°C without significantly degrading the fit to

605 the experimental hornblende-out boundary, the latter being only a weak function of M_{H_2O}.

606 A value of $M_{H_2O} = 3.0$ mole% is in fact close to the estimate of bulk H_2O in the starting

607 materials based on mineral modes ($M_{H_2O} \sim 3.3$ mole%, Patiño Douce & Beard, 1995). For

608 a boundary as sensitive to bulk H_2O as the water-undersaturated solidus, it is difficult to

609 make a meaningful comparison between calculations and observations, given that the

610 appropriate value of bulk H_2O in the experimental run products is poorly known.

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Experiments of Beard & Lofgren (1991)

Sample 478 from the study of Beard & Lofgren (1991; BL478) is a naturally occurring low-K_2O andesite, less siliceous and less potassic than the SQA material of Patiño Douce & Beard (1995) and with higher bulk $FeO/(FeO+MgO)$. Hydrate-breakdown melting experiments, conducted in an IHPV, produced assemblages of pl + melt + Fe-Ti oxides ± cpx ± opx ± hb ± q, as shown in Fig. 4a.

Calculations on this bulk composition again describe an amphibolite to granulite facies transition that is broadly consistent with the experiments, summarised in Fig. 4b. As for the SQA composition, the calculated prediction of clinopyroxene stability conflicts with the lowest-temperature experiment at 850°C, 6.9 kbar. This experiment yielded pargasitic amphibole + q + pl + Fe-Ti oxides + 6.2 wt% L, whereas the starting assemblage was actinolitic amphibole + q + pl + Fe-Ti oxides. We tentatively suggest that the small quantity of melt present in an otherwise dry experiment may again have been insufficient to allow the stable crystalline assemblage to form. If this is the case, the experiments again primarily define an upper temperature limit on the hornblende-out boundary. The calculated quartz-out boundary lies at too high a temperature, but is shown in Fig. 4c and d to be particularly sensitive to M_O and M_{H_2O}. At 900°C and 1 kbar the calculations predict H_2O as a free phase, so they are compared with the results of an H_2O-saturated experiment on the same starting material, but fail to reproduce the observed amphibole + quartz assemblage. This is not a significant concern, as the focus of the model calibration was on the more geologically relevant situation of hydrate-breakdown melting (Brown & Fyfe, 1970).

The value of M_O chosen for the calculations in Fig. 4a corresponds to $X_{Fe^{3+}} = 0.2$, which was assumed to be plausible for the natural starting material, and consistent with exposure to the IHPV assembly over moderate run durations of around 90–120 hours. The T–M_O plot (Fig. 4c) shows that, for the relatively oxidised conditions imposed, the calculated 7

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637 kbar position of the hornblende-out boundary varies only from 885°C at $M_O = 0.76$ mole%

638 ($X_{Fe^{3+}} = 0.15$) to 902°C at $M_O = 1.27$ mole% ($X_{Fe^{3+}} = 0.25$). The hornblende-out boundary

639 is also almost indifferent to M_{H_2O} in the range 0.5 to 4.5 mole% (Fig. 4d). The value of

640 M_{H_2O} chosen for Fig. 4a is 3.42 mole%, larger than the 1.72 mole% estimated by loss on

641 ignition from the starting materials by Beard & Lofgren (1991). In our modelling, this

642 choice of M_{H_2O} leads to the coexistence of orthopyroxene and hornblende over a narrow

643 (~ 50°C) temperature range, whereas for values of $M_{H_2O} < 3.1$ mole%, orthopyroxene joins

644 the assemblage at rather low temperatures and creates a wide field of hornblende-granulite.

Hornblende-out boundaries in various experimental studies

646 Since only two bulk compositions from TTG-genesis experiments were used in the model

647 calibration, Fig. 5 summarises the results of calculations on the hornblende-out boundary in

648 four additional bulk compositions that were not involved in the calibration process, taken

649 from the hydrate-breakdown melting studies of Beard & Lofgren (1991); Rushmer (1991);

650 Wolf & Wyllie (1994) and Skjerlie & Patiño Douce (1995). Comparable calculations for

651 SQA and BL478, the compositions used in calibration, are also shown. In each case, the

652 true temperature of the hornblende-out boundary could be inferred with some confidence

653 from an isobaric sequence of experiments, in which the final hornblende coexisted with a

654 moderate melt fraction and had an apparently equilibrated composition. The calculations,

655 shown as blue bars, locate the hornblende-out boundary for each experimental phase

656 assemblage. Where possible, calculations were performed over generous ranges of M_{H_2O}

657 (3.5–6.5 mole%, equivalent to $\sim 1-2$ wt%) and M_O (such that $0.1 < X_{Fe^{3+}} < 0.25$), varied

658 simultaneously, which we expect to encompass the true experimental values in most cases.

659 For bulk compositions WW94 and BL571, the experimental assemblage could only be

660 calculated over a reduced range of M_O or M_{H_2O}; see Fig. 5 and Table 1.

661 The calculations generally reproduce the experimental hornblende-out temperatures

27

662 well, although they considerably overestimate the temperature for the IAT (island arc

663 tholeiite) composition of Rushmer (1991). Temperatures are probably underestimated for

664 the natural amphibolite composition AGS11.1 of Skjerlie & Patiño Douce (1995), and the

665 calibration composition SQA. Over- or under-estimation of hornblende-out temperature

666 may be correlated with molar bulk values of $Al_2O_3/(CaO + Na_2O + K_2O)$, of which IAT

667 has the highest value and AGS11.1 and SQA relatively low values.

668   To a considerable extent the variation of modelled boundaries with bulk composition is

669 a function of the well established Holland & Powell (2011) dataset calibration, combined

670 with the superimposed ΔG_i^{mod} and ΔG_i^{make} terms. Therefore it is perhaps unsurprising that

671 the results of these calculations are reasonable, even though only two of the TTG-genesis

672 studies were incorporated into the fitting.

673 **DISCUSSION**

674 The newly calibrated a–x relations extend the scope of phase-equilibrium forward-modelling

675 methods to include metabasic rocks at high temperature. A pseudosection approach to

676 thermobarometry is now feasible for such rocks, and other questions that incorporate a bulk

677 composition constraint, such as limits on melt loss, may now be addressed. Methods of this

678 kind have previously brought insight into metamorphic processes in metapelites (e.g. White

679 *et al.*, 2003; Kelsey *et al.*, 2003; Johnson & Brown, 2004; Halpin *et al.*, 2007; Streule *et al.*,

680 2010; Korhonen *et al.*, 2010; Palin *et al.*, 2012). Strictly the calibration of the a–x relations

681 described in this paper was limited to ≤13 kbar, owing to the lack of a thermodynamic

682 model for aqueous fluid containing dissolved silicate material. However, it is reasonable to

683 use the metabasite models with caution whenever the results can be compared with

684 observations to demonstrate that appropriate stable assemblages are calculated. In the

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companion paper, Palin *et al.* (2016b), we examine calculations with the metabasite models on a variety of natural compositions, comparing the calculated assemblages and melt compositions with expectations drawn from observation and experiment.

Through the above comparison of phase diagram calculations with experiments, it is possible to comment on the uncertainties and limitations of the models. The models can probably be expected to give a correct sequence of up-temperature assemblages, with respect to major phases. Within the calibration range of the $a–x$ relations, phase-in/phase-out boundaries are likely to be constrained to within 50–100°C, or 1–2 kbar for a strongly pressure-dependent boundary, allowing for the difficulty of assessing M_O and M_{H_2O} during model calibration. Comparable magnitudes of uncertainty are associated with estimating a representative bulk composition for an equilibrium assemblage in a natural rock sample (Palin *et al.*, 2016a). As in all forward modelling of phase equilibria, careful consideration of the sensitivity of results to M_O and M_{H_2O} will be essential for meaningful interpretation.

As metabasic rocks typically contain fewer phases than metapelites, fields on $P–T$ pseudosections tend to be larger, providing a less useful constraint on the pressure and temperature of mineral preservation. It may therefore be desirable to estimate $P–T$ more precisely by comparing the observed and calculated compositions of phases. An appropriate way to do this, that correctly takes account of the uncertainties in the thermodynamic modelling, is the 'average $P–T$' method of Powell & Holland (1988) and Powell & Holland (1994). This can be carried out in THERMOCALC, using the standard input files for the Holland & Powell (2011) dataset and metabasite set of $a–x$ relations, just as for pseudosection calculations (Powell & Holland, 2008). The average $P–T$ method finds the least-squares best estimate of P-at-T or T-at-P using the thermobarometric information contained in multiple independent reactions among model end-members. Starting from the activities calculated for the model end-members at the analytical phase compositions, it makes minimal uncertainty-weighted adjustments to the activities and enthalpies of the

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712 end-members, until the constraint is satisfied that all end-member reactions must meet at
713 an equilibrium P or T (both P and T can be constrained using the uncertainty output).
714 When good statistical diagnostics are obtained from the procedure, they suggest both that
715 the analysed phases are well equilibrated, and that the thermodynamic models are
716 sufficiently well calibrated to reflect this.

717   The a–x relations presented in this paper should be considered only as a starting point
718 for the modelling of high-temperature metabasic assemblages. Future a–x development is
719 expected to include a single model for clinopyroxene, replacing the current omphacite and
720 augite models, and a single model for tonalitic–trondjhemitic to granitic melt, replacing the
721 current metabasite and metapelite melt models. The set of metabasite a–x models will be
722 refined over time, as was the metapelite set of models before it, to correct systematic
723 problems that emerge in calculated phase equilibria. We welcome feedback from users on
724 the performance of the models.

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APPENDIX

1053 The thermodynamic models discussed in this paper may be conveniently used with the

1054 software THERMOCALC (Powell & Holland, 1988). The THERMOCALC software may be

1055 downloaded from the University of Mainz THERMOCALC website at

1056 http://www.metamorph.geo.uni-mainz.de/thermocalc/, along with input files containing

1057 the a–x relations, versions of the Holland & Powell (2011) dataset, and explanatory notes.

1058 THERMOCALC versions tc340 and above should be used. Versions ds62 and ds63 of the

1059 Holland & Powell (2011) dataset have not been formally published, so anyone wishing to

1060 use them independently of THERMOCALC must extract parameters from the THERMOCALC

1061 input files. To assist in doing so, THERMOCALC may be run in mode 0 with the appropriate

1062 dataset and a–x relations, generating tables of G values as functions of P and T for each

1063 end-member, including those that do not appear explicitly in the dataset. The G values

1064 include any ΔG_i expressions applied to the end-members (identified in a–x input files by

1065 the script 'DQF').

1066   Full thermodynamic descriptions of the new a–x relations for clinopyroxene (augite

1067 model), clinoamphibole and metabasite melt are given below. ΔG_i terms are specified

1068 relative to end-members that appear in the Holland & Powell (2011) dataset. Interaction

1069 energies $W_{i,j}$ and ΔG_i parameters are specified as functions of pressure P in kilobar and T

1070 in kelvin: $W_{i,j} = W_{i,j}^a + W_{i,j}^b\,T + W_{i,j}^c\,P$ and $\Delta G_i = \Delta G_i^a + \Delta G_i^b\,T + \Delta G_i^c\,P$.

