

1 **The effect of Mn on mineral stability in metapelites revisited:**
2 **new $a-x$ relations for manganese-bearing minerals**

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12 ABSTRACT

13 The $a-x$ relations recently presented in White *et al.* 2014, *Journal of Metamorphic*
14 *Geology*, **32**, 261–286 are extended to include MnO. This provides a set of internally
15 consistent $a-x$ relations for metapelitic rocks in the MnO–Na₂O–CaO–K₂O–FeO–MgO–
16 Al₂O₃–SiO₂–H₂O–TiO₂–O₂ (MnNCKFMASHTO) system. The mixing parameters for the
17 Mn-bearing minerals were estimated using the new micro- ϕ approach of Powell *et al.* 2014,
18 *Journal of Metamorphic Geology*, **32**, 245–260. Then the Mn-end-member thermodynamic
19 properties were calibrated using a database of co-existing minerals involving literature data
20 from rocks and from experiments on natural materials. Mn-end-members were calibrated
21 for orthopyroxene, cordierite, staurolite, chloritoid, chlorite, biotite, ilmenite and hematite,
22 assuming known properties for the garnet end-member spessartine. The addition of MnO
23 to phase diagram calculations results in a marked expansion of the stability of
24 garnet-bearing assemblages. At greenschist facies conditions garnet stability is extended
25 down temperature. At amphibolite facies conditions the garnet-in boundary shifts to lower
26 pressure. While the addition of MnO greatly influences the stability of garnet, it has
27 relatively little effect on the stability of other common metapelitic minerals, with the
28 resultant diagrams being topologically very similar to those calculated without MnO.
29 Furthermore, the addition of MnO in the amounts measured in most metapelites has only a
30 small effect on the mode of garnet, with calculated garnet modes remaining smaller than
31 1% in the $P-T$ range outside its predicted Mn-free $P-T$ range.

32 INTRODUCTION

33 While the key equilibria that control the metamorphic mineral assemblages in metapelites
34 can be shown graphically in systems as simple as $\text{K}_2\text{O}\text{--}\text{FeO}\text{--}\text{MgO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2\text{--}\text{H}_2\text{O}$
35 (KFMASH), the quantitative analysis of such rocks using phase equilibria requires larger
36 systems (e.g. White *et al.*, 2000, 2007, 2014; Diener *et al.*, 2007; Smye *et al.*, 2010). These
37 larger systems are necessary to accommodate relatively minor components such as TiO_2 ,
38 Na_2O , CaO Fe_2O_3 and MnO that nevertheless may exhibit a strong influence over the
39 stability of certain common minerals. For example, TiO_2 is known to strongly affect the
40 stability of biotite at higher temperature.

41 Manganese is well known to affect mineral assemblages in metasedimentary rocks via
42 its strong stabilising effect on garnet (e.g. Atherton, 1964; Osberg, 1971; Symmes & Ferry,
43 1992; Droop & Harte, 1995; Mahar *et al.*, 1997; Tinkham *et al.*, 2001). Thus, despite its
44 typically low concentration ($\approx 0.1\text{--}0.3$ wt %) in metasediments (e.g. Ague, 1991; Atherton
45 & Brotherton, 1982) manganese forms a critical component in phase equilibria and the
46 interpretation of metamorphic assemblages (e.g. Symmes & Ferry, 1992; Droop & Harte,
47 1995; Mahar *et al.*, 1997). Calculations in manganese-free systems ranging from KFMASH
48 to NCKFMASHTO ($\text{Na}_2\text{O}\text{--}\text{CaO}\text{--}\text{K}_2\text{O}\text{--}\text{FeO}\text{--}\text{MgO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2\text{--}\text{H}_2\text{O}\text{--}\text{TiO}_2\text{--}\text{O}_2$) show a
49 relatively restricted stability of garnet, even in relatively Fe-rich bulk compositions (e.g.
50 Powell *et al.*, 1998; White *et al.*, 2000, 2014). For example, the NCKFMASHTO
51 calculations presented in White *et al.* (2014) for the amphibolite facies average metapelite
52 composition from Ague (1991) have garnet stability restricted to pressures above ≈ 7.5 kbar
53 and temperatures above ≈ 570 °C. These calculations contrast markedly with the common
54 occurrence of manganese-bearing garnet in many greenschist and amphibolite facies rocks,
55 including those from contact aureoles and low-*P* Buchan type terrains (e.g. Harte &
56 Hudson, 1979; Hudson, 1985; Pattison & Tinkham, 2009)

