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

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Short title: $A-x$ relations for metabasic rocks

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 $\text{Na}_2\text{O}–\text{CaO}–\text{K}_2\text{O}–\text{FeO}–\text{MgO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{H}_2\text{O}–\text{TiO}_2–\text{Fe}_2\text{O}_3$. 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.

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

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, K₂O-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 K₂O and TiO₂, while the clinopyroxene model of Green *et al.* (2007) does not allow for Al on the tetrahedral site, or for Mg or Fe²⁺ 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).

This paper presents the development and calibration of the new a - x relations, while in a companion paper (Palin *et al.*, 2016b, this issue), we examine their application to forward modelling in a range of basic to intermediate bulk compositions. Calibration of the a - x relations ultimately made use of experiments in natural systems, modelled in the system Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O–TiO₂–Fe₂O₃ (NCKFMASHTO). A large body of experimental work has explored phase relations in partially molten metabasic rocks, frequently seeking to determine the origins of tonalite–trondhjemite–granodiorite (TTG) magmas (e.g. Beard & Lofgren, 1991; Rapp *et al.*, 1991; Rushmer, 1991; Sen & Dunn, 1994; Wolf & Wyllie, 1994; Patiño Douce & Beard, 1995; Rapp & Watson, 1995; Skjerlie & Patiño Douce, 1995; Springer & Seck, 1997; López & Castro, 2001; Skjerlie & Patiño Douce, 2002; Foley *et al.*, 2003; Auzanneau *et al.*, 2006; Qian & Hermann, 2013; Zhang *et al.*, 2013; Ziaja *et al.*, 2014). During the calibration process, for a subset of the experimental studies, forward calculations of phase relations at the experimental bulk compositions were compared with the observations. The primary goal was to reproduce major phase-in/phase-out boundaries, which, it is hoped, ensures that the behaviour of the models will be broadly realistic in the forward-modelling context for which they are intended.

GENERAL NOTES ON THE THERMODYNAMIC MODELS

The set of a - x relations presented here will be referred to as the ‘metabasite set’. It is suitable for use with versions 6.2 or 6.3 of the Holland & Powell (2011) dataset (ds62, ds63), created 6 February 2012 and 15 January 2015 respectively. The figures in this paper were calculated with version 6.2. The update to version 6.3 includes a key refinement to the thermodynamics of the H₂O end-member in the melt, and is expected to give slightly more realistic results at the wet solidus. In other respects, differences between calculations with ds62 and ds63 are believed to be insignificant. The a - x relations should not however be

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 $x^{\text{an}} > 0.8$),
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 $[\text{Ca}, \text{Na}, \text{Mg}, \text{Fe}^{2+}]^{\text{M2}} [\text{Mg}, \text{Fe}^{2+}, \text{Al}, \text{Fe}^{3+}]^{\text{M1}} [\text{Si}, \text{Al}]_2^{\text{tet}}$, while diopside (di),
127 jadeite (jd) and omphacite (o) have the general formula $[\text{Ca}, \text{Na}]^{\text{M2}} [\text{Mg}, \text{Fe}^{2+}, \text{Al}, \text{Fe}^{3+}]^{\text{M1}}$
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

(aug and pig) and clinoamphibole (hb, gl and act) are newly calibrated to address partial melting of metabasitic rocks. Of the clinoamphiboles, only hornblende is normally relevant to supersolidus amphibolite–granulite facies conditions, but the new amphibole a – x model is also appropriate for actinolite and glaucophane at lower temperatures. The remaining a – x models in the metabasite set, for the phases garnet, orthopyroxene, feldspar, spinel–magnetite and ilmenite, were taken from the metapelite ds6-set.

Additionally, the existing a – x model for the potentially ordered sodic–calcic pyroxenes jd, di and o (from Green *et al.*, 2007, for use with ds55), has been updated for use with ds6 of the Holland & Powell dataset (Holland & Powell, 2011). This model, the ‘omphacite’ model, remains the appropriate clinopyroxene model to use under subsolidus conditions where co-existing clinopyroxenes might occur. It should not be used in calculations that also involve the augitic clinopyroxene model.

Form of the a – x relations

Like the metapelite ds55- and ds6-sets, the a – x relations developed in this paper are macroscopic regular solution models, in which non-ideal enthalpic interactions are present between pairs of end-members, expressed as interaction energies $W_{i,j}$. The mixing-on-sites approach is adopted, in order to give an approximately correct form for the ideal entropy of mixing. The regular solution paradigm is modified by allowing the $W_{i,j}$ in principle to be linear functions of P and T , though in practice it is almost never possible to resolve these two dependencies, and the $W_{i,j}$ are usually treated as constant or functions of P only. The formulation is discussed extensively by Powell & Holland (1993) and Holland & Powell (1996a,b), under the name ‘symmetric formalism’. A further modification, the asymmetric formalism (Holland & Powell, 2003), introduced asymmetry in the manner of van Laar (1906) via ‘volume’ parameters, α_i , associated with each end-member i .

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

introduced via activity coefficients written as

$$RT \ln \gamma_l = - \sum_i^{n-1} \sum_{j>i}^n (p'_i - p_i)(p'_j - p_j) W_{i,j}, \quad (1)$$

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 $p'_k = 1$ where $k = \ell$ and $p'_k = 0$ 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

$$RT \ln \gamma_l = - \sum_i^{n-1} \sum_{j>i}^n (\phi'_i - \phi_i)(\phi'_j - \phi_j) W_{i,j} \left(\frac{2\alpha_i}{\alpha_i + \alpha_j} \right), \quad (2)$$

where ϕ_i is the proportion of end-member i weighted by the van Laar parameters, $\phi_i = (p_i \alpha_i) / (\sum_k^n p_k \alpha_k)$, and ϕ'_i is likewise the van Laar-weighted equivalent of p'_i .

The free parameters available for fitting are therefore the $W_{i,j}$ 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 $G_i(P, T)$ 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:

- ΔG_i^{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.
- ΔG_i^{mod} . This is a modification made to the thermodynamics 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.

- ΔG_i^{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 ΔG_i^{make} expression is added that can be calibrated to represent the ΔG between the combination of dataset end-members and the fictive end-member.
- ΔG_i^{tran} . This is a special case of ΔG_i^{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 ΔG_i^{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 $j, k, \dots$ in the same phase are represented as $W_{i,[j,k,\dots]}$; (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

TTG-generation. The choice of TTG-generation studies was limited to those with multiple hydrate-breakdown melting runs at ≤ 13 kbar, placing constraints on significant phase-in/phase-out boundaries, with bulk compositions that could reasonably be modelled in NCKFMASHTO (for example, they should be nominally carbon-free).

In general (for variance > 2), the calculations performed during the calibration process mimicked those performed when the finished models are used; they were forward calculations that gave the compositions and modal proportions of phases at equilibrium, subject to the constraint of the experimental bulk composition. In some cases the calculations took place at the P – T conditions of an experiment, for direct comparison with the experimental run products. However, the highest priority for the calibration was to make good predictions of the major features of phase relations across P – T space, rather than to make accurate predictions of phase compositions. Consequently, the interpolated positions of key phase field boundaries (e.g. orthopyroxene-in, hornblende-out) were used directly in calibration. The final step in calibration was to calculate full P – T pseudosections for key experimental bulk compositions, ensuring that the assemblages specified during the calibration were the most stable that could be modelled.

Calibrations that are new in this work were carried out either by manual trial and error or by using a Monte Carlo method, MCTC, within the THERMOCALC software. When MCTC is invoked, THERMOCALC calculates a set of phase equilibria repeatedly, using a – x models with parameters drawn randomly from within specified distributions. ‘Successful’ sets of model parameters are identified by comparing the resulting calculated phase equilibria with the observations, and the distribution of successful model parameters is reviewed, leading to refinement of the initial distribution. Over the course of many MCTC runs, the user will first widen the initial distributions of model parameters until, for each parameter, a peak is visible in the distribution of successful values. Then, certain model parameters may be given fixed values, especially those that are weakly constrained (their ‘successful’ distributions are wide), or strongly correlated with other parameters. The distributions of

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

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

In order to use phase equilibrium experiments as constraints, it is necessary to infer bulk compositions that represent the experimental run products at equilibrium. Two components of bulk composition in particular are hard to estimate: those of fluid content, assumed to be all water ('molar bulk H_2O ', $M_{\text{H}_2\text{O}}$), and of oxygen ('molar bulk O', M_{O}). Experimental studies routinely provide estimates of H_2O content in the starting material, though these are uncertain, and unlikely to include H_2O gained by adsorption during the pulverisation of the sample, which may be retained even during storage under desiccation (London *et al.*, 2012). M_{O} may be equated directly to molar bulk Fe_2O_3 , via the reaction $\text{Fe}_2\text{O}_3 = 2 \text{FeO} + \text{O}$, if iron is the only element considered to have variable oxidation state. The fraction of iron present as Fe_2O_3 in the starting material is rarely estimated. During experimental runs, values of $M_{\text{H}_2\text{O}}$ and M_{O} in the capsule are subject to interdependent changes. The experiments considered in this work were not formally buffered to specified $f\text{O}_2$, but even in such cases, the experimental apparatus has an 'intrinsic $f\text{O}_2$ ' that influences the oxidation state of the starting material during the run; hence M_{O} is not conserved. The process of oxidation or reduction of starting materials primarily involves diffusion of H_2 , to which experimental capsules are effectively open. If the apparatus provides an environment that is reducing with respect to the oxidation state of the starting materials, H_2 will enter the capsule and may form H_2O by reduction of iron oxides, constituting an increase in $M_{\text{H}_2\text{O}}$ and decrease in M_{O} (carbon, derived from graphite furnaces, may play a under-acknowledged role in this process; see Brooker *et al.*, 1998;

258 Jakobsson, 2012; Matjuschkin *et al.*, 2015). Finally, apparent loss or gain of both H₂ and
 259 O₂, or possibly molecular H₂O, 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 $(Ca_{\frac{1}{2}}^{M2}Na_{\frac{1}{2}}^{M2}Mg_{\frac{1}{2}}^{M1}Al_{\frac{1}{2}}^{M1}Si_2^{tet}O_6)$, it treats the M1 and M2 sites as ‘split’. That is, Mg, Fe²⁺,
 280 Al and Fe³⁺ mix on a M1m and a M1a site, with cations preferentially partitioned onto the

281 M1m site in the order $\text{Fe}^{2+} > \text{Mg} > \text{Al} > \text{Fe}^{3+}$, 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 $\Delta G_{\text{acm}}^{\text{mod}}$ 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.

298 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 $[\text{Mg}, \text{Fe}^{2+}, \text{Al}, \text{Fe}^{3+}]^{\text{M1}} [\text{Ca}, \text{Na}, \text{Mg}, \text{Fe}^{2+}]^{\text{M2}} [\text{Si}, \text{Al}]_2^{\text{tet}}$. 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 allow order-disorder to take place on either of these sites

individually, unlike the split M1 and M2 sites of the omphacite model. In partial compensation for this, different values of ΔG^{mod} are used for some end-members that are common to both models.

The heart of the augite model is the pyroxene quadrilateral $\text{CaMgSi}_2\text{O}_6$ – $\text{Mg}_2\text{Si}_2\text{O}_6$ – $\text{Fe}_2\text{Si}_2\text{O}_6$ – $\text{CaFeSi}_2\text{O}_6$. Figure 1 shows the modelled fit to the experimental work of Lindsley (1981, 1983) and Turnock & Lindsley (1981) on clinopyroxene–orthopyroxene equilibria in this system, including the binary subsystem $\text{CaFeSi}_2\text{O}_6$ – $\text{Fe}_2\text{Si}_2\text{O}_6$. The clinopyroxene a – x relations cover the whole of the quadrilateral composition space, with the compositional end-members in appropriate $C2/c$ symmetry being diopside (di), clinoenstatite (cenh), clinoferrosilite (cfs) and hedenbergite (hed). The clinoenstatite and clinoferrosilite end-members are polymorphs that exist at low-pressure, high-temperature in the unary systems, and their stability fields and properties are little known. They are generated via ΔG^{tran} expressions from the $Pbca$ end-members en (enstatite) and fs (ferrosilite) in the Holland & Powell dataset. An ordered intermediate end-member, fmc ($\text{Mg}^{\text{M1}}\text{Fe}^{\text{M2}}\text{Si}_2\text{O}_6$), allows non-equal partitioning of $[\text{Mg}, \text{Fe}^{2+}]$ over the M1 and M2 sites (Holland & Powell, 2006). Since a reaction $\text{di} + \frac{1}{2} \text{cfs} = \text{hed} + \frac{1}{2} \text{cenh}$ can be written among the compositional end-members, the thermodynamic properties of one must be treated as dependent, and hedenbergite was chosen for this purpose. Values for model parameters on the $\text{CaMgSi}_2\text{O}_6$ – $\text{Mg}_2\text{Si}_2\text{O}_6$ join, including $\Delta G_{\text{cenh}}^{\text{tran}}$, were taken from the CMAS clinopyroxene model of Green *et al.* (2012a), where they were calibrated against the experimental work of Brey & Huth (1984); Carlson & Lindsley (1988); Lindsley & Dixon (1976); Mori & Green (1975); Nickel & Brey (1984); Perkins & Newton (1980) and Schweitzer (1982).