Clinopyroxene models

1072 In the augite model, the following independent set of end-members is used, with the cations

1073 shown on their mixing sites, and the tetrahedral site split into T1 and T2 in order to

1074 describe Si–Al ordering in the cats end-member (the latter is an intrinsic property of the

1075 cats end-member of the Holland & Powell (2011) dataset, written out explicitly in the a–x

1076 model):

45

	M1				M2			T1		T2	
	Mg	Fe	Al	Fe3	Mg	Fe	Ca	Na	Si	Al	Si	Al
di	1	0	0	0	0	0	1	0	1	0	1	0
cenh	1	0	0	0	1	0	0	0	1	0	1	0
cfs	0	1	0	0	0	1	0	0	1	0	1	0
jd	0	0	1	0	0	0	0	1	1	0	1	0
acm	0	0	0	1	0	0	0	1	1	0	1	0
ocats	0	0	1	0	0	0	1	0	1	0	0	1
dcats	0	0	1	0	0	0	1	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
fmc	1	0	0	0	0	1	0	0	1	0	1	0

Cenh and cfs are the $C2/c$ polymorphs of the dataset $Pbca$ end-members en and fs, and are derived from them via $\Delta G_{\text{cenh}}^{\text{tran}} = G_{\text{cenh}} - G_{\text{en}} = 3.5 - 0.002T + 0.048P$ kJ and $\Delta G_{\text{cfs}}^{\text{tran}} = G_{\text{cfs}} - G_{\text{fs}} = 2.1 - 0.002T + 0.045P$ kJ. Fmc is the ordered end-member for which $G_{\text{fmc}} = \frac{1}{2}(G_{\text{cenh}} + G_{\text{cfs}}) + \Delta G_{\text{ordering}}$. Because ΔG_{i} terms are described relative to dataset end-members, $\Delta G_{\text{fmc}}^{\text{od}}$ incorporates $\Delta G_{\text{ordering}}$, $\Delta G_{\text{cenh}}^{\text{tran}}$ and $\Delta G_{\text{cfs}}^{\text{tran}}$: $\Delta G_{\text{fmc}}^{\text{od}} = \frac{1}{2}(\Delta G_{\text{cenh}}^{\text{tran}} + \Delta G_{\text{cfs}}^{\text{tran}}) + \Delta G_{\text{ordering}} = -1.6 - 0.002T + 0.0465P$ kJ. Ocats and dcats are the fully ordered and fully disordered forms respectively of the dataset cats end-member. Together they reproduce the thermodynamics of the cats end-member via prescribed values for $W_{\text{ocats,dcats}}$ and the term $\Delta G_{\text{dcats}} = 3.8 - 0.0028816T + 0.01P$ kJ. $W_{\text{ocats,dcats}}$, $\Delta G_{\text{dcats}}^{a}$ and $\Delta G_{\text{dcats}}^{c}$ can be found in Holland & Powell (2011), table 2c, while $\Delta G_{\text{dcats}}^{b}$ represents the configurational entropy involved in disordering. Jd and acm are subject to $\Delta G_{\text{i}}^{\text{mod}}$ terms of 2 kJ and -5 kJ respectively.

Composition is described by the variables

$$
\begin{aligned}
x &= \frac{\text{Fe}}{\text{Fe} + \text{Mg}} \\
&= \frac{x_{\text{Fe}}^{\text{M1}} + x_{\text{Fe}}^{\text{M2}}}{x_{\text{Fe}}^{\text{M1}} + x_{\text{Fe}}^{\text{M2}} + x_{\text{Mg}}^{\text{M1}} + x_{\text{Mg}}^{\text{M2}}} \\
y &= x_{\text{Al}}^{\text{T1}} + x_{\text{Al}}^{\text{T2}} \\
f &= x_{\text{Fe3}}^{\text{M1}} \\
z &= x_{\text{Ca}}^{\text{M2}} \\
j &= x_{\text{Na}}^{\text{M2}},
\end{aligned}
$$

46

1091 and order-disorder by the parameters

$$
\begin{aligned}
Q_{fm} &= 2\left(\frac{x_{\text{Fe}}^{\text{M2}}}{x_{\text{Fe}}^{\text{M2}} + x_{\text{Mg}}^{\text{M2}}} - x\right) \\
Q_{al} &= x_{\text{Al}}^{\text{T2}} - x_{\text{Al}}^{\text{T1}},
\end{aligned}
$$

1092 which are found by solving the internal equilibria via which the corresponding order-disorder

1093 end-members are formed, i.e. fmc = $\frac{1}{2}$ (cenh + cfs) and dcats = ocats. The site fractions are

$$
\begin{aligned}
x_{\text{Mg}}^{\text{M1}} &= 1 - j - x - y + jx + xy + \frac{Q_{fm}}{2}(1 - j - z) \\
x_{\text{Fe}}^{\text{M1}} &= x - jx - xy - \frac{Q_{fm}}{2}(1 - j - z) \\
x_{\text{Al}}^{\text{M1}} &= j + y - f \\
x_{\text{Fe3}}^{\text{M1}} &= f \\
x_{\text{Mg}}^{\text{M2}} &= 1 - j - x - z - \frac{Q_{fm}}{2}(1 - j - z) + jx + xz \\
x_{\text{Fe}}^{\text{M2}} &= x + \frac{Q_{fm}}{2}(1 - j - z) - jx - xz \\
x_{\text{Ca}}^{\text{M2}} &= z \\
x_{\text{Na}}^{\text{M2}} &= j \\
x_{\text{Si}}^{\text{T1}} &= 1 - \frac{1}{2}(y - Q_{al}) \\
x_{\text{Al}}^{\text{T1}} &= \frac{1}{2}(y - Q_{al}) \\
x_{\text{Si}}^{\text{T2}} &= 1 - \frac{1}{2}(y + Q_{al}) \\
x_{\text{Al}}^{\text{T2}} &= \frac{1}{2}(y + Q_{al}),
\end{aligned}
$$

1094 and the ideal activities are

$$
\begin{aligned}
a_{\text{di}}^{\text{ideal}} &= x_{\text{Mg}}^{\text{M1}} x_{\text{Ca}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}}\right)^{\frac{1}{4}} \\
a_{\text{cenh}}^{\text{ideal}} &= x_{\text{Mg}}^{\text{M1}} x_{\text{Mg}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}}\right)^{\frac{1}{4}} \\
a_{\text{cfs}}^{\text{ideal}} &= x_{\text{Fe}}^{\text{M1}} x_{\text{Fe}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}}\right)^{\frac{1}{4}}
\end{aligned}
$$

47

$$a_{\mathrm{jd}}^{\mathrm{ideal}} = x_{\mathrm{Al}}^{\mathrm{M1}} x_{\mathrm{Na}}^{\mathrm{M2}} \left(x_{\mathrm{Si}}^{\mathrm{T1}} x_{\mathrm{Si}}^{\mathrm{T2}} \right)^{\frac{1}{4}}$$

$$a_{\mathrm{acm}}^{\mathrm{ideal}} = x_{\mathrm{Fe3}}^{\mathrm{M1}} x_{\mathrm{Na}}^{\mathrm{M2}} \left(x_{\mathrm{Si}}^{\mathrm{T1}} x_{\mathrm{Si}}^{\mathrm{T2}} \right)^{\frac{1}{4}}$$

$$a_{\mathrm{ocats}}^{\mathrm{ideal}} = x_{\mathrm{Al}}^{\mathrm{M1}} x_{\mathrm{Ca}}^{\mathrm{M2}} \left(x_{\mathrm{Si}}^{\mathrm{T1}} x_{\mathrm{Al}}^{\mathrm{T2}} \right)^{\frac{1}{4}}$$

$$a_{\mathrm{dcats}}^{\mathrm{ideal}} = \sqrt{2}\, x_{\mathrm{Al}}^{\mathrm{M1}} x_{\mathrm{Ca}}^{\mathrm{M2}} \left(x_{\mathrm{Si}}^{\mathrm{T1}} x_{\mathrm{Al}}^{\mathrm{T1}} x_{\mathrm{Si}}^{\mathrm{T2}} x_{\mathrm{Al}}^{\mathrm{T2}} \right)^{\frac{1}{8}}$$

$$a_{\mathrm{fmc}}^{\mathrm{ideal}} = x_{\mathrm{Mg}}^{\mathrm{M1}} x_{\mathrm{Fe}}^{\mathrm{M2}} \left(x_{\mathrm{Si}}^{\mathrm{T1}} x_{\mathrm{Si}}^{\mathrm{T2}} \right)^{\frac{1}{4}},$$

₁₀₉₅ including the entropy reduction factor. Non-ideal activities are given by equation 2. The

₁₀₉₆ end-member proportions for use in equation 2 are

$$p_{\mathrm{di}} = z - y$$

$$p_{\mathrm{cenh}} = 1 - j - x - z - \frac{Q_{fm}}{2}\left(1 - j - z\right) + jx + xz$$

$$p_{\mathrm{cfs}} = x - \frac{Q_{fm}}{2}\left(1 - j - z\right) - jx - xy$$

$$p_{\mathrm{jd}} = j - f$$

$$p_{\mathrm{acm}} = f$$

$$p_{\mathrm{ocats}} = Q_{al}$$

$$p_{\mathrm{dcats}} = y - Q_{al}$$

$$p_{\mathrm{fmc}} = Q_{fm}\left(1 - j - z\right) + xy - xz.$$

₁₀₉₇ The interaction energies are:

₁₀₉₈

$W_{\mathrm{i,j}}$ (kJ)	cenh	cfs	jd	acm	ocats	dcats	fmc
di	$29.8 - 0.03P$	$25.8 - 0.03P$	26	21	$12.3 - 0.01P$	$12.3 - 0.01P$	$20.6 - 0.03P$
cenh		2.3	50	62	$45.7 - 0.29P$	$45.7 - 0.29P$	4
cfs			60	58	48	48	3.5
jd				5	40	40	40
acm					35	35	60
ocats						$3.8 + 0.01P$	50
dcats							50

₁₀₉₉

48

1100 with asymmetry introduced by the van Laar parameters $\alpha_{\text{cenh}} = \alpha_{\text{cfs}} = \alpha_{\text{fmc}} = 1$, $\alpha_{\text{di}} = \alpha_{\text{jd}}$

1101 $= \alpha_{\text{acm}} = 1.2$, and $\alpha_{\text{ocats}} = \alpha_{\text{dcats}} = 1.9$.

1102 We reiterate that the augite model does not have a structure suitable for calculations

1103 where coexisting clinopyroxenes may be expected. To calculate two-clinopyroxene

1104 equilibria, the 'omphacite' model should be used for both phases, using appropriate starting

1105 guesses for the compositional parameters in each. The omphacite model is described in

1106 Green *et al.* (2007), with new $W_{\text{acm},n}$ values given in Diener & Powell (2012) and a new

1107 value for $\Delta G_{\text{acm}}^{\text{mod}}$, of -7 kJ, given in this paper. The change to $\Delta G_{\text{acm}}^{\text{mod}}$ entails a

1108 corresponding change to the parameter $\Delta G_{\text{jac}}^{\text{od}}$. The jac end-member is the ordered

1109 intermediate $Na_{\frac{1}{2}}^{\text{M2}}Na_{\frac{1}{2}}^{\text{M2}}Fe_{\frac{1}{2}}^{3+\text{M1}}Al_{\frac{1}{2}}^{\text{M1}}Si_{2}^{\text{tet}}O_6$, and is formed through the reaction jac $= \frac{1}{2}$ (jd

1110 + acm) $+ \Delta G_{\text{jac}}^{\text{od}}$, such that $\Delta G_{\text{jac}}^{\text{od}} = \frac{1}{2} (\Delta G_{\text{jd}}^{\text{mod}} + \Delta G_{\text{acm}}^{\text{mod}}) - 1$ kJ. With $\Delta G_{\text{jd}}^{\text{mod}} = 0$, the

1111 change to $\Delta G_{\text{acm}}^{\text{mod}}$ leads to $\Delta G_{\text{jac}}^{\text{od}} = -4.5$ kJ, rather than the previous value of -5 kJ.

1112 For comparison between the omphacite and augite models, the dependent parameters

1113 associated with the hed end-member, $CaFeSi_2O_6$, in the augite model are compared here

1114 with their equivalents in the omphacite model.