57 Some of the first studies to undertake quantitative phase diagram calculations beyond
58 the KFMASH system (e.g. Spear & Cheney, 1989; Symmes & Ferry, 1992; Mahar *et al.*,
59 1997) incorporated Mn-end-members in the calculations in order to better predict the
60 stability of garnet. While a large number of studies since have considered MnO in phase
61 diagram calculations in various systems (e.g. Tinkham & Ghent, 2005; White *et al.*, 2005;
62 Wei *et al.*, 2007; Pattison & Tinkham, 2009), these studies generally did not involve the

63 development of new thermodynamic models or recalibration of the Mn end-member data.
64 For example the $a-x$ relations presented in Tinkham *et al.* (2001) and Tinkham & Ghent
65 (2005), are simply the combination of the Mahar *et al.* (1997) MnO relationships to the
66 extant Mn-free $a-x$ relations of the time (e.g. Holland *et al.*, 1998; Holland & Powell, 1998;
67 Powell & Holland 1999; White *et al.*, 2000). Obviously this is not a defensible approach
68 given that the underlying formulation of the Mahar *et al.* (1997) $a-x$ relationships was
69 ideal mixing, while the later models with which they were combined involved the
70 symmetric formalism. Thus, there were large inherent inconsistencies in the $a-x$ relations
71 used in these previous studies.

72 In this paper we develop new end-member properties for the MnO-bearing
73 end-members following a similar approach to Mahar *et al.* (1997). This builds on and
74 extends the thermodynamic descriptions of White *et al.* (2014) and they are compatible
75 with the most recent Holland & Powell (2011) dataset. Thus, for the first time since 1997,
76 the thermodynamic properties of the manganese end-members for phases are consistent
77 with the other end-members in each phase.

78 THE THERMODYNAMICS OF MN-BEARING MINERALS

79 The following phases, with their phase abbreviations, are considered to be Mn-bearing:
80 garnet (g), orthopyroxene (opx), cordierite (cd), staurolite (st), chlorite (chl), chloritoid
81 (ctd), biotite (bi), and ilmenite (ilm). The manganese end-members of these minerals are
82 the same as those whose properties appear in `ds6` (Holland & Powell, 2011), except for the
83 manganese end-member of orthopyroxene which is made from the dataset end-member,
84 pyroxmangite (MnSiO_3): garnet (spessartine, spss, $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), biotite (mnbi,
85 $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$), orthopyroxene (mnopx, $\text{Mn}_2\text{Si}_2\text{O}_6$), cordierite (mncrd,
86 $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), staurolite (mnst, $\text{Mn}_4\text{Al}_{18}\text{Si}_{7.5}\text{O}_{44}(\text{OH})_4$), chloritoid (mnctd,
87 $\text{MnAl}_2\text{SiO}_5(\text{OH})_2$), chlorite (mnchl, $\text{Mn}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$) and ilmenite (pyrophanite, pnt,
88 MnTiO_3).

89 In biotite, orthopyroxene and chlorite, manganese is distributed across non-equivalent
90 octahedral sites such that the site fraction of Mn is the same on the different sites (coined
91 equidistribution). Note that this is not equipartition, which in this case might mean
92 making Mn/Fe^{2+} the same across the sites. Unlike equipartition, equidistribution is not

93 thermodynamically inconsistent (Holland & Powell, 2007). While it is likely that Mn is
94 partitioned between the non-equivalent sites as Mg and Fe²⁺ are, rather than equally
95 distributed, such an approach would require additional ordered manganese end-members,
96 and the enthalpy of ordering would need to be estimated. Although approaches to
97 implement this are available, e.g. Powell *et al.* (2014), given the lack of data on Mn
98 ordering and the fact that Mn is nearly always a minor constituent of these phases, the
99 additional complexity of such an approach is not considered to be warranted.