The MCTC function in THERMOCALC was used to fit the additional CFMS parameters $W_{\text{di},[\text{cfs},\text{fmc}]}$, $W_{\text{cenh},[\text{cfs},\text{fmc}]}$, $W_{\text{cfs},\text{fmc}}$, $\Delta G_{\text{cfs}}^{\text{tran}}$ and $\Delta G_{\text{fmc}}^{\text{od}}$. The pressure dependence of the inherited CMAS parameter $W_{\text{di},\text{cenh}}$ was applied to $W_{\text{di},[\text{cfs},\text{fmc}]}$. $\Delta G_{\text{cfs}}^{\text{tran}}$ was assumed to have the same temperature dependence as $\Delta G_{\text{cenh}}^{\text{tran}}$, and was required to give a $\text{fs} = \text{cfs}$ transition

333 curve consistent with the estimation of Lindsley (1981). $\Delta G_{\text{fmc}}^{\text{od}}$ took the mean pressure and
 334 temperature dependencies of $\Delta G_{\text{cenh}}^{\text{tran}}$ and $\Delta G_{\text{cfs}}^{\text{tran}}$, with the constant term fitted such that
 335 the ordered end-member fmc was more stable than its fully disordered equivalent,
 336 $\text{Mg}_{\frac{1}{2}}^{\text{M1}}\text{Fe}_{\frac{1}{2}}^{\text{M1}}\text{Mg}_{\frac{1}{2}}^{\text{M2}}\text{Fe}_{\frac{1}{2}}^{\text{M2}}\text{Si}_2\text{O}_6$, for which G is given by $\frac{1}{2} (G_{\text{cenh}} + G_{\text{cfs}})$. At 900°C and 8 kbar,
 337 the dependent value of G_{hed} was constrained to be within 2 kJ/mol of the ds62 dataset
 338 value, with a further constraint of $G_{\text{hed}} < G_{\text{ohed}}$. G_{ohed} is the G function for the
 339 *Pbca*-symmetry orthohedenbergite end-member, derived from the quadrilateral a - x
 340 relations for orthopyroxene in the same way as G_{hed} is derived for the hedenbergite
 341 end-member in clinopyroxene; thus the latter condition specified that the monoclinic
 342 polymorph was the more stable of the two.

343 The resulting fit successfully reproduces augite–orthopyroxene tielines in the
 344 quadrilateral, and is notably successful at matching the very sensitive divariant
 345 augite–pigeonite–orthopyroxene equilibrium at 15 kbar, 1000°C (Fig. 1). It somewhat
 346 overestimates the width of the augite–pigeonite solvus towards higher FeO/(FeO+MgO)
 347 values.

348 The quadrilateral model was then combined with the CMAS clinopyroxene model of
 349 Green *et al.* (2012a), introducing the end-member Ca-tschermak’s pyroxene (cats;
 350 $\text{CaAl}_2\text{SiO}_6$) and associated parameters, which allowed for the substitution of Al onto the
 351 M1 and tetrahedral sites simultaneously. The cats end-member exhibits internal
 352 order-disorder of Si-Al on the tetrahedral site, with the energy and entropy of disordering
 353 reduced by a factor of 4 (Holland & Powell, 2011). Finally, the end-members jadeite (jd)
 354 and acmite (acm) were added to the model to accommodate Na, Fe^{3+} , and an excess of Al
 355 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
 356 adopted from the omphacite model. However, the jd and acm end-members serve a different
 357 role in the augite model from in the omphacite model. In the augite model, they are simply
 358 required to admit minor components, whereas in the omphacite model, they may be present
 359 in substantial proportions, with order–disorder between sodic and calcic end-members

contributing heavily to the thermodynamics of mixing. Consequently it is not very significant that the values of the dependent $W_{\text{hed},n}$ parameters in the augite model differ from their independently-calibrated equivalents in the omphacite model (values are compared in the Appendix). With the same justification a $\Delta G_{\text{jd}}^{\text{mod}}$ term was added to the augite jd end-member, and different $\Delta G_{\text{acm}}^{\text{mod}}$ terms were used in the augite and omphacite models.

In addition to $\Delta G_{\text{jd}}^{\text{mod}}$ and $\Delta G_{\text{acm}}^{\text{mod}}$, the free parameters in this second stage of augite model calibration were $W_{\text{cats},[\text{cfs},\text{fmc}]}$, $W_{\text{jd},[\text{cenh},\text{cfs},\text{fmc},\text{cats}]}$ and $W_{\text{acm},[\text{cenh},\text{cfs},\text{fmc},\text{cats}]}$. These interaction energies were not expected to be influential compared with the $\Delta G_{\text{i}}^{\text{mod}}$ terms, so a small number of observed equilibria were carefully chosen to be fitted, primarily with the purpose of finding values for $\Delta G_{\text{jd}}^{\text{mod}}$ and $\Delta G_{\text{acm}}^{\text{mod}}$. The chosen equilibria comprised two natural rock samples, with estimated P and T values, and one experiment; Table 2 shows the equilibria and results. The process of fitting with MCTC revealed very strong multicomponent correlations among the interaction energies. It was not clear *a priori* that these correlations would be relevant for model calculations in general, but in fact, in later calculations on melting equilibria, it was found that violating the correlations for apparently trivial parameters such as $W_{\text{cats},\text{fmc}}$ did indeed have a large and detrimental effect on the calculated compositions of all phases, particularly the anorthite content x^{an} in plagioclase.

Calculations with the augite versus omphacite models

Figure 2 shows pseudosections calculated for an oxidised MORB composition, based on that of Sun & McDonough (1989; SM89, Table 1), in the range 450–700°C and 4–20 kbar. The figure is contoured for $x_{\text{Na}}^{\text{M2}}$ in clinopyroxene. Calculations were carried out with first the augite model (Fig. 2a,b) and then the omphacite model (Fig. 2c,d), in order to compare the two. The comparison demonstrates, firstly, that the omphacite model is the appropriate choice for the relatively low temperatures shown. When modelling is done correctly using

the omphacite model (Fig. 2c,d), $x_{\text{Na}}^{\text{M2}}$ in clinopyroxene rises to > 0.4 towards higher pressures, and the diopside–omphacite solvus is visible at several pressures with closure at $\sim 600^\circ\text{C}$. Meanwhile the augite model has no capacity to model omphacite-like Na contents or coexistence between omphacitic and diopsidic compositions, so no solvus appears in Figs 2a and b. Secondly, it can be seen that the two models give substantially consistent results for $P < 13$ kbar and $T > 600^\circ\text{C}$, where the omphacite model takes on an augitic composition. Phase field boundaries in this region in Figs 2a and c show agreement within 20°C , while the augite model gives values of $x_{\text{Na}}^{\text{M2}}$ that are consistently lower than the omphacite model by ~ 0.05 , within the likely uncertainty in the modelling.

The nature of phase relations in Fig. 2c are discussed in a later section. Subsequent figures will demonstrate the behaviour of the augite model in the $P < 13$ kbar, $T > 600^\circ\text{C}$ regime for which it was calibrated.

CLINOAMPHIBOLE A – X RELATIONS

The clinoamphibole model of Diener *et al.* (2007) and Diener & Powell (2012), in NCFMASHO, is suitable for calculations on metabasic rocks under subsolidus conditions, using version 5.5 of the dataset (Holland & Powell, 1998). As described above, it was updated for use with version 6.2 in conjunction with the omphacite model, by adjustments to the end-member thermodynamics. The resulting modifications affected the following end-members: pargasite ($\Delta G_{\text{parg}}^{\text{mod}}$ changed from 15 kJ to -10 kJ), glaucophane ($\Delta G_{\text{gl}}^{\text{mod}}$ changed from 3 kJ to -3 kJ), cummingtonite ($\Delta G_{\text{cumm}}^{\text{mod}}$ changed from -6.4 kJ to 0 kJ), grunerite ($\Delta G_{\text{grun}}^{\text{mod}}$ changed from -5 kJ to -3 kJ) and magnesioriebeckite ($\Delta G_{\text{mrb}}^{\text{make}}$ changed from 8 kJ to 0 kJ). These were pleasing in that generally the absolute values of the ΔG_i^{mod} terms decreased, making the end-member G curves more similar to the dataset functions.

By granulite facies temperatures, the components K_2O and TiO_2 are significant in hornblende (e.g. Robinson *et al.*, 1982). The core model was therefore expanded to include the components K_2O and TiO_2 , with the intention that the full model in NCKFMASHTO would be applicable both above and below the solidus. K_2O was introduced via a potassium-pargasite end-member (kprg, $KCa_2Mg_4Al_3Si_6O_{22}(OH)_2$), such that K^+ mixes with Na^+ on the partially filled model A site. A deprotonation-style substitution was adopted to introduce TiO_2 via an end-member Ti-tschermakite (tts, $Ca_2Mg_3Ti_2Al_2Si_6O_{22}$), allowing hornblende to persist to higher temperatures in equilibrium with melt by lowering its water activity $a(H_2O)$, although in reality the substitution whereby TiO_2 enters metamorphic hornblende is more likely to be a tschermakite-like and/or glaucophane-like substitution (Schumacher, 2007). The new end-members tts and kprg are not present in the Holland & Powell dataset, but are made via the reactions $kprg = mu - pa + parg + \Delta G_{kprg}^{make}$ and $tts = dsp - 2 ru + ts + \Delta G_{tts}^{make}$ (mu: muscovite; pa: paragonite; ru: rutile; dsp: diaspore).

A key equilibrium is the first introduction of hornblende and glaucophane to the assemblage $act + chl + ep + ab + sph + q + H_2O \pm bi$, i.e. the junction of the greenschist, blueschist and amphibolite facies. This occurs at around 8–10 kbar and 450–500°C on most metamorphic facies diagrams. The presence of three coexisting amphiboles in this equilibrium make the calculated values of P , T and compositional variables extremely sensitive to the parameterisation of the amphibole $a-x$ relations. It was required that minimal amounts of K_2O and TiO_2 should be taken into the amphiboles at this temperature, but the prejudice was nevertheless imposed that the amphibole phases would incorporate K_2O in the order $hb > gl \approx act$, and TiO_2 in the order $hb \approx gl > act$. The full list of P – T and compositional constraints placed on this equilibrium during fitting, and the results obtained, are given in Table 3. The table also compares calculations and observations for several upper-amphibolite facies rocks, for which likely values of P , T and M_O have been established by previous calculations with older versions of the models. Since

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 $\Delta G_{\text{kprg}}^{\text{make}}$, $\Delta G_{\text{tts}}^{\text{make}}$, and the new interaction energies $W_{\text{kprg},n}$ and $W_{\text{tts},n}$. 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 $W_{\text{parg,kprg}} = 0$ and $W_{\text{kprg},n} = W_{\text{parg},n}$. 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 $W_{\text{kprg},n}$ parameters to diverge from the equivalent $W_{\text{parg},n}$ 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 $\alpha_{\text{kprg}} = \alpha_{\text{parg}}$ and $\alpha_{\text{tts}} = \alpha_{\text{ts}}$. 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 $X_{\text{Fe}^{3+}} = \text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+}) = 0.36$. 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

458 compared.

459 Subsolidus phase relations in the greenschist and amphibolite facies remain similar, with
460 hornblende replacing actinolite and chlorite at $\sim 480^\circ\text{C}$ as in the older calculations, and
461 diopside now joining the assemblage at $\sim 550^\circ\text{C}$ rather than 600°C . Calculations at 12–20
462 kbar and $< 550^\circ\text{C}$ now generate $\text{gl} + \text{act} + \text{chl} + \text{ep} \pm \text{law} \pm \text{o}$ 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

treated as a regular solution with the non-ideal enthalpy of mixing expressed using the symmetric formalism. The end-members are mineral-like compounds that mix as molecules.

The metapelite melt model has proved very successful in calculations (e.g. White *et al.*, 2001, 2007; Grant, 2009; Johnson *et al.*, 2008; White *et al.*, 2011). It is desirable that the new metabasite melt model and the metapelite melt model should share a core in NKASH, defined by the end-members qL-abL-kspL-h2oL (see Appendix for end-member definitions). However, with respect to the CaO, FeO and MgO components, the metabasite melt model requires a different parameterisation and structure from the metapelite model, in order to allow the melt composition to become sufficiently calcic, and to become metaluminous if required.

The qL-abL-kspL subsystem of the White *et al.* (2014) metapelite melt model was strongly constrained by the experiments of Boyd & England (1963); Lindsley (1966); Ostrovsky (1966) and Jackson (1976), and could be retained without change to form the core of the metabasite melt model. In the qL-abL-kspL-h2oL subsystem, a number of changes are planned for a forthcoming revision of the White *et al.* (2014) metapelite melt model, and these have been incorporated directly into the metabasite melt model as presented in this study. The changes to the qL-abL-kspL-h2oL core, relative to the White *et al.* (2014) version of the metapelite melt model, are as follows. (1) The interaction energies $W_{h2oL,[qL,abL,kspL]}$ have been refined by comparison with the subsystem experiments of Behrens (1995); Kennedy *et al.* (1962); Stewart (1967); Goldsmith & Peterson (1990) and Goldsmith & Jenkins (1985). (2) In ds63, the constant-pressure heat capacity of the h2oL end-member has been lowered to improve the calculated H₂O isopleths for melts. In fig. 9 of Holland & Powell (2001) the H₂O isopleths in granitic liquid are spuriously concave downwards in pressure, as a result of too high a heat capacity for h2oL; this heat capacity has now been optimised such that the isopleths become approximately straight lines, as required by the experimental data of Holtz *et al.* (1995). (3) The formula of the end-member silL has been changed from $\frac{8}{5}Al_2SiO_5$ to Al_2SiO_5 .