1115

parameter (kJ)	augite model	omphacite model
$W_{\text{di,hed}}$	2.9	4
$W_{\text{cenh,hed}}$	$26.6 - 0.03P$	-
$W_{\text{cfs,hed}}$	$20.9 - 0.03P$	-
$W_{\text{jd,hed}}$	42.4	24
$W_{\text{acm,hed}}$	17.4	20.8
$W_{\text{ocats,hed}}$, $W_{\text{dcats,hed}}$	$8.7 - 0.01P$	-
ΔG_{hed} at 8 kbar, 900°C	1.5	0

1116 There is however no discordance of symmetry between the two models, as they both feature

1117 $\alpha_{\text{di}} = \alpha_{\text{jd}} = \alpha_{\text{acm}} = \alpha_{\text{hed}}$. For the method of determining the dependency relationships, see

1118 Powell & Holland (1999).

1119 **Clinoamphibole model**

1120 The following independent set of end-members is used, based on an amphibole formula

49

calculated for 23 oxygen atoms, with the mixing sites only shown (v=vacancy):

	A			M13		M2					M4				T1		V	
	v	Na	K	Mg	Fe	Mg	Fe	Al	Fe3	Ti	Ca	Mg	Fe	Na	Si	Al	OH	O
tr	1	0	0	3	0	2	0	0	0	0	2	0	0	0	4	0	2	0
ts	1	0	0	3	0	0	0	2	0	0	2	0	0	0	2	2	2	0
parg	0	1	0	3	0	1	0	1	0	0	2	0	0	0	2	2	2	0
gl	1	0	0	3	0	0	0	2	0	0	0	0	0	2	4	0	2	0
cumm	1	0	0	3	0	2	0	0	0	0	0	2	0	0	4	0	2	0
grun	1	0	0	0	3	0	2	0	0	0	0	0	2	0	4	0	2	0
a	1	0	0	3	0	0	2	0	0	0	0	0	2	0	4	0	2	0
b	1	0	0	0	3	2	0	0	0	0	0	0	2	0	4	0	2	0
mrb	1	0	0	3	0	0	0	0	2	0	0	0	0	2	4	0	2	0
kprg	0	0	1	3	0	1	0	1	0	0	2	0	0	0	2	2	2	0
tts	1	0	0	3	0	0	0	0	0	2	2	0	0	0	2	2	0	2

As the end-member thermodynamics are in general not well known, it is assumed that that dataset end-member tr is correct, while the other compositional end-members ts, parg, gl, cumm and grun are modified relative to this via terms $\Delta G_{ts}^{mod} = 10$ kJ, $\Delta G_{parg}^{mod} = -10$ kJ, $\Delta G_{gl}^{mod} = -3$ kJ, $\Delta G_{cumm}^{mod} = 0$ kJ, $\Delta G_{grun}^{mod} = -3$ kJ. Order–disorder of Fe–Mg on the M13, M2 and M4 sites is governed by end-members a $= \frac{3}{7}$ cumm $+ \frac{4}{7}$ grun $+ \Delta G_{a}^{od}$ and b $= \frac{2}{7}$ cumm $+ \frac{5}{7}$ grun $+ \Delta G_{b}^{od}$, where the ΔG relative to the dataset values of the end-members are given by $\Delta G_{a}^{od} = \frac{3}{7} \Delta G_{cumm}^{mod} + \frac{4}{7} \Delta G_{grun}^{mod} - 9.5 = -11.2$ kJ and $\Delta G_{b}^{od} = \frac{2}{7} \Delta G_{cumm}^{mod} + \frac{5}{7} \Delta G_{grun}^{mod} - 11.7 = -13.8$ kJ. The ferric end-member mrb, and the new end-members kprg and tts, have to be 'made' from dataset end-members via the reactions mrb = gl − gr + andr + ΔG_{mrb}^{make}, kprg = mu − pa + parg + ΔG_{kprg}^{make}, and tts = ts + 2 ru − 2 dsp + ΔG_{tts}^{make} respectively, where the dG terms are $\Delta G_{mrb}^{make} = 0$ kJ, $\Delta G_{kprg}^{make} = -7.06 + 0.02\,T$ kJ and $\Delta G_{tts}^{make} = 95$ kJ (gr: grossular; andr: andradite; mu: muscovite; pa: paragonite; ru: rutile; dsp: diaspore). Diener *et al.* (2007) describe the structure and calibration of the core NCFMASHO model more fully.

Composition and order are described by the variables

$$x = \frac{Fe}{Fe + Mg}$$

50

$$= \frac{3x_{\text{Fe}}^{\text{M13}} + 2x_{\text{Fe}}^{\text{M2}} + 2x_{\text{Fe}}^{\text{M4}}}{3x_{\text{Fe}}^{\text{M13}} + 2x_{\text{Fe}}^{\text{M2}} + 2x_{\text{Fe}}^{\text{M4}} + 3x_{\text{Mg}}^{\text{M13}} + 2x_{\text{Mg}}^{\text{M2}} + 2x_{\text{Mg}}^{\text{M4}}}$$

$$y = x_{\text{Al}}^{\text{M2}}$$

$$z = x_{\text{Na}}^{\text{M4}}$$

$$a = x_{\text{K}}^{\text{A}} + x_{\text{Na}}^{\text{A}}$$

$$k = \frac{x_{\text{K}}^{\text{A}}}{x_{\text{K}}^{\text{A}} + x_{\text{Na}}^{\text{K}}}$$

$$c = x_{\text{Ca}}^{\text{M4}}$$

$$f = x_{\text{Fe3}}^{\text{M2}}$$

$$t = x_{\text{Ti}}^{\text{M2}}$$

$$Q_1 = x - \frac{x_{\text{Fe}}^{\text{M13}}}{x_{\text{Fe}}^{\text{M13}} + x_{\text{Mg}}^{\text{M13}}}$$

$$Q_2 = x - \frac{x_{\text{Fe}}^{\text{M2}}}{x_{\text{Fe}}^{\text{M2}} + x_{\text{Mg}}^{\text{M2}}}.$$

1139 The site fractions are

$$x_{\text{v}}^{\text{A}} = 1 - a$$

$$x_{\text{Na}}^{\text{A}} = a(1 - k)$$

$$x_{\text{K}}^{\text{A}} = ak$$

$$x_{\text{Mg}}^{\text{M13}} = 1 - x + Q_1$$

$$x_{\text{Fe}}^{\text{M13}} = x - Q_1$$

$$x_{\text{Mg}}^{\text{M2}} = 1 - x - y - f - t + Q_2(1 - f - t - y) + fx + tx + xy$$

$$x_{\text{Fe}}^{\text{M2}} = x - Q_2(1 - f - t - y) - fx - tx - xy$$

$$x_{\text{Al}}^{\text{M2}} = y$$

$$x_{\text{Fe3}}^{\text{M2}} = f$$

$$x_{\text{Ti}}^{\text{M2}} = t$$

$$x_{\text{Ca}}^{\text{M4}} = c$$

$$x_{\text{Mg}}^{\text{M4}} = 1 - c - x - z - \frac{3Q_1}{2} - Q_2(1 - f - t - y) + xc + xz$$

51

$$x_{\text{Fe}}^{\text{M4}} \;=\; x + \frac{3Q_1}{2} + Q_2\left(1 - f - t - y\right) - xc - xz$$

$$x_{\text{Na}}^{\text{M4}} \;=\; z$$

$$x_{\text{Si}}^{\text{T1}} \;=\; 1 - \frac{1}{2}\left(f + t + y - z + \frac{1}{2}a\right)$$

$$x_{\text{Al}}^{\text{T1}} \;=\; \frac{1}{2}\left(f + t + y - z + \frac{1}{2}a\right)$$

$$x_{\text{OH}}^{\text{V}} \;=\; 1 - t$$

$$x_{\text{O}}^{\text{V}} \;=\; t,$$

₁₁₄₀ and ideal activities

$$a_{\text{tr}}^{\text{ideal}} \;=\; x_{\text{v}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 \left(x_{\text{Mg}}^{\text{M2}}\right)^2 \left(x_{\text{Ca}}^{\text{M4}}\right)^2 x_{\text{Si}}^{\text{T1}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{ts}}^{\text{ideal}} \;=\; 2\,x_{\text{v}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 \left(x_{\text{Mg}}^{\text{M2}}\right)^2 \left(x_{\text{Ca}}^{\text{M4}}\right)^2 \left(x_{\text{Si}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{Al}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{parg}}^{\text{ideal}} \;=\; 8\,x_{\text{Na}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 x_{\text{Mg}}^{\text{M2}}x_{\text{Al}}^{\text{M2}} \left(x_{\text{Ca}}^{\text{M4}}\right)^2 \left(x_{\text{Si}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{Al}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{gl}}^{\text{ideal}} \;=\; x_{\text{v}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 \left(x_{\text{Al}}^{\text{M2}}\right)^2 \left(x_{\text{Na}}^{\text{M4}}\right)^2 x_{\text{Si}}^{\text{T1}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{cumm}}^{\text{ideal}} \;=\; x_{\text{v}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 \left(x_{\text{Mg}}^{\text{M2}}\right)^2 \left(x_{\text{Mg}}^{\text{M4}}\right)^2 x_{\text{Si}}^{\text{T1}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{grun}}^{\text{ideal}} \;=\; x_{\text{v}}^{\text{A}}\left(x_{\text{Fe}}^{\text{M13}}\right)^3 \left(x_{\text{Fe}}^{\text{M2}}\right)^2 \left(x_{\text{Fe}}^{\text{M4}}\right)^2 x_{\text{Si}}^{\text{T1}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{a}}^{\text{ideal}} \;=\; x_{\text{v}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 \left(x_{\text{Fe}}^{\text{M2}}\right)^2 \left(x_{\text{Fe}}^{\text{M4}}\right)^2 x_{\text{Si}}^{\text{T1}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{b}}^{\text{ideal}} \;=\; x_{\text{v}}^{\text{A}}\left(x_{\text{Fe}}^{\text{M13}}\right)^3 \left(x_{\text{Mg}}^{\text{M2}}\right)^2 \left(x_{\text{Fe}}^{\text{M4}}\right)^2 x_{\text{Si}}^{\text{T1}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{mrb}}^{\text{ideal}} \;=\; x_{\text{v}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 \left(x_{\text{Fe3}}^{\text{M2}}\right)^2 \left(x_{\text{Na}}^{\text{M4}}\right)^2 x_{\text{Si}}^{\text{T1}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{kprg}}^{\text{ideal}} \;=\; 8\,x_{\text{K}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 x_{\text{Mg}}^{\text{M2}}x_{\text{Al}}^{\text{M2}} \left(x_{\text{Ca}}^{\text{M4}}\right)^2 \left(x_{\text{Si}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{Al}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{OH}}^{\text{V}}\right)^2$$

$$a_{\text{tts}}^{\text{ideal}} \;=\; 2\,x_{\text{v}}^{\text{A}}\left(x_{\text{Mg}}^{\text{M13}}\right)^3 \left(x_{\text{Ti}}^{\text{M2}}\right)^2 \left(x_{\text{Ca}}^{\text{M4}}\right)^2 \left(x_{\text{Si}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{Al}}^{\text{T1}}\right)^{\frac{1}{2}} \left(x_{\text{O}}^{\text{V}}\right)^2,$$

₁₁₄₁ with non-ideal activities given by equation (2). The end-member proportions are

$$p_{\text{tr}} \;=\; c + z - \frac{a}{2} - f - t - y$$

$$p_{\text{ts}} \;=\; y + f - z - \frac{a}{2}$$

$$p_{\text{parg}} \;=\; a\left(1 - k\right)$$

52

$$p_{gl} = z - f$$

$$p_{cumm} = 1 - c - x - z - \frac{3Q_1}{2} - Q_2\left(1 - f - t - y\right) + cx + xz$$

$$p_{grun} = x - \frac{5Q_1}{2} - 2Q_2\left(1 - f - t - y\right) + cx - fx - tx - xy + xz$$

$$p_a = \frac{5Q_2}{2} + Q_2\left(1 - f - t - y\right) - xc - xz$$

$$p_b = \frac{3Q_1}{2} + 2Q_2\left(1 - f - t - y\right) - xc + fx + tx + xy - xz$$

$$p_{mrb} = f$$

$$p_{kprg} = ak$$

$$p_{tts} = t.$$

1142 The interaction energies are:

$W_{i,j}$ (kJ)	ts	parg	gl	cumm	grun	a	b	mrb	kprg	tts
tr	20	25	65	45	75	57	63	52	30	85
ts		−40	25	70	80	70	72.5	20	−40	35
parg			50	90	106.7	94.8	94.8	40	8	15
gl				100	113.5	100	111.2	0	54	75
cumm					33	18	23	80	87	100
grun						12	8	91	96	65
a							20	80	94	95
b								90	94	95
mrb									50	50
kprg										35

1144 with asymmetry introduced by the van Laar parameters $\alpha_{tr} = \alpha_{cumm} = \alpha_{grun} = \alpha_a = \alpha_b = $
1145 1, $\alpha_{ts} = \alpha_{tts} = 1.5$, $\alpha_{gl} = \alpha_{mrb} = 0.8$, and $\alpha_{parg} = \alpha_{kprg} = 1.7$.