100 The formulation of the a - x relations of the minerals involves ideal-mixing-on-sites and
101 the symmetric formalism (Powell & Holland, 1993; Powell *et al.*, 2014). The
102 parameterisation follows White *et al.* (2014) closely, with the addition of the non-ideality
103 involving Mn substitution in the minerals remaining to be considered. Except for garnet
104 and ilmenite, there are no experimental data that would allow the pairwise macroscopic
105 interaction energies (W) between the manganese and the other end-members in the
106 minerals to be estimated. As argued in Powell *et al.* (2014), the simplification of assuming
107 that all the interaction energies, W , involving the manganese and other end-members are
108 zero is unlikely to be correct, and is likely to bias the results of calculations. Given that
109 even Mg-Fe²⁺ interactions have significant non-zero W , it is much better to give the a - x
110 relations involving Mn a good “shape”, with non-zero W . A way to do this is presented in
111 Powell *et al.* (2014), referred to as micro- ϕ (see below), and this approach has already been
112 used to generate most of the W involving ferrous end-members in the minerals in White *et*
113 *al.* (2014). Once the shape is established, what remains to be determined is the enthalpy
114 adjustment (ΔH , or DQF in THERMOCALC parlance) of the manganese end-members
115 already in the dataset (Holland & Powell, 2011), which involves the “historical” values
116 relating to the ideal-mixing-on-sites approach of Mahar *et al.* (1997).

117 In micro- ϕ , the idea is to implement an expectation that the a - x relations for the X - Y
118 subsystem of a mineral be related to the those of the Mg-Al subsystem, commonly the
119 subsystem that is best known experimentally. In this X might be, for example, Fe²⁺ or
120 Mn, and Y , Fe³⁺ or Cr. Here, the microscopic w of the X - Y subsystem is made
121 proportional to the Mg-Al subsystem with the proportionality represented by ϕ . This
122 allows the X - Y subsystem to be easily made less ($\phi < 1$) or more ($\phi > 1$) non-ideal than
123 the Mg-Al subsystem. The implementation of micro- ϕ starts with disassembling the
124 macroscopic W into their constituent microscopic same-site and cross-site w that arise

125 from pairwise interactions between the cations on the sites in the mineral (Powell &
 126 Holland, 1993). Then simplifications and approximations are made to these w using
 127 heuristics¹, before reassembling the macroscopic W . In Powell *et al.* (2014) and White *et*
 128 *al.* (2014), with $X = \text{Fe}^{2+}$ and $Y = \text{Fe}^{3+}$, the main heuristic values allowing
 129 parameterisation of the a - x relations are;

$$\begin{aligned}
 \phi &= 0.7 \\
 \phi_3 &= 0.8 \\
 w_{\text{FeMg,oct}} &= 4 \text{ kJ} \\
 w_{\text{MgAl,oct}} &= 10 \text{ kJ},
 \end{aligned}
 \tag{1}$$

130 in which ϕ has the effect, $w_{\text{FeX,oct}} = \phi w_{\text{MgX,oct}}$, where Mg, Fe^{2+} , and X are mixing on the
 131 octahedral site, oct. Thus, the Fe subsystem of a mineral can be made to have non-ideality
 132 that is proportional to that of the Mg subsystem with the proportionality arising from ϕ .
 133 Similarly, ϕ_3 has the effect, $w_{\text{YFe3,oct}} = \phi_3 w_{\text{YAl,oct}}$, the Fe^{3+} subsystem being made to have
 134 non-ideality that is proportional to that of the Al subsystem. In this way, for example,
 135 $w_{\text{FeFe3,oct}} = \phi \phi_3 w_{\text{MgAl,oct}}$. The two final values above are the microscopic interaction
 136 energies. These are discussed in detail in Powell *et al.* (2014), along with the additional
 137 necessary approximations involving the cross-site microscopic interaction energies.