In the metapelite model, the Ca-rich vertex of composition space is represented by the anorthite-liquid end-member, anL, but the metabasite model has been extended as far as a wollastonite-liquid end-member, woL, in order to encompass metaluminous compositions. However, the woL end-member is compositionally distant from the melts of metabasic rocks, and its thermodynamics are poorly constrained. To compensate for this, an anL-composition end-member was restored to the metabasite melt model in the form of an ordered intermediate, made via the reaction $\text{anL} = \text{woL} + \text{sillL}$ with a $\Delta G_{\text{anL}}^{\text{od}}$ term applied. The thermodynamic properties of $\text{CaAl}_2\text{Si}_2\text{O}_8$ -composition liquid were approximated by fitting to the anorthite melting curve. This aspect of the model structure follows e.g. Hastie (1983); Hastie & Bonnell (1985); Bonnell & Hastie (1985); Besmann & Spear (2002) and Green *et al.* (2012b), in which the ordered intermediate end-members are termed ‘associate species’. The inclusion of an ordered intermediate end-member, intL, in the melt $a-x$ relations adds flexibility in fitting the available constraints, since the $\Delta G_{\text{intL}}^{\text{od}}$ term provides a free parameter and the presence of the intL compound contributes to model entropy. However it should be stressed that speciation is not represented in any meaningful way in the metabasite melt model, either by the choice of end-member mixing units or by the ordering taking place among them.

To complete the calibration of the metabasite melt model, values had to be found for $\Delta G_{\text{anL}}^{\text{od}}$ and the new interaction energies $W_{\text{woL},n\text{L}}$ and $W_{\text{anL},n\text{L}}$. Parameters such as $W_{\text{anL},q\text{L}}$ are not strictly the same as the equivalently-named parameter in the metapelite melt model, because the anL end-member in the metabasite melt model is not the dataset end-member but an ‘ordered’ end-member that coexists with a 1:1 mixture of woL + sillL ‘molecules’, even at the anorthite composition. Due to the significant difference in composition range between the metapelite and metabasite melt models, the non-core parameters from the metapelite melt model were considered to be potentially subject to variation in MCTC, namely the interaction energies $W_{[\text{sillL},\text{foL},\text{faL}],n\text{L}}$ and the $\Delta G_{[\text{sillL},\text{foL},\text{faL}]}^{\text{mod}}$. A finite $\Delta G_{\text{woL}}^{\text{mod}}$ was also explored.

Calibration in MCTC was carried out simultaneously on (a) the wet and dry melting curves of anorthite (the experiments of Goldsmith (1980); Yoder (1976) and Stewart (1967), constraining the woL–silL and woL–silL–h₂oL compositional joins of the melt model), (b) the inferred position of the hb + di + opx + an + q + L + H₂O invariant point in the CMASH system, from Ellis & Thompson (1986), (c) two reported melt compositions at large melt fraction, from the TTG-genesis studies of Patiño Douce & Beard (1995, SQA composition) and Beard & Lofgren (1991, Sample 478), and (d) nine estimates of phase boundary positions (H₂O-out, orthopyroxene-out, hornblende-out, melt-out, quartz-out, plagioclase-out) in the same two experimental bulk compositions. The studies of Patiño Douce & Beard (1995) and Beard & Lofgren (1991) were chosen because the experiments represent a comprehensive P – T grid for $P \leq 12.5$ kbar. The results of the calibration are shown below.

CALCULATIONS ON EXPERIMENTAL COMPOSITIONS

Figures 3 and 4 present pseudosections calculated for hydrate-breakdown melting using bulk compositions SQA (Patiño Douce & Beard, 1995) and Sample 478 (Beard & Lofgren, 1991, hereafter BL478). Bulk composition is treated as constant for experiments on one starting material in one type of apparatus.

Experiments of Patiño Douce & Beard (1995)

The experiments of Patiño Douce & Beard (1995) on SQA, a synthetic quartz amphibolite, yielded assemblages of q + pl + ilm/ru ± hb ± opx ± g ± cpx. Experiments at > 6 kbar were performed in a piston cylinder and experiments at < 6 kbar in an internally heated pressure vessel (IHPV). In Fig. 3a, calculations at > 6 kbar used a value of M_O that gave

$X_{\text{Fe}^{3+}} = 0.1$, while calculations < 6 kbar took place with $X_{\text{Fe}^{3+}} = 0.25$. These values reflect the more oxidising environment of the IHPV relative to the piston cylinder, and were chosen because they span a range of $X_{\text{Fe}^{3+}}$ values inferred from modelling of natural amphibolites and granulites (see Table 1), although they may not correspond closely to the unknown $X_{\text{Fe}^{3+}}$ values developed in the experimental apparatus. For each of the two bulk compositions, calculated values of fO_2 fall within the ranges estimated in the experiments, but this does not sensitively constrain appropriate values for M_O . A single estimate for $M_{\text{H}_2\text{O}}$ was applied to both high- and low-pressure calculations, obtained by Patiño Douce & Beard (1995) through electron probe analysis of the melted starting mixture. In reality, the starting material likely underwent substantial reduction or oxidation in each of the two assemblies, mediated by infiltration or loss of hydrogen and associated with changes in M_O and $M_{\text{H}_2\text{O}}$. However, we did not attempt to simulate the relationship between $M_{\text{H}_2\text{O}}$ in the high-pressure, low- M_O experiments versus the low-pressure, high- M_O experiments, given that the initial value of $X_{\text{Fe}^{3+}}$ in the starting material is unknown.

The calculations successfully reproduce the major assemblage changes of the amphibolite–granulite transition as characterised by the experiments, specifically through the up-temperature appearance of orthopyroxene and exhaustion of hornblende (summarised in Fig. 3b). The hornblende-out boundary is well defined by the experiments, and the calculations match this constraint reasonably well, although they predict a shallower dP/dT slope for the boundary than the experiments suggest. For the chosen values of M_O and $M_{\text{H}_2\text{O}}$, the calculations progressively underestimate the temperature of hornblende exhaustion towards lower pressure. Garnet appears up to 0.6 kbar below the minimum pressure permitted by the experiments, and at the highest pressures the orthopyroxene-in boundary moves rapidly towards excessive temperatures. In the experiments at 840°C and at 875°C, 10 kbar, the experimental assemblage is hb + pl + q + Fe-Ti oxides, while the calculations additionally contain aug + L $\pm$ opx $\pm$ g. The experimental assemblage is unchanged from that of the starting materials, so an approach

to the stable equilibrium assemblage cannot be demonstrated. Despite the moderate temperatures and very long run durations of 1–2 weeks, the shortage of vapour or a detectable volume of melt may inhibit equilibration, and it is likely that stable assemblages at these conditions do indeed include clinopyroxene $\pm$ orthopyroxene $\pm$ melt.

Figure 3c shows the effect of oxidation state on the calculated assemblages at $P = 7$ kbar, over a range of $0 < M_O < 1.62$ mole% ($0 < X_{\text{Fe}^{3+}} < 0.50$). Under the relatively reduced conditions assumed for the piston cylinder assembly, the temperature of the hornblende-out boundary in particular is a strong function of M_O , rising from 830°C to 905°C over the range $0 < M_O < 0.5$ mole% ($0 < X_{\text{Fe}^{3+}} < 0.15$), although further increase in M_O to 1.62 mole% raises the hornblende-out temperature by only 40°C. The sensitivity of the boundary under low- M_O conditions demonstrates the difficulties of extracting calibration information from even the best devised and most careful experimental study, and also highlights the sensitivity of future forward-modelling results to the assumed bulk O content. This sensitivity should always be quantitatively investigated via T – M_O and P – M_O plots (e.g. White *et al.*, 2000; Diener & Powell, 2010; Korhonen *et al.*, 2012).

The equivalent analysis for $M_{\text{H}_2\text{O}}$ at 7 kbar is shown in Fig. 3d. At $M_{\text{H}_2\text{O}} = 4.6$ mol%, the value used in Fig. 3a, the calculations predict a H_2O -present solidus at 665°C, leading to a volumetric melt fraction of 0.33 at 900°C (Fig. 3e). By contrast, the experiments are thought to represent hydrate-breakdown melting and produce only modest melt fractions at 900°C. However, by reducing the estimate of $M_{\text{H}_2\text{O}}$ in Fig. 3a from 4.6 mole% to 3.0 mole%, a fluid-absent solidus could be calculated at 800°C without significantly degrading the fit to the experimental hornblende-out boundary, the latter being only a weak function of $M_{\text{H}_2\text{O}}$. A value of $M_{\text{H}_2\text{O}} = 3.0$ mole% is in fact close to the estimate of bulk H_2O in the starting materials based on mineral modes ($M_{\text{H}_2\text{O}} \sim 3.3$ mole%, Patiño Douce & Beard, 1995). For a boundary as sensitive to bulk H_2O as the water-undersaturated solidus, it is difficult to make a meaningful comparison between calculations and observations, given that the appropriate value of bulk H_2O in the experimental run products is poorly known.

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 $pl + melt + Fe-Ti\ oxides \pm cpx \pm opx \pm hb \pm q$, 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

kbar position of the hornblende-out boundary varies only from 885°C at $M_O = 0.76$ mole% ($X_{Fe^{3+}} = 0.15$) to 902°C at $M_O = 1.27$ mole% ($X_{Fe^{3+}} = 0.25$). The hornblende-out boundary is also almost indifferent to M_{H_2O} in the range 0.5 to 4.5 mole% (Fig. 4d). The value of M_{H_2O} chosen for Fig. 4a is 3.42 mole%, larger than the 1.72 mole% estimated by loss on ignition from the starting materials by Beard & Lofgren (1991). In our modelling, this choice of M_{H_2O} leads to the coexistence of orthopyroxene and hornblende over a narrow ($\sim 50^\circ\text{C}$) temperature range, whereas for values of $M_{H_2O} < 3.1$ mole%, orthopyroxene joins the assemblage at rather low temperatures and creates a wide field of hornblende-granulite.

Hornblende-out boundaries in various experimental studies

Since only two bulk compositions from TTG-genesis experiments were used in the model calibration, Fig. 5 summarises the results of calculations on the hornblende-out boundary in four additional bulk compositions that were not involved in the calibration process, taken from the hydrate-breakdown melting studies of Beard & Lofgren (1991); Rushmer (1991); Wolf & Wyllie (1994) and Skjerlie & Patiño Douce (1995). Comparable calculations for SQA and BL478, the compositions used in calibration, are also shown. In each case, the true temperature of the hornblende-out boundary could be inferred with some confidence from an isobaric sequence of experiments, in which the final hornblende coexisted with a moderate melt fraction and had an apparently equilibrated composition. The calculations, shown as blue bars, locate the hornblende-out boundary for each experimental phase assemblage. Where possible, calculations were performed over generous ranges of M_{H_2O} (3.5–6.5 mole%, equivalent to $\sim 1\text{--}2$ wt%) and M_O (such that $0.1 < X_{Fe^{3+}} < 0.25$), varied simultaneously, which we expect to encompass the true experimental values in most cases. For bulk compositions WW94 and BL571, the experimental assemblage could only be calculated over a reduced range of M_O or M_{H_2O} ; see Fig. 5 and Table 1.

The calculations generally reproduce the experimental hornblende-out temperatures

well, although they considerably overestimate the temperature for the IAT (island arc
tholeiite) composition of Rushmer (1991). Temperatures are probably underestimated for
the natural amphibolite composition AGS11.1 of Skjerlie & Patiño Douce (1995), and the
calibration composition SQA. Over- or under-estimation of hornblende-out temperature
may be correlated with molar bulk values of $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$, of which IAT
has the highest value and AGS11.1 and SQA relatively low values.

To a considerable extent the variation of modelled boundaries with bulk composition is
a function of the well established Holland & Powell (2011) dataset calibration, combined
with the superimposed ΔG_i^{mod} and ΔG_i^{make} terms. Therefore it is perhaps unsurprising that
the results of these calculations are reasonable, even though only two of the TTG-genesis
studies were incorporated into the fitting.

DISCUSSION

The newly calibrated a - x relations extend the scope of phase-equilibrium forward-modelling
methods to include metabasic rocks at high temperature. A pseudosection approach to
thermobarometry is now feasible for such rocks, and other questions that incorporate a bulk
composition constraint, such as limits on melt loss, may now be addressed. Methods of this
kind have previously brought insight into metamorphic processes in metapelites (e.g. White
et al., 2003; Kelsey *et al.*, 2003; Johnson & Brown, 2004; Halpin *et al.*, 2007; Streule *et al.*,
2010; Korhonen *et al.*, 2010; Palin *et al.*, 2012). Strictly the calibration of the a - x relations
described in this paper was limited to ≤ 13 kbar, owing to the lack of a thermodynamic
model for aqueous fluid containing dissolved silicate material. However, it is reasonable to
use the metabasite models with caution whenever the results can be compared with
observations to demonstrate that appropriate stable assemblages are calculated. In the

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 $M_{\text{H}_2\text{O}}$ 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 $M_{\text{H}_2\text{O}}$ 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

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

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

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APPENDIX

The thermodynamic models discussed in this paper may be conveniently used with the software THERMOCALC (Powell & Holland, 1988). The THERMOCALC software may be downloaded from the University of Mainz THERMOCALC website at <http://www.metamorph.geo.uni-mainz.de/thermocalc/>, along with input files containing the a - x relations, versions of the Holland & Powell (2011) dataset, and explanatory notes. THERMOCALC versions tc340 and above should be used. Versions ds62 and ds63 of the Holland & Powell (2011) dataset have not been formally published, so anyone wishing to use them independently of THERMOCALC must extract parameters from the THERMOCALC input files. To assist in doing so, THERMOCALC may be run in mode 0 with the appropriate dataset and a - x relations, generating tables of G values as functions of P and T for each end-member, including those that do not appear explicitly in the dataset. The G values include any ΔG_i expressions applied to the end-members (identified in a - x input files by the script 'DQF').