1146 These a–x relations are suitable for all of the clinoamphibole solid solutions hornblende,
1147 glaucophane, actinolite and cummingtonite, when appropriate starting guesses are given for
1148 the compositional variables.

Melt model

1150 The end-members are mixing units with mineral-like formulae:

53

end-member	formula
qL	Si_4O_8
abL	$NaAlSi_3O_8$
kspL	$KAlSi_3O_8$
woL	$CaSiO_3$
silL	Al_2SiO_5
faL	$Fe_4Si_2O_8$
foL	$Mg_4Si_2O_8$
h2oL	H_2O
anL	$CaAl_2Si_2O_8$

$\Delta G_i^{\mathrm{mod}}$ terms are imposed on some end-members: $\Delta G_{\mathrm{woL}}^{\mathrm{mod}} = 1.3$ kJ, $\Delta G_{\mathrm{silL}}^{\mathrm{mod}} = -7.8$ kJ,

$\Delta G_{\mathrm{faL}}^{\mathrm{mod}} = -8.2 - 1.4P$ kJ, and $\Delta G_{\mathrm{foL}}^{\mathrm{mod}} = -4$. The end-member anL is made by the reaction

$\mathrm{anL} = \mathrm{woL} + \mathrm{silL} + \Delta G_{\mathrm{anL}}^{\mathrm{od}}$, with $\Delta G_{\mathrm{anL}}^{\mathrm{od}} = -46.5 - 0.25P$.

The composition of the melt is described by the following variables, where

$\Sigma_c = Si_4O_8 + NaAlSi_3O_8 + KAlSi_3O_8 + CaSiO_3 + Al_2SiO_5 + Fe_4Si_2O_8 + Mg_4Si_2O_8 + H_2O$:

$$q = \frac{Si_4O_8}{\Sigma_c}$$

$$fsp = \frac{NaAlSi_3O_8 + KAlSi_3O_8}{\Sigma_c}$$

$$na = \frac{NaAlSi_3O_8}{NaAlSi_3O_8 + KAlSi_3O_8} = \frac{Na}{Na + K}$$

$$wo = \frac{CaSiO_3}{\Sigma_c}$$

$$sil = \frac{Al_2SiO_5}{\Sigma_c}$$

$$ol = \frac{Fe_4Si_2O_8 + Mg_4Si_2O_8}{\Sigma_c}$$

$$x = \frac{Fe_4Si_2O_8}{Fe_4Si_2O_8 + Mg_4Si_2O_8} = \frac{Fe^{2+}}{Fe^{2+} + Mg}.$$

To handle the formation of the associate species anL, an 'order parameter' y_{anL} is defined,

where $y_{\mathrm{anL}} = p_{\mathrm{anL}}$. The full set of end-member proportions can now be written as:

$$p_{\mathrm{qL}} = q\,(1 + y_{\mathrm{anL}})$$

$$p_{\mathrm{abL}} = fsp\,na\,(1 + y_{\mathrm{anL}})$$

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$$p_{\text{kspL}} = fsp \ (1 - na) \ (1 + y_{\text{anL}})$$

$$p_{\text{woL}} = wo \ (1 + y_{\text{anL}}) - y_{\text{anL}}$$

$$p_{\text{silL}} = sil \ (1 + y_{\text{anL}}) - y_{\text{anL}}$$

$$p_{\text{faL}} = ol \ x \ (1 + y_{\text{anL}})$$

$$p_{\text{foL}} = ol \ (1 - x) \ (1 + y_{\text{anL}})$$

$$p_{\text{h2oL}} = 1 - (q + fsp + wo + sil + ol) \ (1 + y_{\text{anL}}) + y_{\text{anL}}$$

$$p_{\text{anL}} = y_{\text{anL}}.$$

1159 The ubiquitous $(1 + y_{\text{anL}})$ terms arise because the reaction woL + silL = anL leads to an

1160 overall change in the number of 'molecules' present, for a fixed number of atoms of liquid.

1161 There are no site fractions in a formal sense since mixing is molecular. However it is

1162 necessary to introduce an equivalent concept in order to formulate ideal activity

1163 expressions. Considering melt as a one-phase site, the 'site fractions' are chosen to be

1164 composed of the end-member proportion expressions p_{qL}, p_{woL}, p_{h2oL}, p_{anL}, $p_{\text{ol}} = p_{\text{faL}} + p_{\text{foL}}$,

1165 $x_{\text{ab}} = p_{\text{abL}}$, $x_{\text{ksp}} = p_{\text{kspL}}$, and additionally the expressions

$$x_{\text{Fe}} = x$$

$$x_{\text{Mg}} = 1 - x$$

$$x_{\text{fac}} = 1 - p_{\text{h2oL}}.$$

1166 The ideal activities are then written as follows, with the x_{Fe} and x_{Mg} terms allowing for an

1167 extra entropic contribution from Fe-Mg mixing in addition to that of the mixing of foL and

1168 faL units, and the x_{fac} term allowing for extra entropy in the addition of H_2O:

$$a_{\text{qL}}^{\text{ideal}} = x_{\text{fac}} \ p_{\text{qL}}$$

$$a_{\text{abL}}^{\text{ideal}} = x_{\text{fac}} \ x_{\text{ab}}$$

$$a_{\text{kspL}}^{\text{ideal}} = x_{\text{fac}} \ x_{\text{ksp}}$$

$$a_{\text{woL}}^{\text{ideal}} = x_{\text{fac}}\, p_{\text{woL}}$$

$$a_{\text{silL}}^{\text{ideal}} = x_{\text{fac}}\, p_{\text{silL}}$$

$$a_{\text{faL}}^{\text{ideal}} = x_{\text{fac}}\, p_{\text{ol}}\,\left(x_{\text{Fe}}\right)^5$$

$$a_{\text{foL}}^{\text{ideal}} = x_{\text{fac}}\, p_{\text{ol}}\,\left(x_{\text{Mg}}\right)^5$$

$$a_{\text{h2oL}}^{\text{ideal}} = \left(p_{\text{h2oL}}\right)^2$$

$$a_{\text{anL}}^{\text{ideal}} = x_{\text{fac}}\, p_{\text{anL}}.$$

¹¹⁶⁹ The non-ideal activities are given by equation (1). The symmetrical interaction energies are:

$W_{i,j}$ (kJ)	abL	kspL	woL	silL	faL	foL	h2oL	anL
qL	$12 - 0.4P$	$-2 - 0.5P$	-5	0	0	$42 + 1.0P$	$18.1 - 0.68P$	$-29.5 - 0.1P$
abL		$-6 + 3.0P$	-12.0	10	$-30 + 0.8P$	$-47.3 + 0.3P$	$-4.4 - 0.17P$	$8.6 + 0.4P$
kspL			-13	0	-11.3	6.8	$10.4 - 0.39P$	$-16 - 0.25P$
woL				-1.6	6.5	4	21	3.5
silL					12	12	$11 - 0.5P$	6.4
faL						18	29	$-43.5 - 0.95P$
foL							$29 - 0.5P$	$-26 - 0.6P$
h2oL								$9.75 - 0.5P$

¹¹⁷⁰ In version 6.3 of the Holland & Powell (2011) dataset, the thermodynamic properties of

¹¹⁷¹ the h2oL end-member, incorporating the new constant-pressure heat capacity, are as

¹¹⁷² follows. Enthalpy of formation ($\Delta_f H$): -281.68 ± 0.26 kJ, entropy (S): 66.60 kJ K^{-1},

¹¹⁷³ volume (V): 1.363 J bar^{-1}, at 1 bar, 298 K. Heat capacity (C_P): 0.0650 kJ K^{-1}. Thermal

¹¹⁷⁴ expansivity (α_0): 57.80 K^{-1}. Bulk modulus at 1 bar, 298 K, and its first and second

¹¹⁷⁵ pressure derivatives (κ_0, κ_0', κ_0''): 47.92 kbar, 4.00, -0.08350 kbar^{-1}.

Other models

¹¹⁷⁷ The a–x relations for biotite, garnet and orthopyroxene were first presented in White *et al.*

¹¹⁷⁸ (2014). As used in White *et al.* (2014), the a–x relations for epidote were taken from

¹¹⁷⁹ Holland & Powell (2011), those for feldspar from Holland & Powell (2003), and those for

¹¹⁸⁰ spinel–magnetite from White *et al.* (2002). For ilmenite, the Mg-bearing model used by

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White *et al.* (2014) has been replaced, in both the metabasite set and the metapelite set, with the older model of White *et al.* (2000) in the system FeO–Fe_2O_3–TiO_2, as the more recent model appears to predict excessive values of $MgO/(FeO+MgO)$ in the phase.

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FIGURE CAPTIONS

Figure 1: Comparison of model calculations with experiments in the pyroxene quadrilateral, diopside (di) – enstatite (en) – ferrosilite (fs) – hedenbergite (hed). (a)–(d) The quadrilateral itself, displaying the data of Turnock & Lindsley (1981) and Lindsley (1983) in black. Black arrowheads show the directions of approach to equilibrium compositions; black lines are tielines defining the miscibility gap and solvus. Grey curves and lines indicate the calculated miscibility limits; dashed grey curves show the metastable extension of the augite–pigeonite solvus within the augite–orthopyroxene miscibility gap. (e)–(f) The fs–hed binary subsystem, displaying the experimental brackets of Lindsley (1981). Fs_{ss} and hed_{ss} are solid solutions rich in the fs and hed end-members respectively.

Figure 2: Pseudosections calculated using the metabasite set of thermodynamic models for an oxidised MORB bulk composition, based on that of Sun & McDonough (1989) but with a greater M_O, giving $X_{Fe^{3+}}$=0.36 (SM89, Table 1). Panels (a), (b): calculations using the augite model for clinopyroxene. Panels (c), (d): correctly modelled using the omphacite model for clinopyroxene. Where clinopyroxene is truly augitic in composition, the two models are substantially consistent, but the augite model is unable to represent moderate to high Na contents or the coexisting clinopyroxene phases highlighted in (b) and (d). H_2O was taken to be in excess below the solidus; above the solidus values of 5.8 mole % were used for (a), (b) and 5.6 mole % for (c), (d), such that assemblages are just H_2O-saturated at the solidus. Removal of K_2O, TiO_2 from the amphibole model has negligible effect on phase boundaries. The bulk composition is the same as in Diener & Powell (2012), fig. 1c, which was calculated with the previous generation of models.