138 If X is Mn, then ϕ_{Mn} needs to be specified, the following chosen heuristics being
 139 discussed below

$$\begin{aligned}
 \phi_{\text{Mn}} &= 0.7 \\
 w_{\text{FeMn,oct}} &= 2 \text{ kJ}
 \end{aligned}
 \tag{2}$$

140 making $w_{\text{MgMn,oct}} \approx 2.9 \text{ kJ}$, or rounded to 3 kJ for phases where little is known about the
 141 overall a - x relations of the mineral, keeping the W as whole numbers. Here, as opposed to
 142 the above, the value for $w_{\text{FeMn,oct}}$ is taken as known and the micro- ϕ approach is used to
 143 derive the value for $w_{\text{MgMn,oct}}$. Regarding the behaviour of Mn in mixing with Fe^{2+} and Mg,
 144 the data is very limited and no data exists for directly constraining Mn mixing properties
 145 involving octahedral sites in silicates. However, there is some information regarding garnet
 146 and ilmenite, through experiments on Fe–Mn exchange experiments (Pownceby *et al.*, 1987;
 147 Feenstra & Peters, 1996). As recognised by Pownceby *et al.* (1987), the sundry correlations

¹Heuristic is used here in the sense of an experience-based rule of thumb or educated guess, commonly in the context of providing a numerical value for a parameter or a relationship between parameters

148 between controlling thermodynamic parameters means that separating information about
 149 garnet from that of ilmenite via the experimental data is difficult. However, Pownceby *et*
 150 *al.* (1987) do argue that Fe–Mn interactions have to be slightly stronger in ilmenite than in
 151 garnet: they suggest on a single site basis $W_{\text{FeMn}}^{\text{ilm}} - \frac{1}{3}W_{\text{FeMn}}^{\text{g}} \approx 1.2$ kJ. Separately, O’Neill
 152 (1998) estimated from Fe–Mn exchange between ilmenite and olivine that
 153 $W_{\text{FeMn}}^{\text{ilm}} = 1.8 \pm 0.1$ kJ, with provisos about the thermodynamics of olivine. This value is
 154 also consistent with O’Neill *et al.* (1989), who derived $W_{\text{FeMn}}^{\text{ilm}} = 2.2 \pm 0.3$ kJ. This leads to
 155 our adoption of $W_{\text{FeMn}}^{\text{ilm}} = 2$ kJ. This then leads to $W_{\text{alm,spss}} = 3(W_{\text{FeMn}}^{\text{ilm}} - 1.2) \approx 2$ kJ.

156 Recently, Dachs *et al.* (2014) undertook a detailed analysis of Fe–Mn mixing in garnet
 157 and suggested almandine-spessartine mixing is asymmetric and a little more non-ideal than
 158 that adopted here, for more almandine-rich garnet. In the light of the discussion of the
 159 various experimental data by O’Neill (1998), adoption of the simpler, symmetric, model is
 160 defensible. Making the unavoidable step of carrying this value across to octahedral sites in
 161 silicates, leads to $w_{\text{MgMn,oct}} = 3$ kJ, once ϕ_{Mn} is chosen to be 0.7, given that this w is likely
 162 to be of the same order as $w_{\text{MgFe,oct}}$. The interaction energies that result from the adoption
 163 of these heuristics are given in Appendix 1. They should be seen in the context of the
 164 Appendix in White *et al.* (2014) for the way in which the approach of Powell & Holland
 165 (1993) and Holland & Powell (1996ab) for writing a - x relations is implemented.