Full thermodynamic descriptions of the new a - x relations for clinopyroxene (augite model), clinoamphibole and metabasite melt are given below. ΔG_i terms are specified relative to end-members that appear in the Holland & Powell (2011) dataset. Interaction energies $W_{i,j}$ and ΔG_i parameters are specified as functions of pressure P in kilobar and T 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

In the augite model, the following independent set of end-members is used, with the cations shown on their mixing sites, and the tetrahedral site split into T1 and T2 in order to describe Si-Al ordering in the cats end-member (the latter is an intrinsic property of the cats end-member of the Holland & Powell (2011) dataset, written out explicitly in the a - x model):

	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 ΔG_i^{mod} terms of 2 kJ and -5 kJ respectively.

Composition is described by the variables

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

1091 and order-disorder by the parameters

$$Q_{fm} = 2 \left(\frac{x_{\text{Fe}}^{\text{M2}}}{x_{\text{Fe}}^{\text{M2}} + x_{\text{Mg}}^{\text{M2}}} - x \right)$$

$$Q_{al} = x_{\text{Al}}^{\text{T2}} - x_{\text{Al}}^{\text{T1}},$$

1092 which are found by solving the internal equilibria via which the corresponding order-disorder
 1093 end-members are formed, i.e. $\text{fmc} = \frac{1}{2} (\text{cenh} + \text{cfs})$ and $\text{dcats} = \text{ocats}$. The site fractions are

$$x_{\text{Mg}}^{\text{M1}} = 1 - j - x - y + jx + xy + \frac{Q_{fm}}{2} (1 - j - z)$$

$$x_{\text{Fe}}^{\text{M1}} = x - jx - xy - \frac{Q_{fm}}{2} (1 - j - z)$$

$$x_{\text{Al}}^{\text{M1}} = j + y - f$$

$$x_{\text{Fe3}}^{\text{M1}} = f$$

$$x_{\text{Mg}}^{\text{M2}} = 1 - j - x - z - \frac{Q_{fm}}{2} (1 - j - z) + jx + xz$$

$$x_{\text{Fe}}^{\text{M2}} = x + \frac{Q_{fm}}{2} (1 - j - z) - jx - xz$$

$$x_{\text{Ca}}^{\text{M2}} = z$$

$$x_{\text{Na}}^{\text{M2}} = j$$

$$x_{\text{Si}}^{\text{T1}} = 1 - \frac{1}{2} (y - Q_{al})$$

$$x_{\text{Al}}^{\text{T1}} = \frac{1}{2} (y - Q_{al})$$

$$x_{\text{Si}}^{\text{T2}} = 1 - \frac{1}{2} (y + Q_{al})$$

$$x_{\text{Al}}^{\text{T2}} = \frac{1}{2} (y + Q_{al}),$$

1094 and the ideal activities are

$$a_{\text{di}}^{\text{ideal}} = x_{\text{Mg}}^{\text{M1}} x_{\text{Ca}}^{\text{M2}} (x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}})^{\frac{1}{4}}$$

$$a_{\text{cenh}}^{\text{ideal}} = x_{\text{Mg}}^{\text{M1}} x_{\text{Mg}}^{\text{M2}} (x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}})^{\frac{1}{4}}$$

$$a_{\text{cfs}}^{\text{ideal}} = x_{\text{Fe}}^{\text{M1}} x_{\text{Fe}}^{\text{M2}} (x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}})^{\frac{1}{4}}$$

$$\begin{aligned}
a_{\text{jd}}^{\text{ideal}} &= x_{\text{Al}}^{\text{M1}} x_{\text{Na}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}} \right)^{\frac{1}{4}} \\
a_{\text{acm}}^{\text{ideal}} &= x_{\text{Fe3}}^{\text{M1}} x_{\text{Na}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}} \right)^{\frac{1}{4}} \\
a_{\text{ocats}}^{\text{ideal}} &= x_{\text{Al}}^{\text{M1}} x_{\text{Ca}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Al}}^{\text{T2}} \right)^{\frac{1}{4}} \\
a_{\text{dcats}}^{\text{ideal}} &= \sqrt{2} x_{\text{Al}}^{\text{M1}} x_{\text{Ca}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Al}}^{\text{T1}} x_{\text{Si}}^{\text{T2}} x_{\text{Al}}^{\text{T2}} \right)^{\frac{1}{8}} \\
a_{\text{fmc}}^{\text{ideal}} &= x_{\text{Mg}}^{\text{M1}} x_{\text{Fe}}^{\text{M2}} \left(x_{\text{Si}}^{\text{T1}} x_{\text{Si}}^{\text{T2}} \right)^{\frac{1}{4}},
\end{aligned}$$

including the entropy reduction factor. Non-ideal activities are given by equation 2. The end-member proportions for use in equation 2 are

$$\begin{aligned}
p_{\text{di}} &= z - y \\
p_{\text{cenh}} &= 1 - j - x - z - \frac{Q_{\text{fm}}}{2} (1 - j - z) + jx + xz \\
p_{\text{cfs}} &= x - \frac{Q_{\text{fm}}}{2} (1 - j - z) - jx - xy \\
p_{\text{jd}} &= j - f \\
p_{\text{acm}} &= f \\
p_{\text{ocats}} &= Q_{\text{al}} \\
p_{\text{dcats}} &= y - Q_{\text{al}} \\
p_{\text{fmc}} &= Q_{\text{fm}} (1 - j - z) + xy - xz.
\end{aligned}$$

The interaction energies are:

$W_{i,j}$ (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

with asymmetry introduced by the van Laar parameters $\alpha_{\text{cenh}} = \alpha_{\text{cfs}} = \alpha_{\text{fmc}} = 1$, $\alpha_{\text{di}} = \alpha_{\text{jd}}$
 $= \alpha_{\text{acm}} = 1.2$, and $\alpha_{\text{ocats}} = \alpha_{\text{dcats}} = 1.9$.

We reiterate that the augite model does not have a structure suitable for calculations
 where coexisting clinopyroxenes may be expected. To calculate two-clinopyroxene
 equilibria, the ‘omphacite’ model should be used for both phases, using appropriate starting
 guesses for the compositional parameters in each. The omphacite model is described in
 Green *et al.* (2007), with new $W_{\text{acm},n}$ values given in Diener & Powell (2012) and a new
 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
 corresponding change to the parameter $\Delta G_{\text{jac}}^{\text{od}}$. The jac end-member is the ordered
 intermediate $\text{Na}_{\frac{1}{2}}^{\text{M2}}\text{Na}_{\frac{1}{2}}^{\text{M2}}\text{Fe}_{\frac{1}{2}}^{3+\text{M1}}\text{Al}_{\frac{1}{2}}^{\text{M1}}\text{Si}_{\frac{1}{2}}^{\text{tet}}\text{O}_6$, and is formed through the reaction $\text{jac} = \frac{1}{2}(\text{jd}$
 $+ \text{acm}) + \Delta G_{\text{jac}}^{\text{od}}$, 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
 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.

For comparison between the omphacite and augite models, the dependent parameters
 associated with the hed end-member, $\text{CaFeSi}_2\text{O}_6$, in the augite model are compared here
 with their equivalents in the omphacite model.

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

There is however no discordance of symmetry between the two models, as they both feature
 $\alpha_{\text{di}} = \alpha_{\text{jd}} = \alpha_{\text{acm}} = \alpha_{\text{hed}}$. For the method of determining the dependency relationships, see
 Powell & Holland (1999).

Clinoamphibole model

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

1121 calculated for 23 oxygen atoms, with the mixing sites only shown (v=vacancy):

1122

	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
1123 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
mrbr	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

1124 As the end-member thermodynamics are in general not well known, it is assumed that that
1125 dataset end-member tr is correct, while the other compositional end-members ts, parg, gl,
1126 cumm and grun are modified relative to this via terms $\Delta G_{ts}^{\text{mod}} = 10$ kJ, $\Delta G_{parg}^{\text{mod}} = -10$ kJ,
1127 $\Delta G_{gl}^{\text{mod}} = -3$ kJ, $\Delta G_{cumm}^{\text{mod}} = 0$ kJ, $\Delta G_{grun}^{\text{mod}} = -3$ kJ. Order-disorder of Fe-Mg on the M13,
1128 M2 and M4 sites is governed by end-members $a = \frac{3}{7}$ cumm + $\frac{4}{7}$ grun + ΔG_a^{od} and $b = \frac{2}{7}$
1129 cumm + $\frac{5}{7}$ grun + ΔG_b^{od} , where the ΔG relative to the dataset values of the end-members
1130 are given by $\Delta G_a^{\text{od}} = \frac{3}{7} \Delta G_{cumm}^{\text{mod}} + \frac{4}{7} \Delta G_{grun}^{\text{mod}} - 9.5 = -11.2$ kJ and $\Delta G_b^{\text{od}} = \frac{2}{7} \Delta G_{cumm}^{\text{mod}} + \frac{5}{7}$
1131 $\Delta G_{grun}^{\text{mod}} - 11.7 = -13.8$ kJ. The ferric end-member mrbr, and the new end-members kprg and
1132 tts, have to be ‘made’ from dataset end-members via the reactions $\text{mrbr} = \text{gl} - \text{gr} + \text{andr} +$
1133 $\Delta G_{mrbr}^{\text{make}}$, $\text{kprg} = \text{mu} - \text{pa} + \text{parg} + \Delta G_{kprg}^{\text{make}}$, and $\text{tts} = \text{ts} + 2 \text{ru} - 2 \text{dsp} + \Delta G_{tts}^{\text{make}}$
1134 respectively, where the dG terms are $\Delta G_{mrbr}^{\text{make}} = 0$ kJ, $\Delta G_{kprg}^{\text{make}} = -7.06 + 0.02 T$ kJ and
1135 $\Delta G_{tts}^{\text{make}} = 95$ kJ (gr: grossular; andr: andradite; mu: muscovite; pa: paragonite; ru: rutile;
1136 dsp: diaspore). Diener *et al.* (2007) describe the structure and calibration of the core
1137 NCFMASHO model more fully.

1138 Composition and order are described by the variables

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

$$\begin{aligned}
&= \frac{3x_{\text{Fe}}^{\text{M13}} + 2x_{\text{Fe}}^{\text{M2}} + 2x_{\text{Fe}}^{\text{M4}}}{3x_{\text{Fe}}^{\text{M13}} + 2x_{\text{Fe}}^{\text{M2}} + 2x_{\text{Fe}}^{\text{M4}} + 3x_{\text{Mg}}^{\text{M13}} + 2x_{\text{Mg}}^{\text{M2}} + 2x_{\text{Mg}}^{\text{M4}}} \\
y &= x_{\text{Al}}^{\text{M2}} \\
z &= x_{\text{Na}}^{\text{M4}} \\
a &= x_{\text{K}}^{\text{A}} + x_{\text{Na}}^{\text{A}} \\
k &= \frac{x_{\text{K}}^{\text{A}}}{x_{\text{K}}^{\text{A}} + x_{\text{Na}}^{\text{K}}} \\
c &= x_{\text{Ca}}^{\text{M4}} \\
f &= x_{\text{Fe3}}^{\text{M2}} \\
t &= x_{\text{Ti}}^{\text{M2}} \\
Q_1 &= x - \frac{x_{\text{Fe}}^{\text{M13}}}{x_{\text{Fe}}^{\text{M13}} + x_{\text{Mg}}^{\text{M13}}} \\
Q_2 &= x - \frac{x_{\text{Fe}}^{\text{M2}}}{x_{\text{Fe}}^{\text{M2}} + x_{\text{Mg}}^{\text{M2}}}.
\end{aligned}$$

1139 The site fractions are

$$\begin{aligned}
x_{\text{v}}^{\text{A}} &= 1 - a \\
x_{\text{Na}}^{\text{A}} &= a(1 - k) \\
x_{\text{K}}^{\text{A}} &= ak \\
x_{\text{Mg}}^{\text{M13}} &= 1 - x + Q_1 \\
x_{\text{Fe}}^{\text{M13}} &= x - Q_1 \\
x_{\text{Mg}}^{\text{M2}} &= 1 - x - y - f - t + Q_2(1 - f - t - y) + fx + tx + xy \\
x_{\text{Fe}}^{\text{M2}} &= x - Q_2(1 - f - t - y) - fx - tx - xy \\
x_{\text{Al}}^{\text{M2}} &= y \\
x_{\text{Fe3}}^{\text{M2}} &= f \\
x_{\text{Ti}}^{\text{M2}} &= t \\
x_{\text{Ca}}^{\text{M4}} &= c \\
x_{\text{Mg}}^{\text{M4}} &= 1 - c - x - z - \frac{3Q_1}{2} - Q_2(1 - f - t - y) + xc + xz
\end{aligned}$$

$$\begin{aligned}
x_{\text{Fe}}^{\text{M4}} &= x + \frac{3Q_1}{2} + Q_2(1 - f - t - y) - xc - xz \\
x_{\text{Na}}^{\text{M4}} &= z \\
x_{\text{Si}}^{\text{T1}} &= 1 - \frac{1}{2} \left(f + t + y - z + \frac{1}{2}a \right) \\
x_{\text{Al}}^{\text{T1}} &= \frac{1}{2} \left(f + t + y - z + \frac{1}{2}a \right) \\
x_{\text{OH}}^{\text{V}} &= 1 - t \\
x_{\text{O}}^{\text{V}} &= t,
\end{aligned}$$