Figure 3: Pseudosections calculated with the metabasite set for the SQA composition of Patiño Douce & Beard (1995) (Table 1). (a) P–T pseudosection compared with

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Figure 4: Pseudosections calculated with the metabasite set for sample 478 of Beard & Lofgren (1991; BL478 in Table 1). (a) P–T pseudosection compared with experiments. Experimental assemblages are pl + mt + ilm $\pm$ hb $\pm$ opx $\pm$ cpx $\pm$ q. The experiments involved hydrate-breakdown melting except for one, marked with a square symbol, which was fluid-saturated. (b) Summary of (a) highlighting the implied facies transition. (c) T–M_O section at 7 kbar, representing values of $X_{Fe^{3+}}$ $\leq$ 0.5. (d) T–M_{H_2O} sections at 7 kbar. Boundaries are ornamented and coloured to highlight the continuation of phase-out curves through different assemblages (colour online). In calculating this figure, the clinoamphibole model was used with $\Delta G_{gl}^{mod}=0$ kJ, rather than the preferred value of -3 kJ; however this affects the position of phase field boundaries by $\leq 10°C$.

Figure 5: Interpreted temperature of the hornblende-out boundary in six experimental bulk compositions (brackets and half-brackets labelled with assemblages; bulk compositions in Table 1), compared with the temperatures obtained from calculations using a range of M_O and M_{H_2O} values (blue bars, colour online). Except in the case of compositions labelled ^{a}, calculations were performed for a range of M_O such that 0.1 $< X_{Fe^{3+}} <$ 0.25, and for 3.5 $< M_{H_2O} <$ 6.5 mole% ($\sim$ 1–2 wt% H_2O), varied simultaneously. For compositions ^{a}, the blue bars represent calculations for the

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restricted range of M_O or M_{H_2O} over which positive modes of phases were predicted (Table 1). For composition WW94, TiO_2 was omitted as hornblende is the only Ti-bearing model involved. In compositions [b], only trace hornblende was detected at the lower-T end of the experimental bracket. Calculations were made on each experimental assemblage without checking that it was the most stable assemblage that the models could generate, except for compositions [c], which were used in calibration. For BL478, the experimental assemblage is ambiguous, while in the calculations, stable assemblages $\pm$ quartz are needed to cover the full range of M_O and M_{H_2O}.

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TABLE CAPTIONS

1245   Table 1: Bulk compositions in mole % used in calculations, expressed in terms of the

1246   chemical components used by THERMOCALC. FeO^{tot} is total iron expressed as FeO. O,

1247   oxygen, combines only with FeO, via the equation $2\,FeO + O = Fe_2O_3$; hence M_O is

1248   identically equal to molar bulk Fe_2O_3, $M_{Fe_2O_3}$, with $X_{Fe^{3+}}$ given by $2\,M_O/M_{FeO^{tot}}$.

1249   Where no value is cited in the M_{H_2O} column, H_2O is assumed to be in excess.

1250   Table 2: Equilibria used in calibrating the augite model (see text), and results of

1251   calculations with the completed set of models. Observed values of compositional

1252   variables are shown in roman font, calculated values in italic. Compositional variables

1253   for the augite model are defined in the Appendix. Bulk compositions used in the

1254   calculations are given in Table 1. Observational $f(\text{aug})$ values (x_{Fe3}^{M1}) obtained using

1255   the rule of Droop (1987).

1256   Table 3: Equilibria used in calibrating the clinoamphibole model, and the results of

1257   calculations with the completed set of models (all with excess q, H_2O). Observed or

1258   other target values (see footnotes) of compositional variables are shown in roman font,

1259   calculated values in italics. Compositional variables for the clinoamphibole and augite

1260   models are defined in the Appendix. Bulk compositions used in the calculations are

1261   given in Table 1. $Phase \rightarrow 0$ indicates the zero-mode isopleth (the *phase*-out
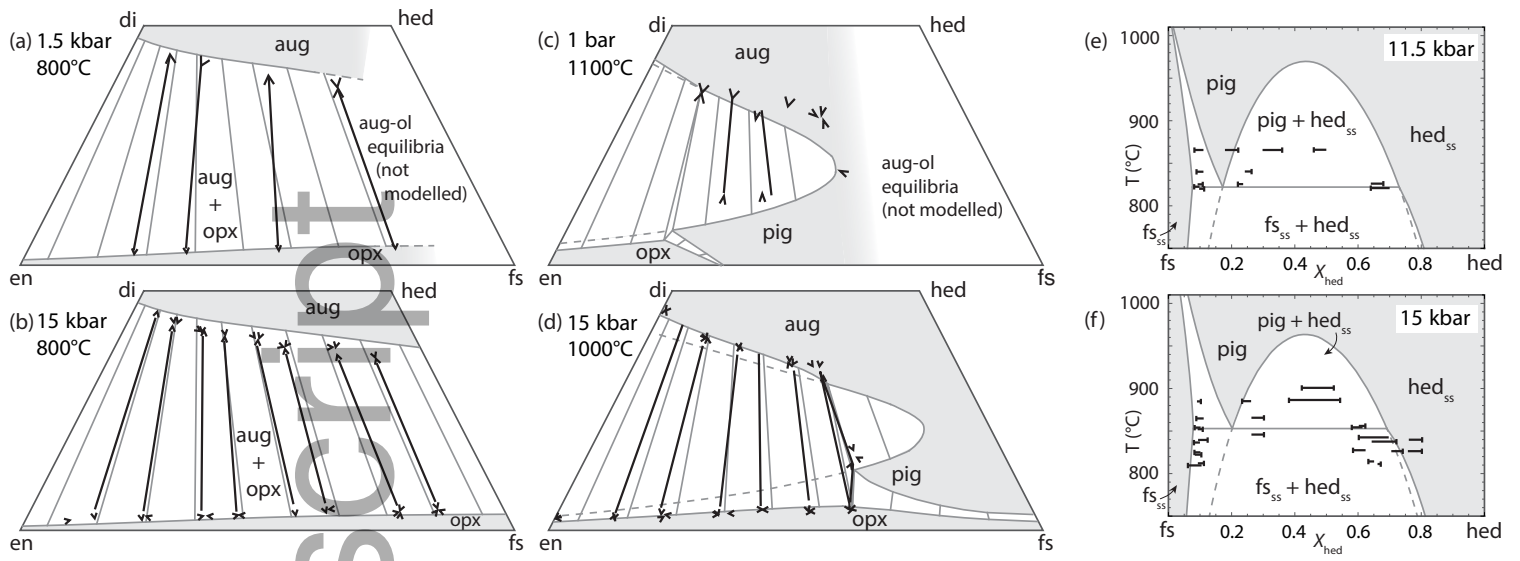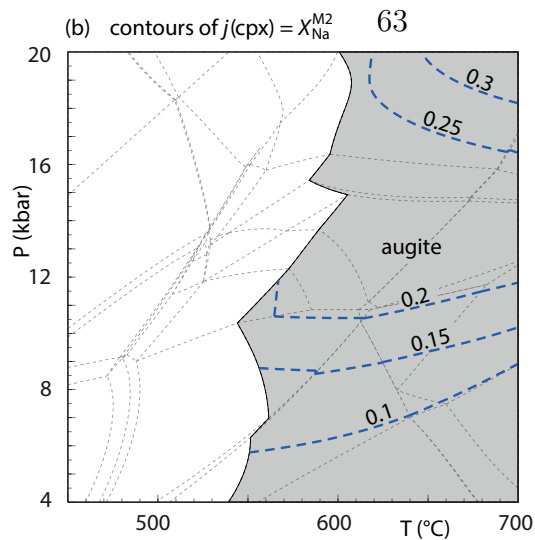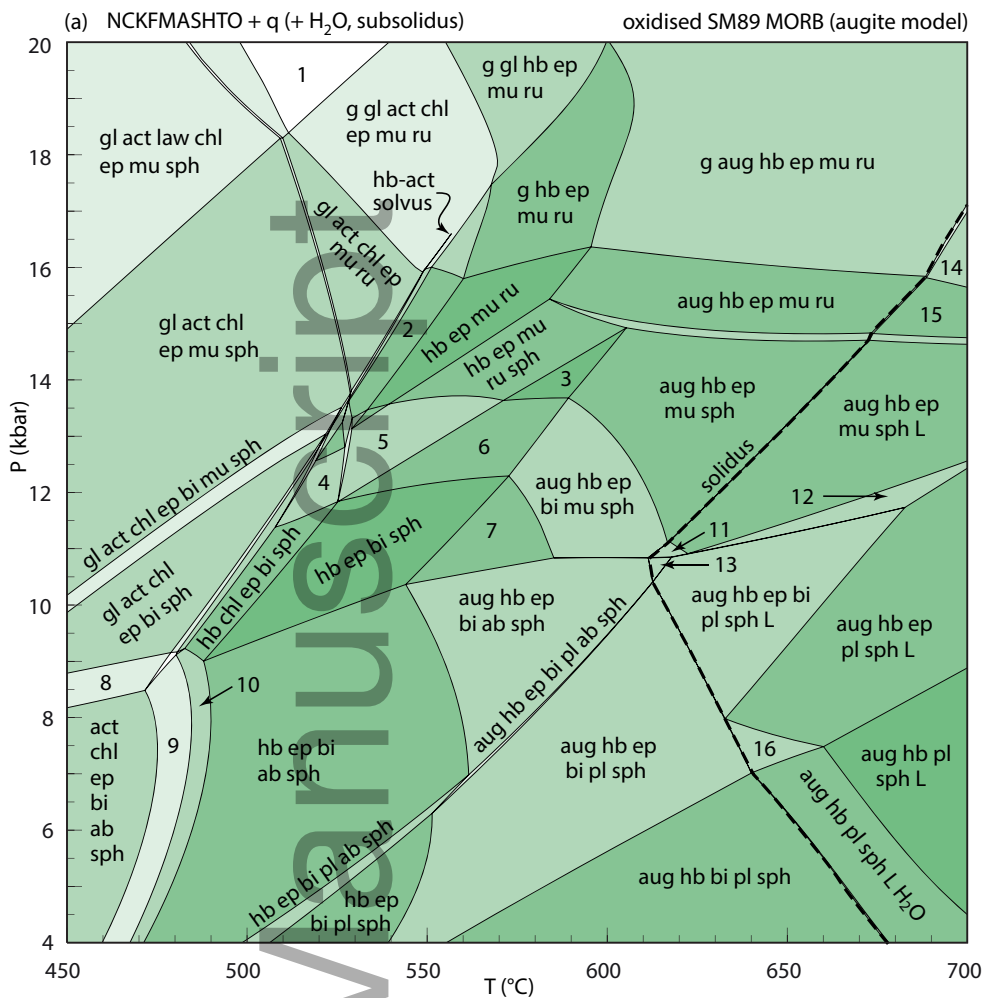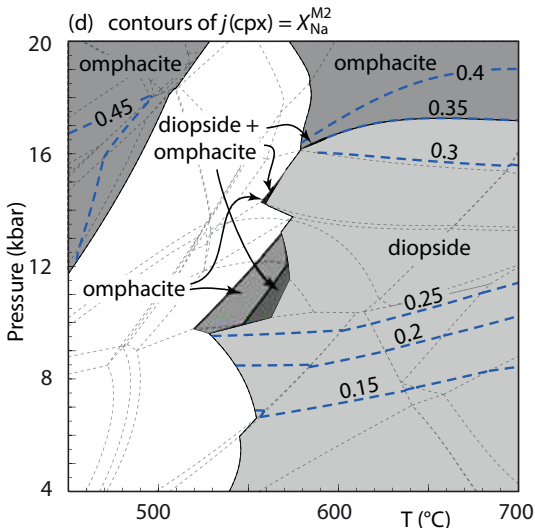
1262   boundary) for *phase*.