166 The dataset of Holland & Powell (2011) contains data for all the manganese
 167 end-members above but their enthalpies are based on the original ideal-mixing calculations
 168 of Mahar *et al.* (1997). As these are superceded by the non-ideal mixing calculations
 169 presented here, the enthalpies of these end-members need to be modified. A reference point
 170 is provided by the properties of the pyrophanite and spessartine dataset end-members
 171 (Holland & Powell, 2011), as they are based on experimental data rather than being from
 172 Mahar *et al.* (1997). They provide an anchor for establishing manganese end-member
 173 properties for the other minerals. As in Mahar *et al.* (1997), the approach taken is to use
 174 Mg–Mn exchange reactions between the minerals using a natural assemblage database
 175 constructed for the purpose (Appendix 2). The database used for calibration is presented
 176 as Supplementary Information. Exchange reactions are good for calibration purposes as the
 177 resulting thermodynamic properties are not sensitive to the chosen P – T of the natural
 178 assemblages. This is the converse of saying that exchange reactions make bad thermometers
 179 because they are so sensitive to the thermodynamics. Such thermometers can easily lead to

180 strong bias in thermometric results (e.g. through poor thermodynamic formulation or
181 when ferric is ignored), e.g. Powell & Holland (2008). The exchange reactions used are the
182 Mg–Mn ones so as to minimise the consequences of difficulties with respect to ferric iron.
183 The derivation of the enthalpy modifications of the dataset via the Mn–Mg exchange
184 reactions is given in Appendix 3, completing the thermodynamic descriptions of the phases.

185 PHASE DIAGRAM CALCULATIONS

186 The phase diagrams presented here using the new a – x relations were calculated using
187 THERMOCALC version 3.37 and the internally-consistent end-member dataset of Holland &
188 Powell (2011), ds62 (created 6th February 2011). Calculations were undertaken in a range
189 of chemical systems ranging from MnO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O (MnKFMASH)
190 to MnO–Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O–TiO₂–O₂ (MnNCKFMASHTO).
191 The version of the Holland & Powell dataset used here is slightly newer than that used in
192 White *et al.* (2014) for modelling in NCKFMASHTO (ds61), though the differences in the
193 resulting diagrams from this are very minor.

194 In addition to the Mn-bearing minerals, garnet, orthopyroxene, cordierite, staurolite,
195 chlorite, chloritoid, biotite and ilmenite, the following minerals were considered in the
196 phase diagram calculations: sillimanite/kyanite/andalusite (sill/ky/and), spinel (sp),
197 muscovite (mu), paragonite (pa), margarite (ma), K-feldspar (ksp), plagioclase (pl), albite
198 (ab), epidote (ep), sphene (sph), magnetite (mt), rutile (ru), quartz (q) and melt (liq). For
199 the minerals not considered to be Mn-bearing, the a – x relationships of White *et al.* (2014)
200 were used for the white micas and silicate melt; Holland & Powell (2003) for feldspar,
201 White *et al.* (2000) for magnetite at subsolidus conditions, White *et al.* (2002) for
202 magnetite and spinel at suprasolidus conditions, and Holland & Powell (2011) for epidote.

203 MnKFMASH

204 P–T Projections and compatibility diagrams

205 In adding MnO to the KFMASH system, each of the invariant points in KFMASH becomes
206 a univariant line extending away from the KFMASH invariant, typically to lower P – T
207 conditions. The Mn content of the phases increase away from the invariant point. Where

208 the KFMASH invariant point is garnet bearing, the univariant that emanates from it may
 209 extend a considerable distance in P - T . By contrast, MnKFMASH univariant reactions
 210 that lack garnet typically only extend a short distance from their KFMASH origins before
 211 garnet appears at a new MnKFMASH invariant. A MnKFMASH grid is shown in Fig. 1
 212 for subsolidus (450 °C) to suprasolidus (950 °C) conditions. The Mn content of garnet
 213 ($m(g)$) along four of the univariant reactions is shown via the horizontal ticks along each
 214 reaction. The grid is relatively simple with only two invariant points. The suprasolidus
 215 univariant reactions extend only a short distance from their KFMASH origins before
 216 terminating in another subsystem. The first invariant point [opx cd ksp liq]—using the
 217 [absent phase] notation—occurs at ≈ 0.8 kbar and ≈ 480 °C and links the main univariant
 218 reactions seen in the subsolidus part of the grid. Details of the reactions that emanate from
 219 this point are shown in the oval shaped inset in Fig. 1. The second invariant point [opx st
 220 chl ctd] occurs where the muscovite breakdown reaction intersects the wet solidus (≈ 5.8
 221 kbar, ≈ 725 °C). For P - T conditions below the solidus and the muscovite breakdown
 222 reaction there are four univariant reactions that could be seen under typical crustal
 223 metamorphic conditions. These reactions, in order of increasing T are;