1140 and ideal activities

$$\begin{aligned}
a_{\text{tr}}^{\text{ideal}} &= x_{\text{v}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 (x_{\text{Mg}}^{\text{M2}})^2 (x_{\text{Ca}}^{\text{M4}})^2 x_{\text{Si}}^{\text{T1}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{ts}}^{\text{ideal}} &= 2 x_{\text{v}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 (x_{\text{Mg}}^{\text{M2}})^2 (x_{\text{Ca}}^{\text{M4}})^2 (x_{\text{Si}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{Al}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{parg}}^{\text{ideal}} &= 8 x_{\text{Na}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 x_{\text{Mg}}^{\text{M2}} x_{\text{Al}}^{\text{M2}} (x_{\text{Ca}}^{\text{M4}})^2 (x_{\text{Si}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{Al}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{gl}}^{\text{ideal}} &= x_{\text{v}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 (x_{\text{Al}}^{\text{M2}})^2 (x_{\text{Na}}^{\text{M4}})^2 x_{\text{Si}}^{\text{T1}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{cumm}}^{\text{ideal}} &= x_{\text{v}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 (x_{\text{Mg}}^{\text{M2}})^2 (x_{\text{Mg}}^{\text{M4}})^2 x_{\text{Si}}^{\text{T1}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{grun}}^{\text{ideal}} &= x_{\text{v}}^{\text{A}} (x_{\text{Fe}}^{\text{M13}})^3 (x_{\text{Fe}}^{\text{M2}})^2 (x_{\text{Fe}}^{\text{M4}})^2 x_{\text{Si}}^{\text{T1}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{a}}^{\text{ideal}} &= x_{\text{v}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 (x_{\text{Fe}}^{\text{M2}})^2 (x_{\text{Fe}}^{\text{M4}})^2 x_{\text{Si}}^{\text{T1}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{b}}^{\text{ideal}} &= x_{\text{v}}^{\text{A}} (x_{\text{Fe}}^{\text{M13}})^3 (x_{\text{Mg}}^{\text{M2}})^2 (x_{\text{Fe}}^{\text{M4}})^2 x_{\text{Si}}^{\text{T1}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{mrb}}^{\text{ideal}} &= x_{\text{v}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 (x_{\text{Fe3}}^{\text{M2}})^2 (x_{\text{Na}}^{\text{M4}})^2 x_{\text{Si}}^{\text{T1}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{kprg}}^{\text{ideal}} &= 8 x_{\text{K}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 x_{\text{Mg}}^{\text{M2}} x_{\text{Al}}^{\text{M2}} (x_{\text{Ca}}^{\text{M4}})^2 (x_{\text{Si}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{Al}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{OH}}^{\text{V}})^2 \\
a_{\text{tts}}^{\text{ideal}} &= 2 x_{\text{v}}^{\text{A}} (x_{\text{Mg}}^{\text{M13}})^3 (x_{\text{Ti}}^{\text{M2}})^2 (x_{\text{Ca}}^{\text{M4}})^2 (x_{\text{Si}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{Al}}^{\text{T1}})^{\frac{1}{2}} (x_{\text{O}}^{\text{V}})^2,
\end{aligned}$$

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

$$\begin{aligned}
p_{\text{tr}} &= c + z - \frac{a}{2} - f - t - y \\
p_{\text{ts}} &= y + f - z - \frac{a}{2} \\
p_{\text{parg}} &= a(1 - k)
\end{aligned}$$

$$\begin{aligned}
p_{\text{gl}} &= z - f \\
p_{\text{cumm}} &= 1 - c - x - z - \frac{3Q_1}{2} - Q_2(1 - f - t - y) + cx + xz \\
p_{\text{grun}} &= x - \frac{5Q_1}{2} - 2Q_2(1 - f - t - y) + cx - fx - tx - xy + xz \\
p_{\text{a}} &= \frac{5Q_2}{2} + Q_2(1 - f - t - y) - xc - xz \\
p_{\text{b}} &= \frac{3Q_1}{2} + 2Q_2(1 - f - t - y) - xc + fx + tx + xy - xz \\
p_{\text{mrb}} &= f \\
p_{\text{kprg}} &= ak \\
p_{\text{tts}} &= t.
\end{aligned}$$

1142 The interaction energies are:

W_{ij} (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 $\alpha_{\text{tr}} = \alpha_{\text{cumm}} = \alpha_{\text{grun}} = \alpha_{\text{a}} = \alpha_{\text{b}} =$
1145 1 , $\alpha_{\text{ts}} = \alpha_{\text{tts}} = 1.5$, $\alpha_{\text{gl}} = \alpha_{\text{mrb}} = 0.8$, and $\alpha_{\text{parg}} = \alpha_{\text{kprg}} = 1.7$.

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.

1149 Melt model

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

end-member	formula
qL	Si ₄ O ₈
abL	NaAlSi ₃ O ₈
kspL	KAlSi ₃ O ₈
woL	CaSiO ₃
silL	Al ₂ SiO ₅
faL	Fe ₄ Si ₂ O ₈
foL	Mg ₄ Si ₂ O ₈
h2oL	H ₂ O
anL	CaAl ₂ Si ₂ O ₈

1152 ΔG_i^{mod} terms are imposed on some end-members: $\Delta G_{\text{woL}}^{\text{mod}} = 1.3 \text{ kJ}$, $\Delta G_{\text{silL}}^{\text{mod}} = -7.8 \text{ kJ}$,

1153 $\Delta G_{\text{faL}}^{\text{mod}} = -8.2 - 1.4P \text{ kJ}$, and $\Delta G_{\text{foL}}^{\text{mod}} = -4$. The end-member anL is made by the reaction

1154 $\text{anL} = \text{woL} + \text{silL} + \Delta G_{\text{anL}}^{\text{od}}$, with $\Delta G_{\text{anL}}^{\text{od}} = -46.5 - 0.25P$.

1155 The composition of the melt is described by the following variables, where

1156 $\Sigma_c = \text{Si}_4\text{O}_8 + \text{NaAlSi}_3\text{O}_8 + \text{KAlSi}_3\text{O}_8 + \text{CaSiO}_3 + \text{Al}_2\text{SiO}_5 + \text{Fe}_4\text{Si}_2\text{O}_8 + \text{Mg}_4\text{Si}_2\text{O}_8 + \text{H}_2\text{O}$:

$$\begin{aligned}
 q &= \frac{\text{Si}_4\text{O}_8}{\Sigma_c} \\
 fsp &= \frac{\text{NaAlSi}_3\text{O}_8 + \text{KAlSi}_3\text{O}_8}{\Sigma_c} \\
 na &= \frac{\text{NaAlSi}_3\text{O}_8}{\text{NaAlSi}_3\text{O}_8 + \text{KAlSi}_3\text{O}_8} = \frac{\text{Na}}{\text{Na} + \text{K}} \\
 wo &= \frac{\text{CaSiO}_3}{\Sigma_c} \\
 sil &= \frac{\text{Al}_2\text{SiO}_5}{\Sigma_c} \\
 ol &= \frac{\text{Fe}_4\text{Si}_2\text{O}_8 + \text{Mg}_4\text{Si}_2\text{O}_8}{\Sigma_c} \\
 x &= \frac{\text{Fe}_4\text{Si}_2\text{O}_8}{\text{Fe}_4\text{Si}_2\text{O}_8 + \text{Mg}_4\text{Si}_2\text{O}_8} = \frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg}}.
 \end{aligned}$$

1157 To handle the formation of the associate species anL, an ‘order parameter’ y_{anL} is defined,

1158 where $y_{\text{anL}} = p_{\text{anL}}$. The full set of end-member proportions can now be written as:

$$\begin{aligned}
 p_{\text{qL}} &= q (1 + y_{\text{anL}}) \\
 p_{\text{abL}} &= fsp \, na \, (1 + y_{\text{anL}})
 \end{aligned}$$

$$\begin{aligned}
p_{\text{kspL}} &= f_{\text{sp}} (1 - na) (1 + y_{\text{anL}}) \\
p_{\text{woL}} &= w_{\text{o}} (1 + y_{\text{anL}}) - y_{\text{anL}} \\
p_{\text{silL}} &= s_{\text{il}} (1 + y_{\text{anL}}) - y_{\text{anL}} \\
p_{\text{faL}} &= o_{\text{l}} x (1 + y_{\text{anL}}) \\
p_{\text{foL}} &= o_{\text{l}} (1 - x) (1 + y_{\text{anL}}) \\
p_{\text{h2oL}} &= 1 - (q + f_{\text{sp}} + w_{\text{o}} + s_{\text{il}} + o_{\text{l}}) (1 + y_{\text{anL}}) + y_{\text{anL}} \\
p_{\text{anL}} &= y_{\text{anL}}.
\end{aligned}$$

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

$$\begin{aligned}
x_{\text{Fe}} &= x \\
x_{\text{Mg}} &= 1 - x \\
x_{\text{fac}} &= 1 - p_{\text{h2oL}}.
\end{aligned}$$

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 :

$$\begin{aligned}
a_{\text{qL}}^{\text{ideal}} &= x_{\text{fac}} p_{\text{qL}} \\
a_{\text{abL}}^{\text{ideal}} &= x_{\text{fac}} x_{\text{ab}} \\
a_{\text{kspL}}^{\text{ideal}} &= x_{\text{fac}} x_{\text{ksp}}
\end{aligned}$$

$$\begin{aligned}
a_{\text{woL}}^{\text{ideal}} &= x_{\text{fac}} p_{\text{woL}} \\
a_{\text{silL}}^{\text{ideal}} &= x_{\text{fac}} p_{\text{silL}} \\
a_{\text{faL}}^{\text{ideal}} &= x_{\text{fac}} p_{\text{ol}} (x_{\text{Fe}})^5 \\
a_{\text{foL}}^{\text{ideal}} &= x_{\text{fac}} p_{\text{ol}} (x_{\text{Mg}})^5 \\
a_{\text{h2oL}}^{\text{ideal}} &= (p_{\text{h2oL}})^2 \\
a_{\text{anL}}^{\text{ideal}} &= x_{\text{fac}} p_{\text{anL}}.
\end{aligned}$$

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 ($\kappa_0, \kappa'_0, \kappa''_0$): 47.92 kbar, 4.00 , -0.08350 kbar⁻¹.

1176 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

1181 White *et al.* (2014) has been replaced, in both the metabasite set and the metapelite set,
1182 with the older model of White *et al.* (2000) in the system FeO–Fe₂O₃–TiO₂, as the more
1183 recent model appears to predict excessive values of MgO/(FeO+MgO) in the phase.

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 $X_{\text{Fe}^{3+}}=0.36$ (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

experiments. Experimental assemblages are q + pl + ilm/ru ± hb ± opx ± cpx ± g ± L. Two different M_O values are used at higher and lower pressure, corresponding to different sets of experimental apparatus (see text). (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. (e) Melt fraction as a function of T at 7 kbar; melt fraction is molar with phases represented on a 1-cation basis, approximating the volumetric melt fraction. Boundaries are ornamented and coloured to highlight the continuation of phase-out curves through different assemblages (colour online).

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 ± hb ± opx ± cpx ± 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 $\leq 10^\circ\text{C}$.

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% (~ 1 – 2 wt% H_2O), varied simultaneously. For compositions ^a, the blue bars represent calculations for the

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} .

TABLE CAPTIONS

Table 1: Bulk compositions in mole % used in calculations, expressed in terms of the chemical components used by THERMOCALC. FeO^{tot} is total iron expressed as FeO. O, oxygen, combines only with FeO, via the equation $2 \text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$; hence M_{O} is identically equal to molar bulk Fe_2O_3 , $M_{\text{Fe}_2\text{O}_3}$, with $X_{\text{Fe}^{3+}}$ given by $2 M_{\text{O}}/M_{\text{FeO}^{\text{tot}}}$. Where no value is cited in the $M_{\text{H}_2\text{O}}$ column, H_2O is assumed to be in excess.

Table 2: Equilibria used in calibrating the augite model (see text), and results of calculations with the completed set of models. Observed values of compositional variables are shown in roman font, calculated values in italic. Compositional variables for the augite model are defined in the Appendix. Bulk compositions used in the calculations are given in Table 1. Observational $f(\text{aug})$ values ($x_{\text{Fe}_3}^{\text{M1}}$) obtained using the rule of Droop (1987).

Table 3: Equilibria used in calibrating the clinoamphibole model, and the results of calculations with the completed set of models (all with excess q, H_2O). Observed or other target values (see footnotes) of compositional variables are shown in roman font, calculated values in italics. Compositional variables for the clinoamphibole and augite models are defined in the Appendix. Bulk compositions used in the calculations are given in Table 1. $\text{Phase} \rightarrow 0$ indicates the zero-mode isopleth (the *phase-out* boundary) for *phase*.