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Figure 1:

(a) NCKFMASHTO + q (+ H₂O, subsolidus)   oxidised SM89 MORB (augite model)

(b) contours of j(cpx) = X_{Na}^{M2}
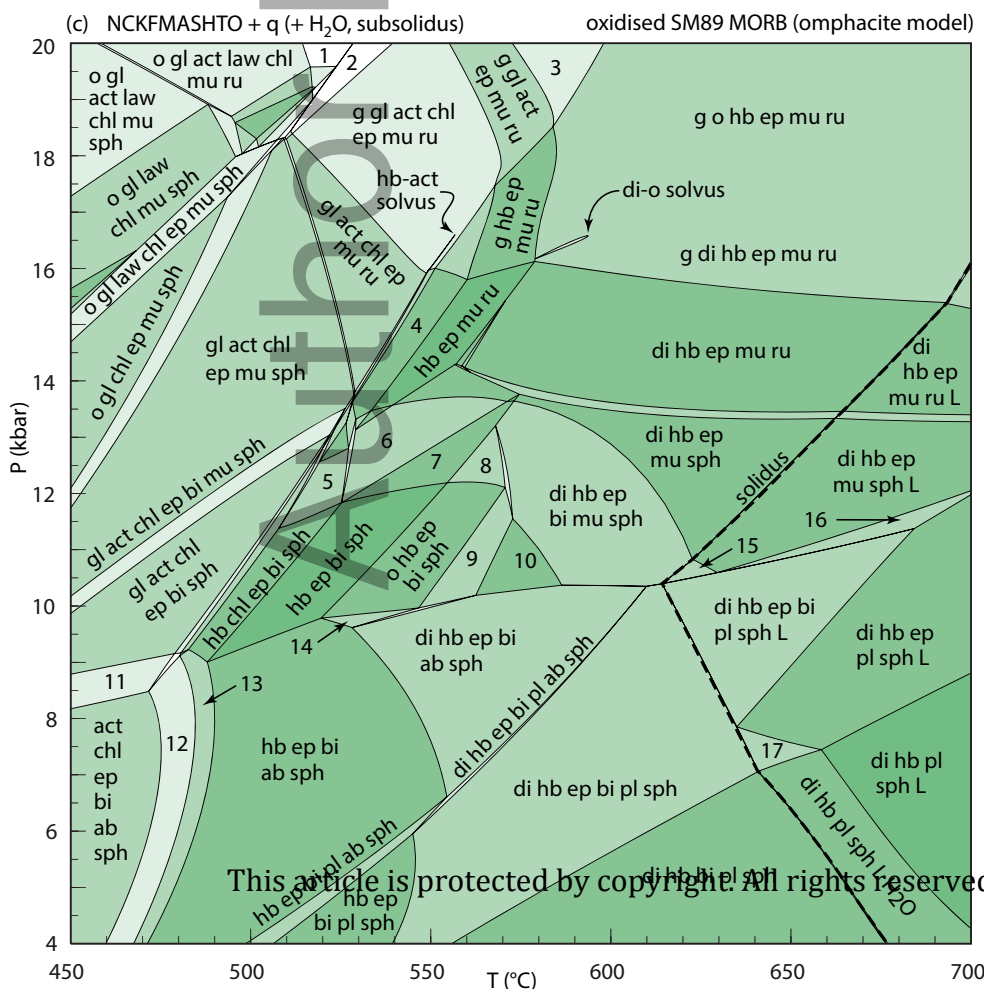
1) g gl act law chl ep mu ru
2) hb chl ep mu ru
3) hb ep mu sph
4) hb chl ep bi mu sph
5) hb ep mu bi ru sph
6) hb ep bi mu sph
7) aug hb ep bi sph
8) gl act chl ep bi ab sph
9) hb act chl ep bi ab sph
10) hb chl ep bi ab sph
11) aug hb ep bi mu sph L
12) aug hb ep mu pl sph L
13) aug hb ep bi ab sph L
14) g aug hb ep mu ru L
15) aug hb ep mu ru L
16) aug hb ep pl sph L H₂O

(c) NCKFMASHTO + q (+ H₂O, subsolidus)   oxidised SM89 MORB (omphacite model)

(d) contours of j(cpx) = X_{Na}^{M2}

1) g o gl act law chl mu ru
2) g gl act law chl ep mu ru
3) g o gl act ep mu ru
4) hb chl ep mu ru
5) hb chl ep mu bi sph
6) hb ep mu bi ru sph
7) hb ep mu bi sph
8) o hb ep mu bi sph
9) o di hb ep bi sph
10) di hb ep bi sph
11) gl act chl ep bi ab sph
12) hb act chl ep bi ab sph
13) hb chl ep bi ab sph
14) o hb ep bi ab sph
15) di hb ep bi mu sph L
16) di hb ep mu pl sph L
17) di hb ep pl sph L H₂O

(a)

1) aug hb bi pl ep q sph H2O
2) aug hb bi ep q sph H2O
3) aug hb mu bi ep q sph H2O
4) aug hb bi ep q sph L
5) aug hb mu bi q sph L

(b) garnet amphibolite, garnet granulite, amphibolite, hornblende granulite, granulite

(e) 7 kbar

(c) 7 kbar

1) opx aug hb bi pl ilm q L
2) aug hb pl ru sph q L
3) aug hb ksp pl sph q L
4) aug hb pl ilm sph q L
5) hb ksp pl ilm sph q L

(d) 7 kbar

1) opx aug bi pl q ilm L
2) opx aug pl q ilm ru L
3) opx aug hb bi pl q ilm ru L
4) opx aug pl ilm ru L
5) opx aug ru L
6) aug hb pl q ilm L

Figure 3:

Figure 4:

Figure 5:

Table 1:

	M_{SiO_2}	M_{TiO_2}	$M_{Al_2O_3}$	$M_{FeO^{tot}}$	M_{MgO}	M_{CaO}	M_{Na_2O}	M_{K_2O}	M_O	M_{H_2O}
Mcal	55.21	1.01	8.75	7.84	12.22	11.75	2.51	0.22	0.47	
SM89	52.47	1.05	9.10	8.15	12.71	12.21	2.61	0.23	1.47	
IZ100	52.05	1.29	13.24	10.18	7.70	12.14	2.89		0.51	
dP0669	58.29	0.99	11.55	6.45	7.18	8.97	4.59	1.14	0.84	
DR9734	47.05	0.18	8.77	5.43	19.02	17.52	1.39	0.04	0.60	
SKA101	58.26	1.42	9.15	11.98	8.80	8.61	0.49	0.70	0.60	
SKB116	53.72	1.75	9.10	12.40	7.43	10.85	2.95	0.42	1.38	
PM13013	52.95	1.70	8.42	11.61	9.86	11.22	2.72	0.62	0.89	
PM13083	53.24	0.83	8.62	9.71	11.32	12.48	2.41	0.19	1.19	
PM13161	53.13	1.08	8.01	9.05	11.71	12.31	3.14	0.43	1.15	
AG9	51.08	1.37	9.68	11.66	11.21	13.26	0.79	0.16	0.80	
SQA (high-P)	60.05	1.27	6.62	6.57	9.93	8.31	1.83	0.44	0.33	4.64
SQA (low-P)	59.76	1.26	6.59	6.54	9.88	8.27	1.82	0.44	0.81	4.62
BL478	53.96	1.35	9.26	10.14	8.11	10.15	2.54	0.11	0.98	3.42
WW94	50.09	0.31	8.91	7.27	16.50	15.86	1.00	0.07	0.35–0.86	3.50–5.00
AGS11.1	58.31	0.75	8.62	10.90	8.44	11.44	1.14	0.41	0.52–1.30	3.50–6.50
IAT	55.99	0.81	10.41	6.90	12.12	10.33	3.24	0.18	0.33–0.82	3.50–6.50
BL571	56.03	1.28	10.17	11.15	7.18	10.46	3.49	0.26	1.20–1.30	3.50–6.50

Mcal: MORB-like composition used in calibration. **SM89**: oxidised average MORB composition of Sun & McDonough (1989) (the analysed composition has M_O=0.5 mole %). **IZ100**: natural metabasite sample of Kunz *et al.* (2014), M_O estimate from pseudosection modelling. **dP0669**: Breaksea Orthogneiss sample 0669 (dioritic gneiss), De Paoli (2006), M_O from wet chemistry. **DR9734**: microprobe analysis of experimental glass, ground from a garnet pyroxenite xenolith, by Adam *et al.* (1992); M_O was assumed for the current study. **SKA101**, **SKB116**, **PM13013**, **PM13083**, **PM13161**, **AG9**: Natural amphibolites and low-temperature granulites (unpublished), $X_{Fe^{3+}}$ estimated at 0.10–0.25 from previous pseudosection modelling. **SQA**: Synthetic amphibolite composition of Patiño Douce & Beard (1995) (glass analysis). The compositions at high and low P are the same except for different assumed M_O values at high-P (piston cylinder apparatus) and low-P (internally heated pressure vessel); see text. M_{H_2O} from analysis of starting material. In Fig. 5, $0.33 < M_O < 0.82$, $3.50 < M_{H_2O} < 6.50$. **BL478**: Sample 478 of Beard & Lofgren (1991). See text for M_{H_2O}, M_O estimates. In Fig. 5, $0.52 < M_O < 1.30$, $3.50 < M_{H_2O} < 6.50$. **WW94**: natural amphibolite composition of Wolf & Wyllie (1994). **AGS11.1**: natural amphibolite composition of Skjerlie & Patiño Douce (1995). **IAT**: meta island arc tholeiite of Rushmer (1991). **BL571**: Sample 571 of Beard & Lofgren (1991).
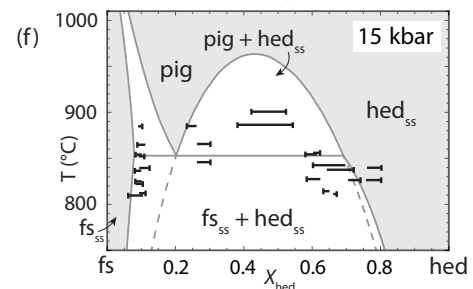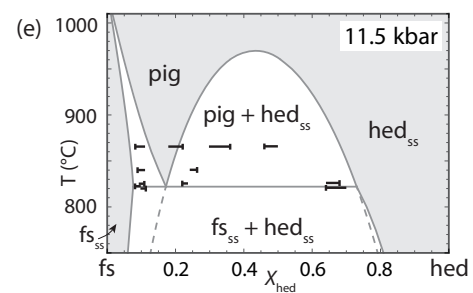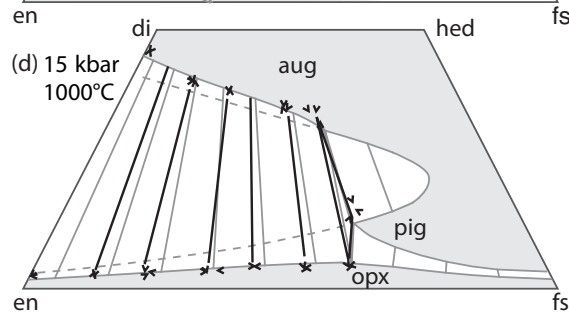
Table 2:

	Assemblage	P (kbar)	T (°C)	x(aug)	y(aug)	f(aug)	z(aug)	j(aug)	$x^{\mathrm{X}}_{\mathrm{Ca}}(g)$	$x^{\mathrm{an}}(pl)$
IZ100[1]	cpx opx g pl ilm	9	900	0.26	0.08	0.06	0.89	0.04	0.19	0.53
				0.34	*0.06*	*0.07*	*0.81*	*0.05*	*0.20*	*0.56*
dP0669[2]	cpx opx g pl bi ilm q H_2O	11	880	0.25	0.10	0.05	0.80	0.05	0.20	0.50
				0.25	*0.01*	*0.11*	*0.73*	*0.15*	*0.20*	*0.31*
1303/DR9734[3]	cpx g pl sp	10	1000	0.17	0.19	0.03	0.77	0.07	0.21	0.64
				0.14	*0.09*	*0.06*	*0.81*	*0.06*	*0.18*	*0.57*

[1]Natural sample (Kunz *et al.*, 2014). *P–T* estimate from pseudosection forward modelling of intercalated metapelitic rocks using the ds55 models. [2]Natural sample from De Paoli (2006). *P–T* estimate from the author's pseudosection forward modelling using the ds55 models. Representative values of compositional variables given to nearest 0.05. [3]Experimental run 1303 of Adam *et al.* (1992), with starting material DR9734.