and



224 where als represents the stable aluminosilicate of and, sill and ky. A singularity occurs
 225 along reaction 6 involving als swapping sides of the reaction at lower pressure. For
 226 reactions 3–5, which all emanate from KFMASH invariant points, each represents a
 227 garnet-bearing equivalent to the garnet-absent reaction from each KFMASH invariant
 228 (White *et al.*, 2014), with the KFMASH and MNKFMASH reactions typically occurring
 229 only a few degrees apart for most of their length because the incorporation of Mn is minor

230 in all of the phases apart from garnet. As a consequence, the garnet-absent assemblage
231 possible for each MnKFMASH reaction (e.g. ky–st–ctd–chl for below reaction 3) typically
232 has a very limited P – T stability range between the KFMASH and MNKFMASH reactions.

233 The phase relationships relating to the low variance MnKFMASH equilibria (with $v =$
234 1–3) can also be shown in compatibility diagrams, that additionally show the composition
235 space that these equilibria occupy. A series of AFM and MnFM compatibility triangles are
236 shown in Fig. 2 and Fig. 3 respectively for the P – T conditions shown on Fig. 1 as small
237 triangles. The AFM triangles (Fig. 2) have garnet, quartz, muscovite and H₂O in excess
238 and the MnFM diagrams (Fig. 3) have aluminosilicate, quartz, muscovite and H₂O in
239 excess.

240 The AFM compatibility diagrams are shown for an isobaric transect at 4.5 kbar (Fig.
241 2a–f) at the P – T conditions shown as open triangles in Fig. 1. As garnet is taken as
242 in-excess, these diagrams show the changing stable divariant to quadrivariant equilibria
243 amongst the remaining ferromagnesian phases and aluminosilicate. The sequence of AFM
244 diagrams shows the changes in stable tie-triangles on crossing each of the univariant
245 reactions 3–5. For example Fig. 2a and Fig. 2b illustrate the breakdown of the ky–ctd
246 tie-line and the formation of the st–chl tie line on crossing reaction 3, with the phases
247 involved having very similar compositions to those expected in the MnO-free system.

248 The mineral composition relationships either side of reaction 3 are shown in a sequence
249 of MnFM compatibility triangles (Fig. 3) calculated for pressures of 12 kbar and 6 kbar
250 (filled triangles on Fig 1). These diagrams show the varying size of the garnet one-phase
251 field as a function of pressure along the reaction. As these diagrams are calculated with
252 kyanite in excess, they are only appropriate for rather aluminous compositions. For the
253 diagrams at 12 kbar (Fig. 3a, b), the garnet one-phase field is relatively large and extends
254 a considerable distance from the MnO apex towards the FeO apex. Chlorite, staurolite
255 and, where present, chloritoid all plot at low MnO contents. Thus, rocks with only small
256 amounts of MnO may contain garnet at these conditions. At T below the reaction, two
257 stable divariant assemblages occur (g–st–ctd and g–chl–ctd). As discussed above, the
258 garnet-absent tie triangle (st–ctd–chl) is not stable at these conditions, but appears from
259 the base of the compatibility triangle less than 0.1 °C below the MnKFMASH univariant.
260 Above the reaction only one stable tie triangle exists, and, as kyanite is in excess, this
261 reaction is a terminal chloritoid reaction.