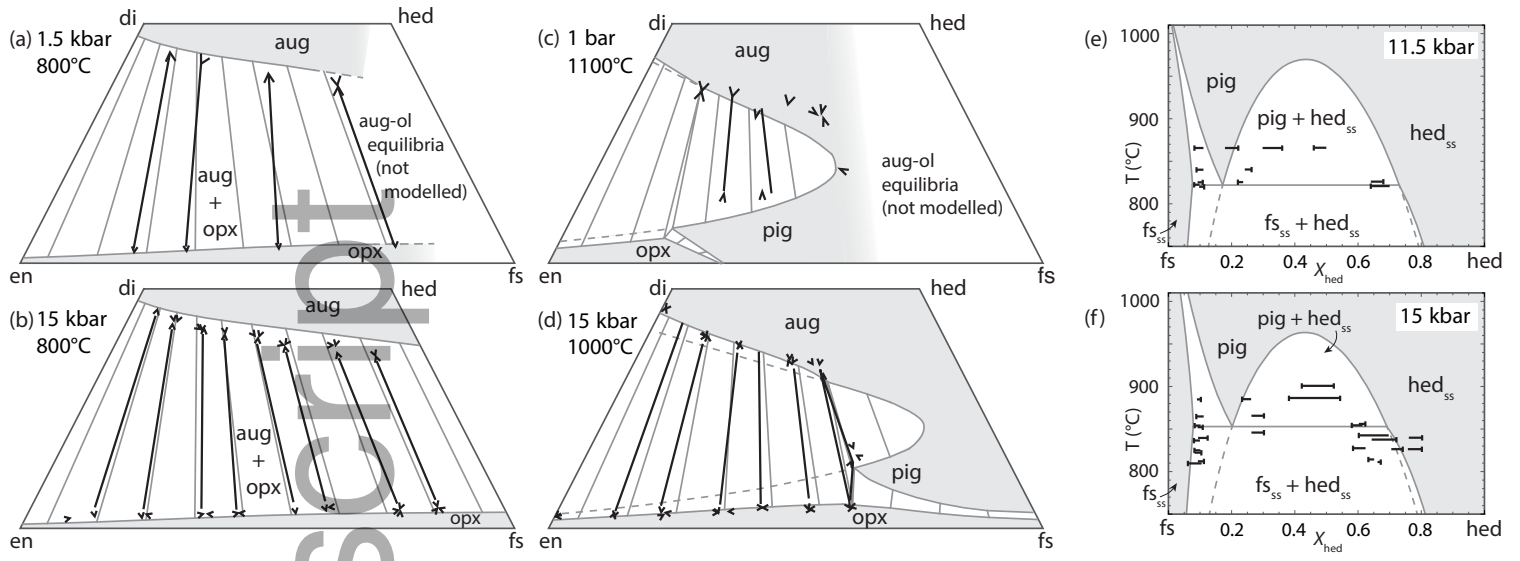
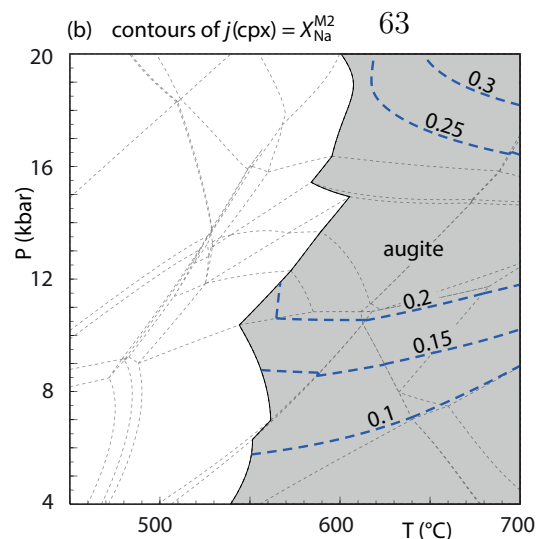
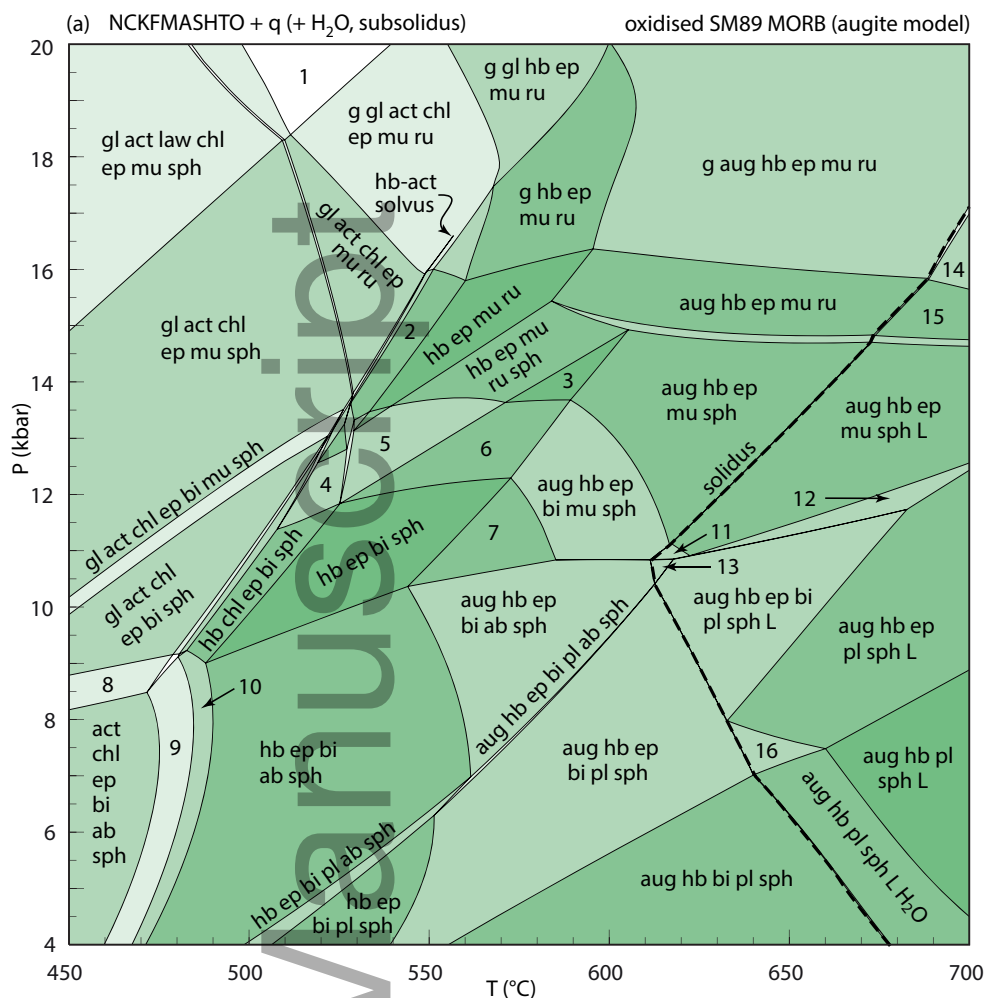
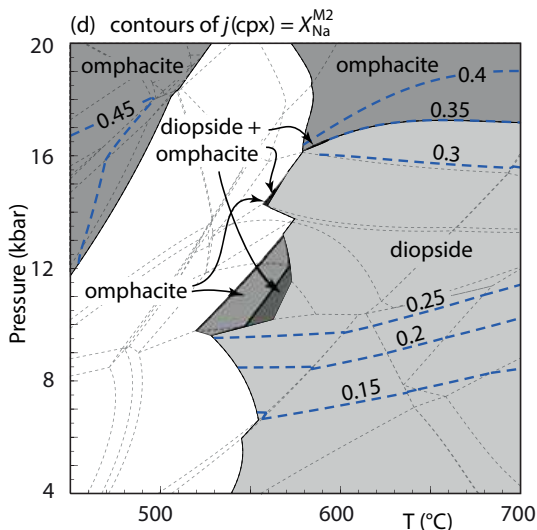
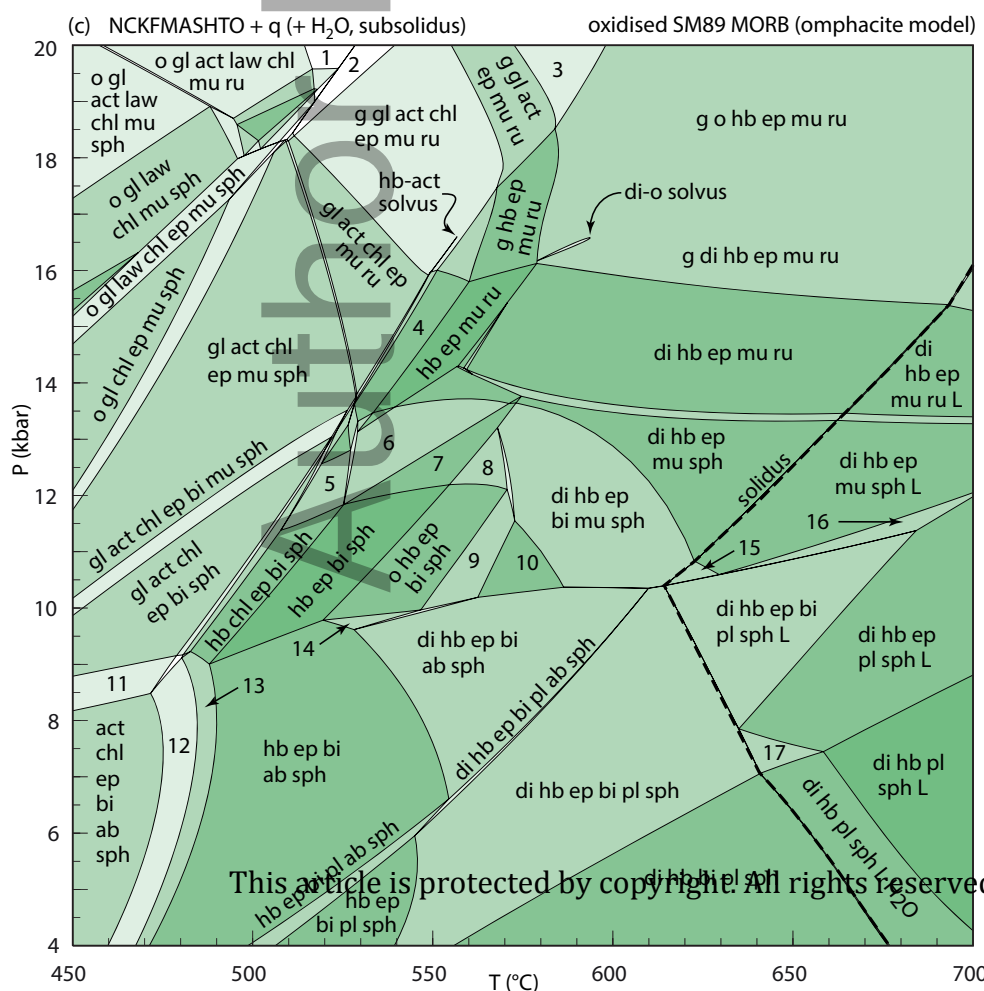


Figure 1:



- 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 H₂O



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

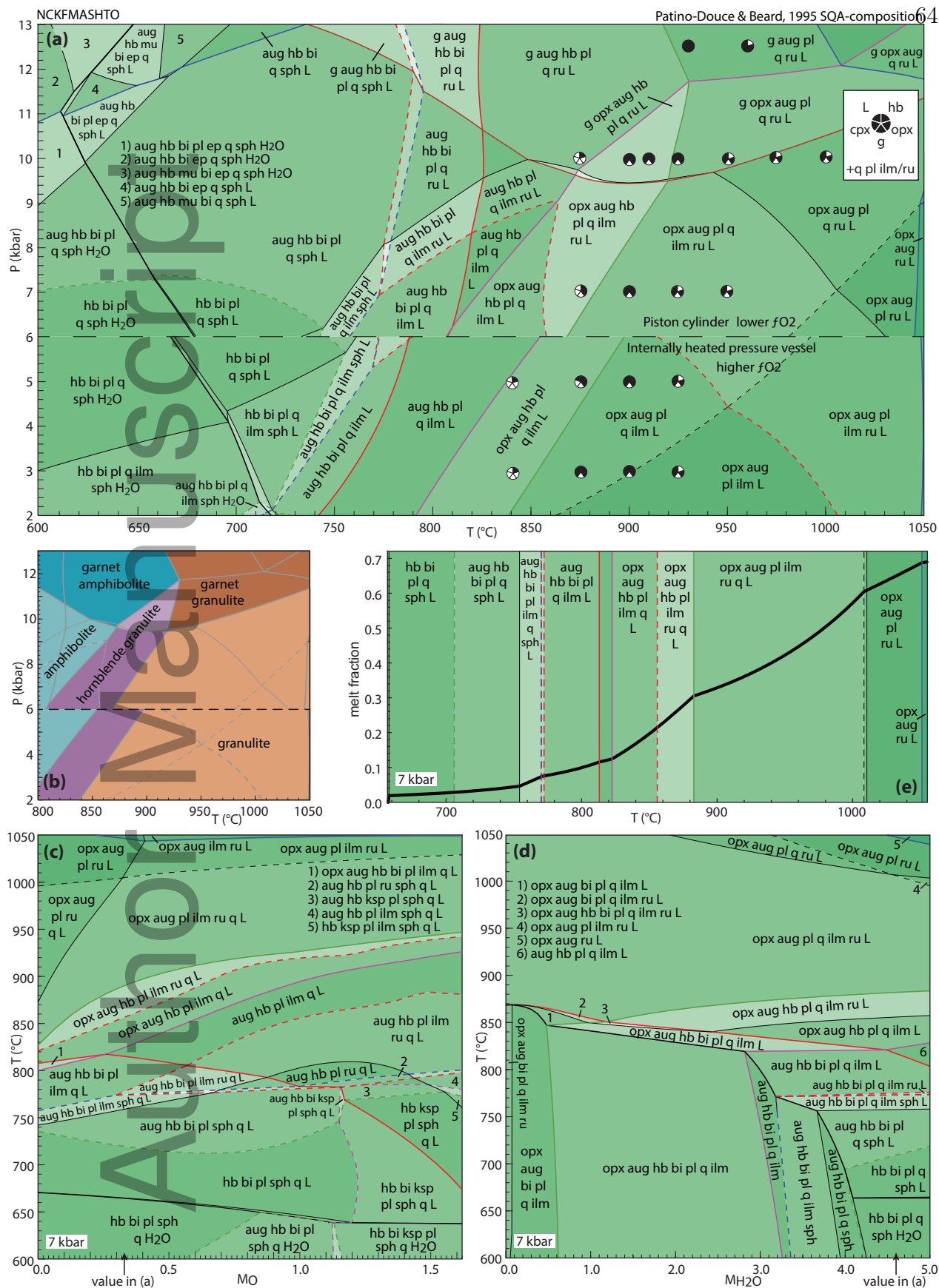


Figure 3:

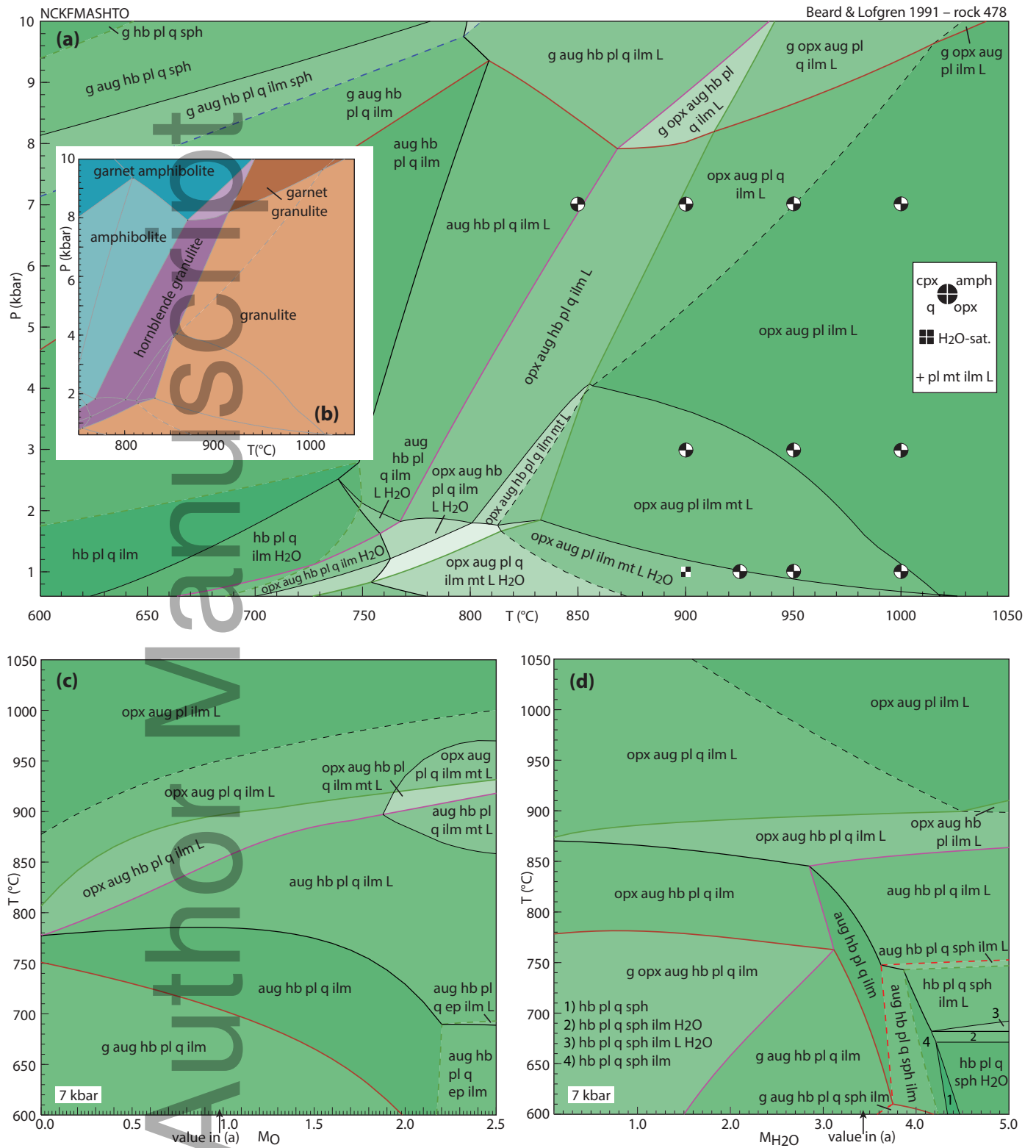


Figure 4:

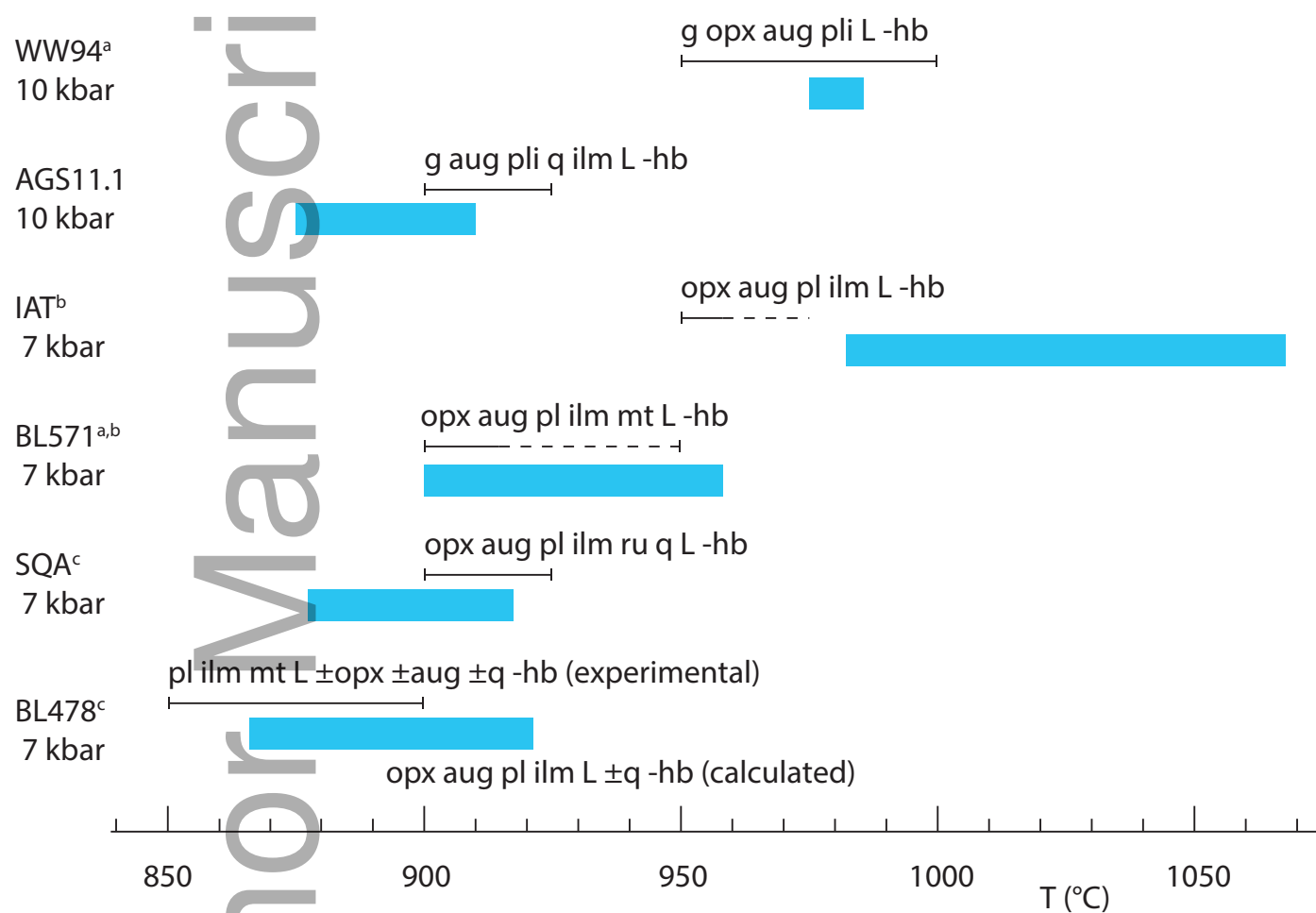


Figure 5:

Table 1:

	M_{SiO_2}	M_{TiO_2}	$M_{\text{Al}_2\text{O}_3}$	$M_{\text{FeO}^{\text{tot}}}$	M_{MgO}	M_{CaO}	$M_{\text{Na}_2\text{O}}$	$M_{\text{K}_2\text{O}}$	M_{O}	$M_{\text{H}_2\text{O}}$
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 $M_{\text{O}}=0.5$ 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), $X_{\text{Fe}^{3+}}$ 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. $M_{\text{H}_2\text{O}}$ from analysis of starting material. In Fig. 5, $0.33 < M_{\text{O}} < 0.82$, $3.50 < M_{\text{H}_2\text{O}} < 6.50$. **BL478**: Sample 478 of Beard & Lofgren (1991). See text for $M_{\text{H}_2\text{O}}$, M_{O} estimates. In Fig. 5, $0.52 < M_{\text{O}} < 1.30$, $3.50 < M_{\text{H}_2\text{O}} < 6.50$. **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:

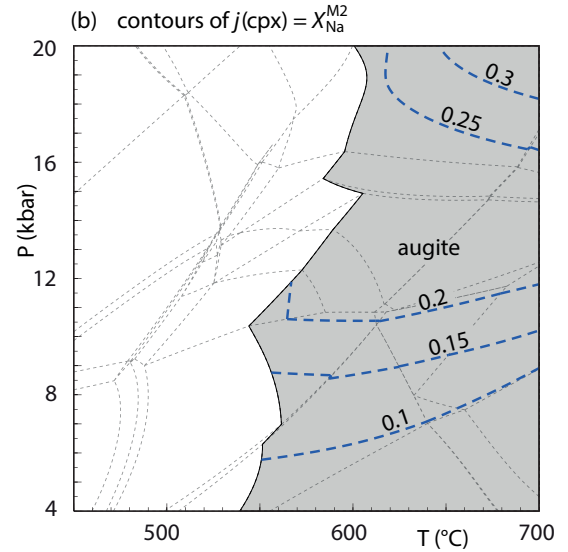
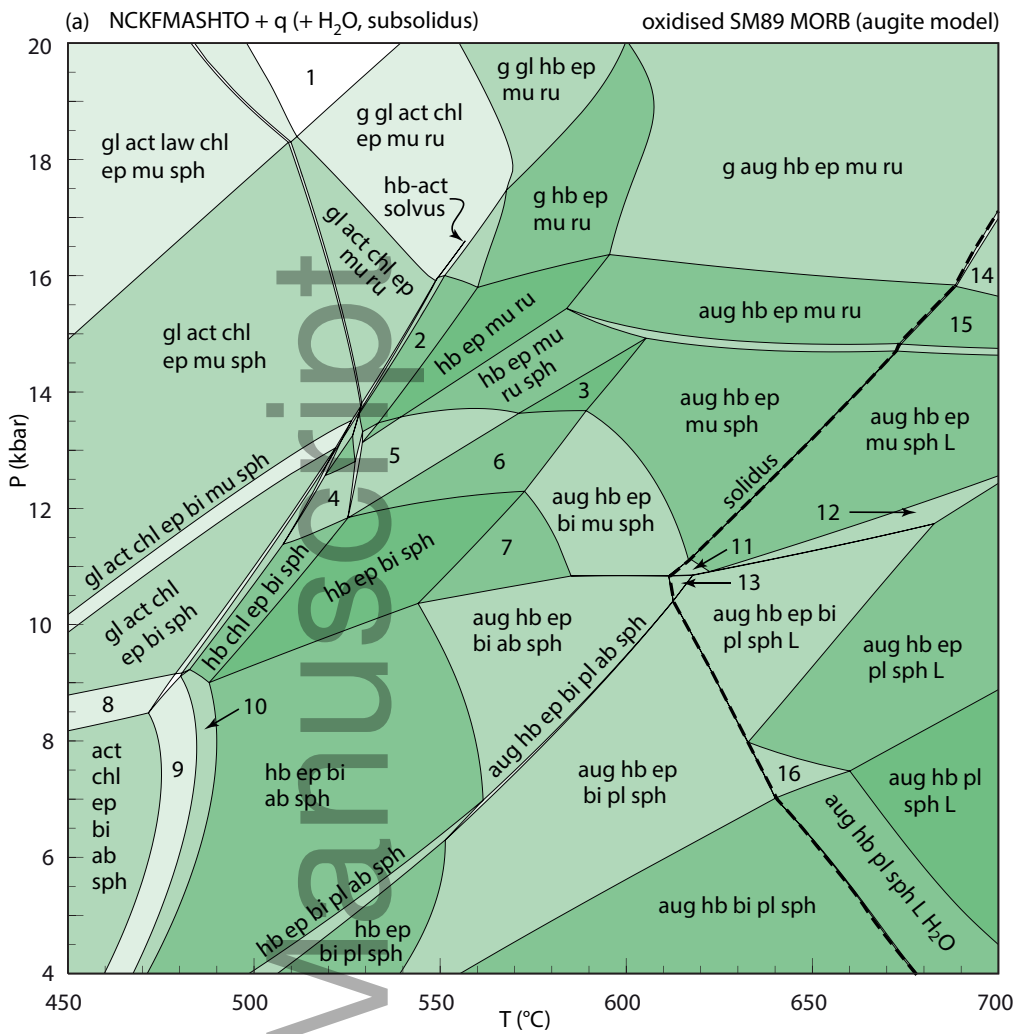
	Assemblage	P (kbar)	T ($^{\circ}\text{C}$)	$x(\text{aug})$	$y(\text{aug})$	$f(\text{aug})$	$z(\text{aug})$	$j(\text{aug})$	$x_{\text{Ca}}^{\text{X}}(g)$	$x^{\text{an}}(pl)$
IZ100 ¹	cpx opx g pl ilm	9	900	0.26	0.08	0.06	0.89	0.04	0.19	0.53
				<i>0.34</i>	<i>0.06</i>	<i>0.07</i>	<i>0.81</i>	<i>0.05</i>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

¹Natural sample (Kunz *et al.*, 2014). P – T estimate from pseudosection forward modelling of intercalated metapelitic rocks using the ds55 models. ²Natural 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. ³Experimental run 1303 of Adam *et al.* (1992), with starting material DR9734.