Table 3:

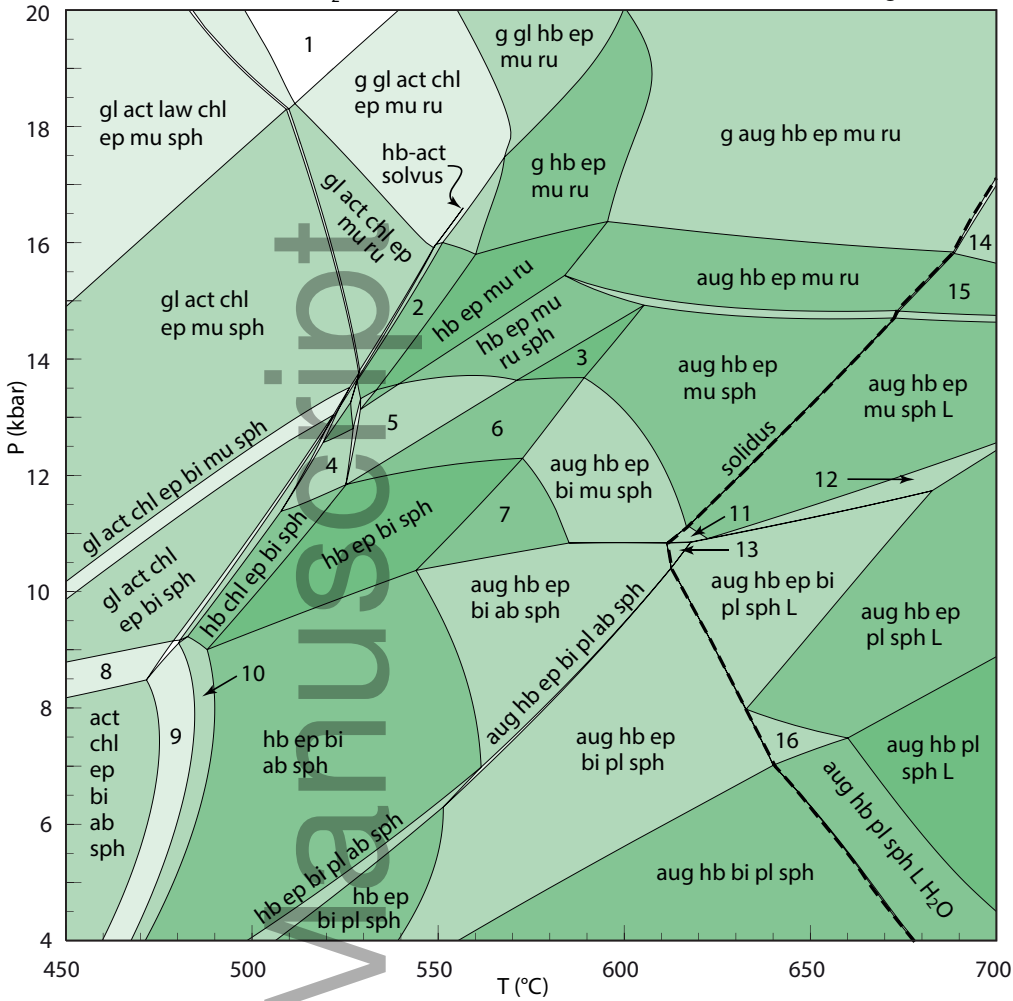|	Assemblage	P (kbar)	T (°C)	Composition variables									
				y(hb)	z(hb)	a(hb)	c(hb)	f(hb)	y(gl)	z(gl)	a(gl)	c(gl)	f(gl)
Mcal[1]	hb gl act bi ep chl	10±1	480±20	0.55–0.70	0.3–0.4	0.35–0.45	0.6–0.7	0.1	0.7–0.8	0.8–0.9	0.1	0.1	0.1
	ab sph;	9.3	474	0.63	0.38	0.37	0.61	0.08	0.78	0.89	0.07	0.11	0.09
	hb, gl→0												
				y(act)	z(act)	a(act)	c(act)	f(act)					
				0.15–0.25	0.15–0.25	0.1	0.75–0.80	0.05					
				0.17	0.22	0.07	0.78	0.03					

	Assemblage	P (kbar)	T (°C)	a(hb)	k(hb)	t(hb)	y(aug)	z(aug)	j(aug)	$x^{\mathrm{X}}_{\mathrm{Ca}}$(g)	x^{an}(pl)
SKA101[2]	hb g pl bi ilm sph	10	770	0.41	0.31	0.08	-	-	-	0.27	0.86
				0.65	0.34	0.07				0.28	0.83
SKB116[2]	hb cpx g pl bi sph	11	770	0.56	0.38	0.12	0.03	0.87	0.02	0.30	0.47
				0.72	0.16	0.07	0.09	0.86	0.11	0.43	0.26
PM13013[2]	hb pl ilm	4	700	0.71	0.31	0.11	-	-	-	-	0.36
				0.39	0.35	0.05					0.38
PM13083[2]	hb cpx pl sph	4	700	0.44	0.11	0.07	0.07	0.93	0.04	-	0.51
				0.51	0.14	0.05	0.06	0.92	0.04		0.49
PM13161[2,3]	hb cpx pl sph	4	700	0.65	0.18	0.07	0.08	0.52	0.02	-	0.26
				0.49	0.19	0.04	0.02	0.89	0.08		0.29
AG9[4]	hb g pl ilm;	6±3	650	0.29	0.17	0.04	-	-	-		0.96
	g→0	6.3		0.32	0.19	0.04				0.47	0.95

[1]Hb, gl, act were assumed to have negligible K_2O, TiO_2, with k(hb) > k(gl) ≈ k(act) and t(hb) ≈ t(gl) > t(act); calculated values are $0.02 < k < 0.04$, $t \leq 0.01$, with appropriate differences among the three phases. [2]P–T estimated from pseudosection forward modelling with ds55 models. [3]Measured j(aug) looks suspect. [4]Garnet has 20% spessartine, unmodelled.
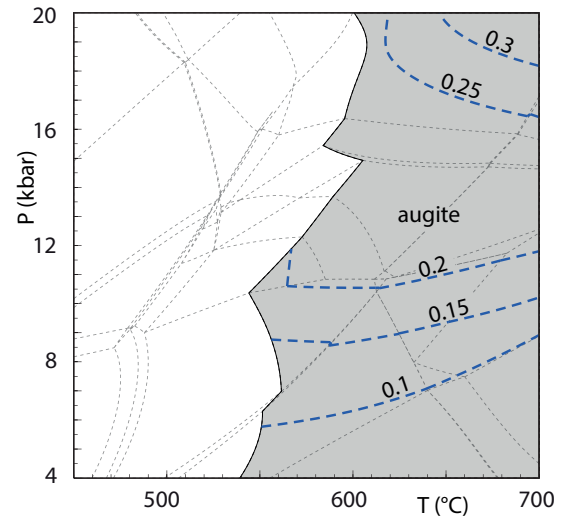
jmg_12211_f1.eps

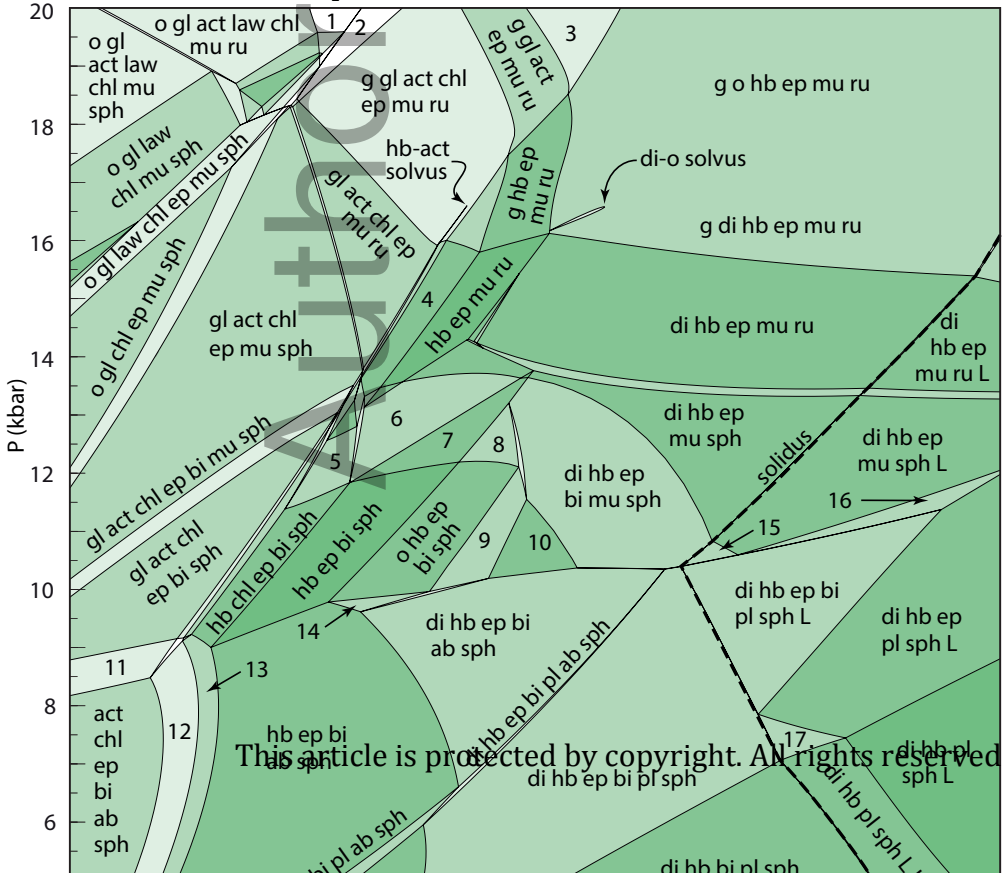**(a)** NCKFMASHTO + q (+ H$_2$O, subsolidus) oxidised SM89 MORB (augite model)