262 The diagrams at 6 kbar (Fig. 3c, d) show substantially reduced garnet one-phase fields
 263 in comparison with those at 12 kbar and the other phases (especially staurolite and
 264 chloritoid) may incorporate substantially more MnO before garnet must become stable.
 265 Thus, garnet is limited to somewhat higher bulk rock MnO contents and is considerably
 266 more MnO rich than at higher P .

267 Pseudosections

268 The MnKFMASH system is useful for demonstrating the effect of adding MnO on the
 269 stability of key assemblages. Figure 4 shows the predicted assemblages for three different
 270 bulk compositions with different $x_{\text{Fe}} = \text{FeO}/(\text{FeO} + \text{MgO})$ and $x_{\text{Al}} = \text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{FeO}$
 271 $+ \text{MgO})$ proportions. Figure 4a is a P - T pseudosection from 450 °C to 950 °C and for the
 272 same composition as used for fig. 4 in White *et al.* (2014) but with 0.1 mol. % MnO.
 273 Pseudosections are also presented for subsolidus conditions for a more magnesian
 274 composition (Fig. 4b) and a more magnesian and more aluminous composition (Fig. 4c),
 275 each with an MnO content of ≈ 0.1 mol. % (see Table 1 for exact compositions used). The
 276 two lower x_{Al} pseudosections (Fig. 4a, b) are topologically similar, containing largely the
 277 same assemblage fields.

278 The pseudosections are dominated by divariant to quadrivariant fields. However, a
 279 short segment of the MnKFMASH reaction 5 is seen in each pseudosection. This reaction
 280 controls the disposition of the main divariant fields seen in each diagram. Each of these
 281 divariant fields is equivalent to a univariant equilibria stable in the KFMASH system and
 282 are little displaced in P - T from the KFMASH univariants. For example the divariant
 283 g-st-chl-bi field in each pseudosection is equivalent to the KFMASH univariant reaction:



284 In Fig. 4, the garnet-in lines for a bulk rock MnO content of 0.05 (dashed red line
 285 labelled MnO=0.05) and for the MnO-free system (red line labelled MnO=0) are also
 286 shown. These garnet-in lines illustrate the relationship between the bulk MnO content and
 287 the P - T stability of garnet, with the garnet-in lines moving down T and P relative to the
 288 MnO-absent garnet-in lines. At lower T (greenschist facies) the garnet-in boundaries are
 289 relatively steep such that the main effect of adding MnO is a shift to lower T of the
 290 garnet-in line. Under amphibolite facies conditions, the garnet-in line is somewhat flatter

291 such that the main effect of adding MnO is to increase garnet stability down P . The
292 combination of these two features results in the greatest displacement of the garnet-in line
293 occurring at close to 500 °C where it forms a distinct wedge that may extend to the base of
294 the diagram. Thus, at low P the calculations predict the appearance of garnet soon
295 followed by its disappearance. However, in reality, such a narrow field could conceivably be
296 crossed with no garnet growth having occurred.

297 A noticeable feature of all three pseudosections is the small triangular field of
298 garnet-absent assemblages within the overall garnet stability field. These garnet-absent
299 fields each emanate from the divariant g–st–chl–bi fields in Figs 4a–c and reflect the fact
300 that garnet is a reactant in reaction 7. The high- T boundary of this garnet absent field is
301 defined by the equivalent to the garnet producing KFMASH reaction,



302 Thus, along a prograde path, the calculations predict the appearance, disappearance and
303 reappearance of garnet.

304 While the stability of subsolidus garnet-bearing assemblages is strongly influenced by
305 MnO, the high temperature assemblages are significantly less so. At temperatures above
306 about 750 °C the addition of 0.1 mol. % MnO to the bulk rock composition stabilises
307 garnet down pressure by less than 1 kbar (Fig. 4a). For upper amphibolite facies
308 conditions, manganese can have significant effect on garnet stability, particularly at 3–5
309 kbar where the presence of MnO may substantially extend g–sill–bi and
310 g–sill–cd–bi-bearing assemblages to lower P – T .