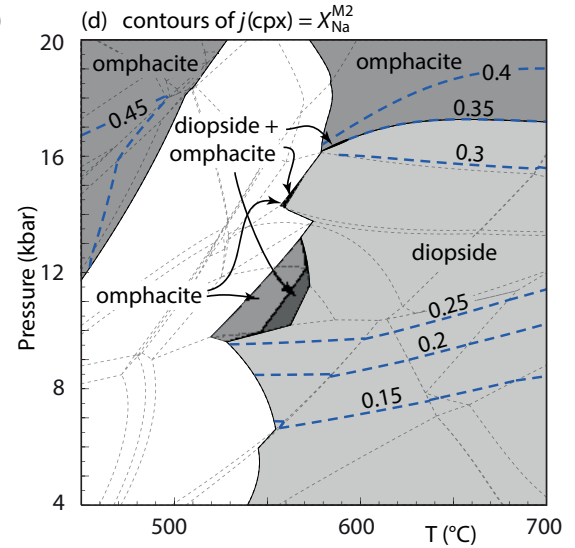
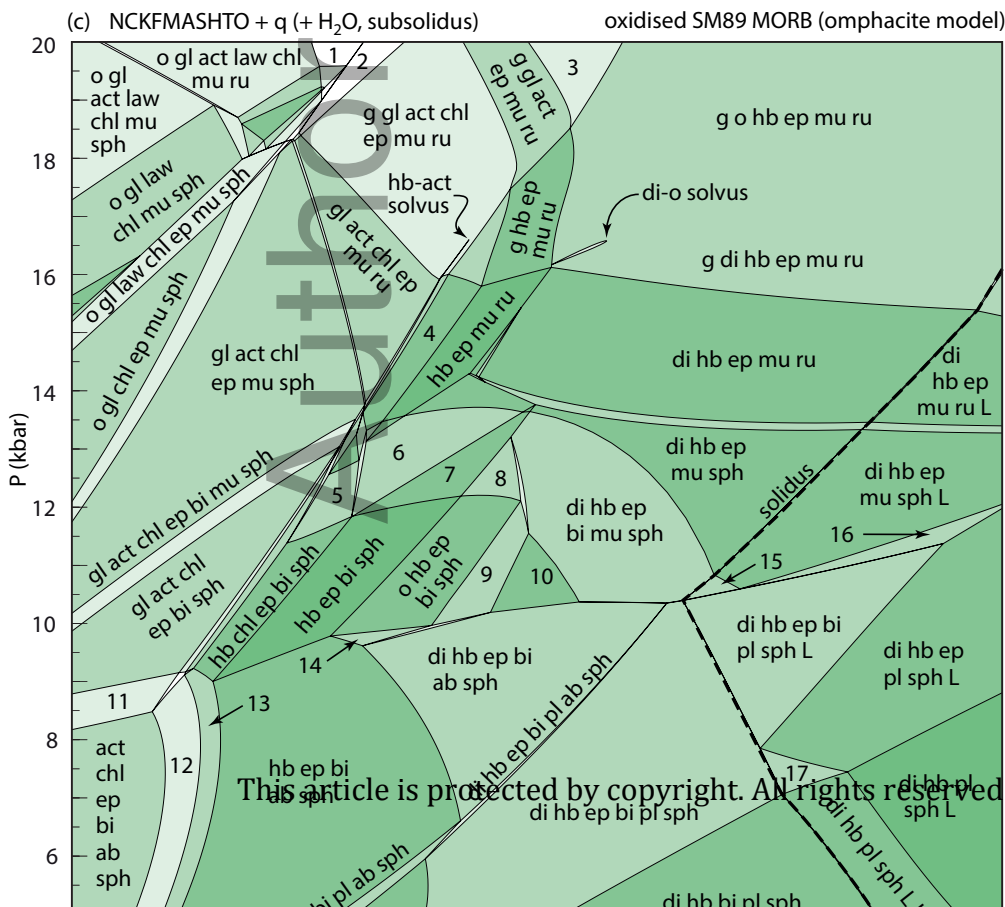
Table 3:

Assemblage		P (kbar)	T (°C)	Composition variables									
Mcal ¹	hb gl act bi ep chl	10±1	480±20	<i>y</i> (hb)	<i>z</i> (hb)	<i>a</i> (hb)	<i>c</i> (hb)	<i>f</i> (hb)	<i>y</i> (gl)	<i>z</i> (gl)	<i>a</i> (gl)	<i>c</i> (gl)	<i>f</i> (gl)
	ab sph;	<i>9.3</i>	<i>474</i>	<i>0.55–0.70</i>	<i>0.3–0.4</i>	<i>0.35–0.45</i>	<i>0.6–0.7</i>	<i>0.1</i>	<i>0.7–0.8</i>	<i>0.8–0.9</i>	<i>0.1</i>	<i>0.1</i>	<i>0.1</i>
	hb, gl→0			<i>0.63</i>	<i>0.38</i>	<i>0.37</i>	<i>0.61</i>	<i>0.08</i>	<i>0.78</i>	<i>0.89</i>	<i>0.07</i>	<i>0.11</i>	<i>0.09</i>
				<i>y</i> (act)	<i>z</i> (act)	<i>a</i> (act)	<i>c</i> (act)	<i>f</i> (act)					
				<i>0.15–0.25</i>	<i>0.15–0.25</i>	<i>0.1</i>	<i>0.75–0.80</i>	<i>0.05</i>					
				<i>0.17</i>	<i>0.22</i>	<i>0.07</i>	<i>0.78</i>	<i>0.03</i>					
				<i>a</i> (hb)	<i>k</i> (hb)	<i>t</i> (hb)	<i>y</i> (aug)	<i>z</i> (aug)	<i>j</i> (aug)	<i>x</i> _{Ca} ^X (g)	<i>x</i> ^{an} (pl)		
SKA101 ²	hb g pl bi ilm sph	10	770	<i>0.41</i>	<i>0.31</i>	<i>0.08</i>	-	-	-	<i>0.27</i>	<i>0.86</i>		
				<i>0.65</i>	<i>0.34</i>	<i>0.07</i>				<i>0.28</i>	<i>0.83</i>		
SKB116 ²	hb cpx g pl bi sph	11	770	<i>0.56</i>	<i>0.38</i>	<i>0.12</i>	<i>0.03</i>	<i>0.87</i>	<i>0.02</i>	<i>0.30</i>	<i>0.47</i>		
				<i>0.72</i>	<i>0.16</i>	<i>0.07</i>	<i>0.09</i>	<i>0.86</i>	<i>0.11</i>	<i>0.43</i>	<i>0.26</i>		
PM13013 ²	hb pl ilm	4	700	<i>0.71</i>	<i>0.31</i>	<i>0.11</i>	-	-	-	-	<i>0.36</i>		
				<i>0.39</i>	<i>0.35</i>	<i>0.05</i>					<i>0.38</i>		
PM13083 ²	hb cpx pl sph	4	700	<i>0.44</i>	<i>0.11</i>	<i>0.07</i>	<i>0.07</i>	<i>0.93</i>	<i>0.04</i>	-	<i>0.51</i>		
				<i>0.51</i>	<i>0.14</i>	<i>0.05</i>	<i>0.06</i>	<i>0.92</i>	<i>0.04</i>		<i>0.49</i>		
PM13161 ^{2,3}	hb cpx pl sph	4	700	<i>0.65</i>	<i>0.18</i>	<i>0.07</i>	<i>0.08</i>	<i>0.52</i>	<i>0.02</i>	-	<i>0.26</i>		
				<i>0.49</i>	<i>0.19</i>	<i>0.04</i>	<i>0.02</i>	<i>0.89</i>	<i>0.08</i>		<i>0.29</i>		
AG9 ⁴	hb g pl ilm;	6±3	650	<i>0.29</i>	<i>0.17</i>	<i>0.04</i>	-	-	-		<i>0.96</i>		
	g→0	<i>6.3</i>		<i>0.32</i>	<i>0.19</i>	<i>0.04</i>				<i>0.47</i>	<i>0.95</i>		

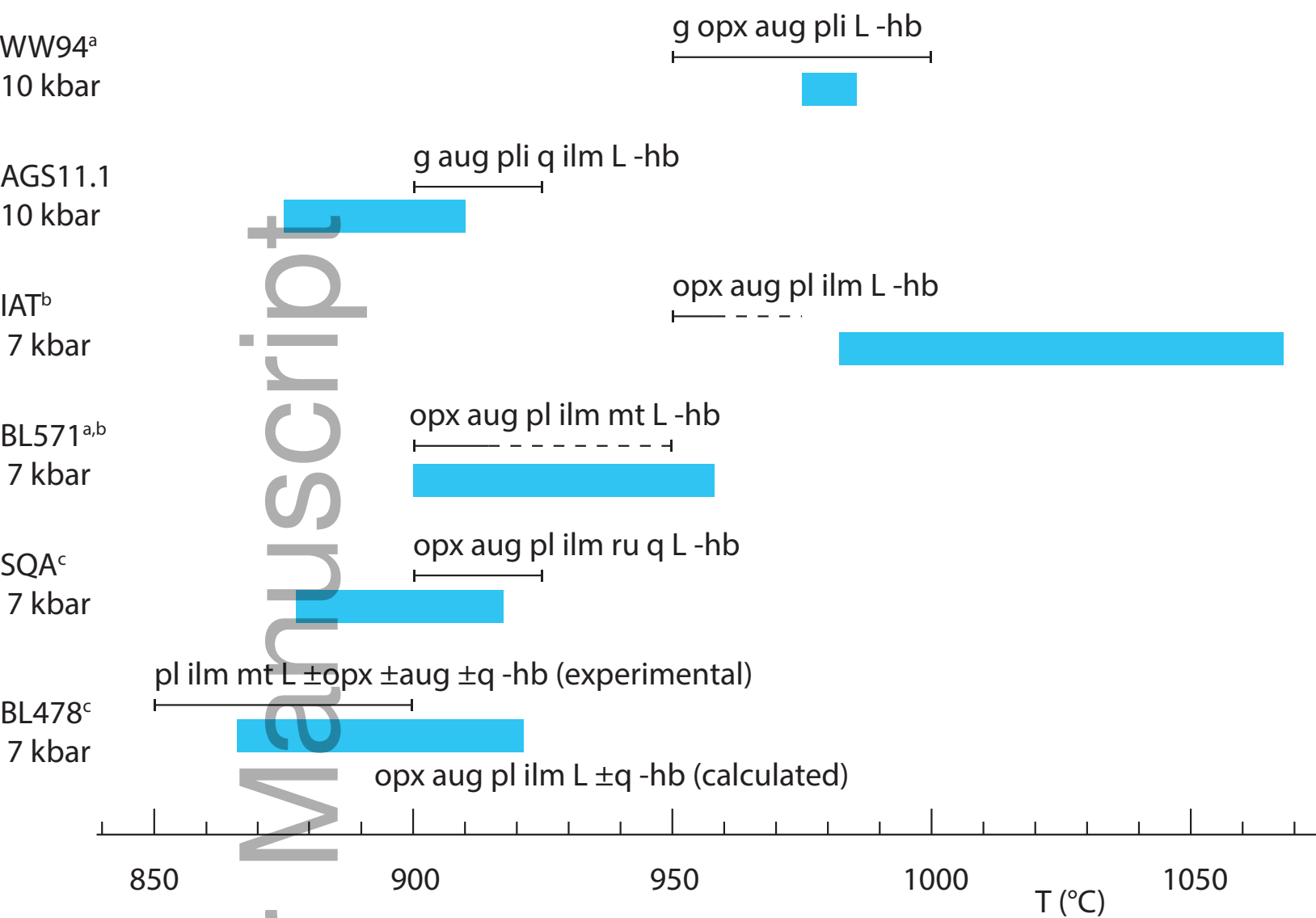
¹Hb, gl, act were assumed to have negligible K₂O, TiO₂, with $k(\text{hb}) > k(\text{gl}) \approx k(\text{act})$ and $t(\text{hb}) \approx t(\text{gl}) > t(\text{act})$; calculated values are $0.02 < k < 0.04$, $t \leq 0.01$, with appropriate differences among the three phases. ² P – T estimated from pseudosection forward modelling with ds55 models. ³Measured $j(\text{aug})$ looks suspect. ⁴Garnet has 20% spessartine, unmodelled.



- 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



- 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



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