1

gl act law chl ep mu sph

g gl act chl ep mu ru

g gl hb ep mu ru

hb-act solvus

gl act chl ep mu ru

g hb ep mu ru

g aug hb ep mu ru

gl act chl ep mu sph

2

hb ep mu ru

hb ep mu ru sph

aug hb ep mu ru

14

15

3

aug hb ep mu sph

aug hb ep mu sph L

gl act chl ep bi mu sph

5

6

aug hb ep bi mu sph

solidus

12

gl act chl ep bi sph

4

hb ep bi sph

7

11

13

gl act chl ep bi sph

hb chl ep bi sph

aug hb ep bi ab sph

aug hb ep bi pl sph L

aug hb ep pl sph L

8

10

aug hb ep bi pl ab sph

9

hb ep bi ab sph

aug hb ep bi pl sph

16

aug hb pl sph L

act chl ep bi ab sph

aug hb pl sph L H$_2$O

hb ep bi pl ab sph

hb ep bi pl sph

aug hb bi pl sph

(b) contours of j(cpx) $= X_{Na}^{M2}$

0.3
0.25

augite

0.2
0.15
0.1

1) g gl act law chl ep mu ru
2) hb chl ep mu ru
3) hb ep mu sph
4) hb chl ep bi mu sph
5) hb ep mu bi ru sph
6) hb ep bi mu sph
7) aug hb ep bi sph
8) gl act chl ep bi ab sph
9) hb act chl ep bi ab sph
10) hb chl ep bi ab sph
11) aug hb ep bi mu sph L
12) aug hb ep mu pl sph L
13) aug hb ep bi ab sph L
14) g aug hb ep mu ru L
15) aug hb ep mu ru L
16) aug hb ep pl sph L H$_2$O

(c) NCKFMASHTO + q (+ H$_2$O, subsolidus) oxidised SM89 MORB (omphacite model)

o gl act law chl mu ru
1
2
g gl act ep mu ru
3

o gl act law chl mu sph

g gl act chl ep mu ru

hb-act solvus

g gl act chl ep mu ru

g o hb ep mu ru

o gl law chl mu sph

g hb ep mu ru

di-o solvus

o gl law chl ep mu sph

gl act chl ep mu ru

g di hb ep mu ru

o gl chl ep mu sph

gl act chl ep mu sph

4

hb ep mu ru

di hb ep mu ru

di hb ep mu ru L

6

7

8

di hb ep mu sph

di hb ep mu sph L

gl act chl ep bi mu sph

5

di hb ep bi mu sph

16

solidus

gl act chl ep bi sph

hb chl ep bi sph

hb ep bi sph

o hb ep bi sph

9

10

15

di hb ep bi mu sph L

11

13

14

di hb ep bi ab sph

di hb ep bi pl sph L

di hb ep pl sph L

act chl ep bi ab sph

12

hb ep bi ab sph

hb ep bi pl ab sph

17

di hb pl sph L

di hb ep bi pl sph

di hb bi pl sph

(d) contours of j(cpx) $= X_{Na}^{M2}$

omphacite

omphacite

0.45

0.4
0.35

diopside + omphacite

0.3

diopside

omphacite

0.25
0.2

0.15

1) g o gl act law chl mu ru
2) g gl act law chl ep mu ru
3) g o gl act ep mu ru
4) hb chl ep mu ru
5) hb chl ep mu bi sph
6) hb ep mu bi ru sph
7) hb ep mu bi sph
8) o hb ep mu bi sph
9) o di hb ep bi sph
10) di hb ep bi sph
11) gl act chl ep bi ab sph
12) hb act chl ep bi ab sph
13) hb chl ep bi ab sph

(a)

3

aug hb mu bi ep q sph L

5

2

4

aug hb bi pl ep q sph L

1

aug hb bi q sph L

g aug hb bi pl q sph L

g aug hb bi pl q ru L

g aug hb pl q ru L

g aug pl q ru L

g opx aug q ru L

1) aug hb bi pl ep q sph H2O
2) aug hb bi ep q sph H2O
3) aug hb mu bi ep q sph H2O
4) aug hb bi ep q sph L
5) aug hb mu bi q sph L

aug hb bi pl q ru L

g opx aug hb pl q ru L

g opx aug pl q ru L

g opx aug q ru L

L   hb
cpx ⊛ opx
g
+q pl ilm/ru

aug hb bi pl q sph H2O

aug hb bi pl q sph L

aug hb bi pl q ilm ru L

aug hb bi pl q ilm ru L

aug hb pl q ilm ru L

aug hb pl q ilm L

opx aug hb pl q ilm ru L

opx aug pl q ilm ru L

opx aug pl q ru L

opx aug pl ru L

hb bi pl q sph H2O

hb bi pl q sph L

aug hb bi pl q ilm sph L

aug hb bi pl q ilm L

opx aug hb pl q ilm L

Piston cylinder lower ƒO2

opx aug pl ru L

hb bi pl q sph H2O

hb bi pl q sph L

aug hb bi pl q ilm sph L

Internally heated pressure vessel higher ƒO2

hb bi pl q ilm sph L

aug hb bi pl q ilm L

aug hb pl q ilm L

opx aug hb pl q ilm L

opx aug pl q ilm L

opx aug pl ilm ru L

hb bi pl q ilm sph H2O

aug hb bi pl q ilm sph H2O

opx aug pl ilm L

P (kbar): 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2

T (°C): 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1050

(b)

garnet amphibolite

garnet granulite

amphibolite

hornblende granulite

granulite

P (kbar): 12, 10, 8, 6, 4, 2

T (°C): 800, 850, 900, 950, 1000, 1050

(e)

hb bi pl q sph L

aug hb bi pl q sph L

aug hb bi pl ilm q sph L

aug hb bi pl q ilm L

opx aug hb pl ilm q L

opx aug hb pl ilm ru q L

opx aug pl ilm ru q L

opx aug pl ru L

opx aug ru L

7 kbar

melt fraction: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7

T (°C): 700, 800, 900, 1000

(c)

opx aug pl ru L

opx aug ilm ru L

opx aug pl ilm ru L

opx aug pl ru q L

opx aug pl ilm ru q L

1) opx aug hb bi pl ilm q L
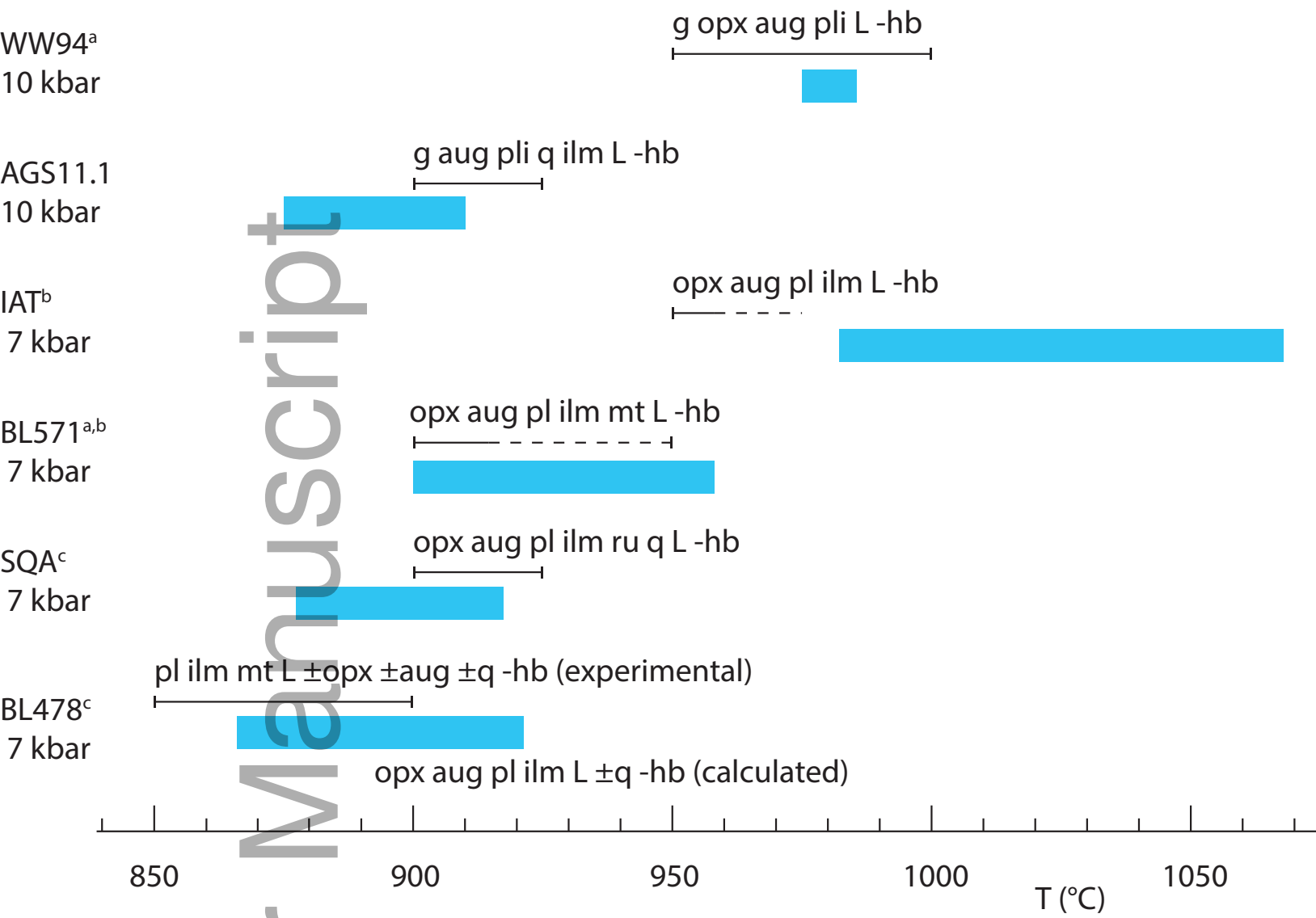2) aug hb pl ru sph q L
3) aug hb ksp pl sph q L
4) aug hb pl ilm sph q L
5) hb ksp pl ilm sph q L

opx aug hb pl ilm ru q L

opx aug hb pl ilm q L

aug hb pl ilm q L

aug hb pl ilm ru q L

1

aug hb bi pl ilm q L

aug hb bi pl ilm ru q L

aug hb pl ru q L

2

aug hb bi pl ilm sph q L

aug hb bi ksp pl sph q L

3

hb ksp pl sph

4

5

aug hb bi pl sph q L

hb bi pl sph q L

hb bi ksp pl sph q L

T (°C): 1050, 1000, 950, 900, 850, 800, 750, 700

(d)

opx aug pl q ru L

opx aug pl ru L

5

4

1) opx aug bi pl q ilm L
2) opx aug bi pl q ilm ru L
3) opx aug hb bi pl q ilm ru L
4) opx aug pl ilm ru L
5) opx aug ru L
6) aug hb pl q ilm L

opx aug pl q ilm ru L

opx aug hb pl q ilm ru L

opx aug hb bi pl q ilm L

opx aug hb pl q ilm L

1

2

3

aug hb bi pl q ilm L

6

aug hb bi pl q ilm ru L

opx aug bi pl q ilm ru L

opx aug hb bi pl q ilm

aug hb bi pl q ilm ru L

aug hb bi pl q ilm sph L

aug hb bi pl q sph L

opx aug bi pl q ilm

aug hb bi pl q ilm

hb bi pl q sph L

T (°C): 1050, 1000, 950, 900, 850, 800, 750, 700, 650

jmg_12211_f4.eps

WW94[a]
10 kbar

g opx aug pli L -hb

AGS11.1
10 kbar

g aug pli q ilm L -hb

IAT[b]
7 kbar

opx aug pl ilm L -hb

BL571[a,b]
7 kbar

opx aug pl ilm mt L -hb

SQA[c]
7 kbar

opx aug pl ilm ru q L -hb

BL478[c]
7 kbar

pl ilm mt L ±opx ±aug ±q -hb (experimental)

opx aug pl ilm L ±q -hb (calculated)

850   900   950   1000   1050

T (°C)

jmg_12211_f5.eps

Author/s:
Green, ECR; White, RW; Diener, JFA; Powell, R; Holland, TJB; Palin, RM

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