311 **MnNCKFMASHTO**

312 The addition of MnO to the NCKFMASHTO calculations presented in White *et al.* (2014)
313 results in the MnNCKFMASHTO system that closely approximates the composition space
314 of natural metapelites. Thus, this system is potentially useful for applied phase equilibria
315 modelling studies.

316 Figure 5 is a P – T pseudosection based on the composition used for fig. 5b presented in
317 White *et al.* (2014), but with 0.1 mol % MnO. Garnet-in lines are additionally shown for
318 the MnO-free system and for MnO contents of 0.05 and 0.15. As with the MnKFMASH
319 calculations, the addition of MnO has a profound affect on the stability of garnet with

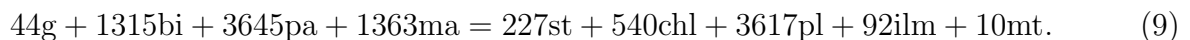
320 garnet-bearing assemblages stabilised to lower P and T . Otherwise, Fig. 5 is very similar
321 to the equivalent pseudosection in White *et al.* (2014), with the same main assemblages
322 present. Garnet-bearing assemblages are limited to pressures above about 7 kbar and
323 temperatures above about 550 °C for the MnO-free system but stabilised to pressures as
324 low as 2 kbar and temperatures close to 500 °C with 0.1 mol % MnO. As with the
325 MnKFMASH calculations, the main effect of adding MnO is to lower the temperature of
326 garnet stability in greenschist-facies assemblages and to lower the pressure of garnet
327 stability in amphibolite-facies assemblages. At pressures above 2 kbar, garnet first appears
328 in a series of g–chl–bi-bearing fields that may additionally involve combinations of
329 paragonite, epidote, plagioclase, ilmenite and magnetite. At higher temperature, the lower
330 pressure limit of garnet-bearing assemblages involves g–and–bi- and g–sill–bi-bearing
331 assemblages, in contrast to its restriction to ky-bearing assemblages in the MnO-free
332 system. A small, triangular garnet-absent field is also present in Fig. 5 related to the
333 higher variance equivalent to reaction 7.

334 Figure 6 shows the phase relations for a more aluminous composition, based on that of
335 fig. 7 in White *et al.* (2014). As with the pseudosection in fig. 7 of White *et al.* (2014),
336 Fig. 6 contains a series of chloritoid-bearing fields, a restricted stability range for biotite
337 and an enhanced stability field for the aluminosilicates compared with Fig. 5. At pressures
338 above about 4 kbar, the first appearance of garnet occurs in a series of biotite-absent
339 assemblages involving combinations of garnet, chlorite, staurolite and chloritoid. Under
340 greenschist-facies conditions the effect of MnO on garnet stability is less profound than in
341 the less aluminous composition, with the garnet-in line moving down T by about 30 °C
342 with the addition of 0.1 mol. % MnO. A large embayment in the garnet-in boundary exists
343 at close to 4 kbar, with the garnet-in line trending from about 540 °C at \approx 3.8 kbar up to
344 about 640 °C at \approx 5.8 kbar before trending back down P and T to about 510 °C and 1.6
345 kbar. This embayment can also be seen in the garnet-in line for the bulk MnO content of
346 0.05 mol. %, shown as a dashed red line. Like with the triangular garnet-absent fields
347 described above, this embayment is controlled by the higher variance equivalents of
348 reaction 7 consuming garnet and reaction 8 producing it.

349 Ague (1991) compiled two average metapelite compositions, one for greenschist facies
350 metapelites and one for amphibolite facies metapelites. Although these two compositions
351 are broadly similar, there are notable differences in composition between the two, including

352 in the bulk MnO content (Ague, 1991). In comparison with the compositions used above,
353 the average metapelite compositions in Ague (1991) have higher CaO and Na₂O contents,
354 but are otherwise similar to the composition used for Fig. 5, albeit with a lower x_{Fe} .

355 Figure 7 is a P - T pseudosection for the low-grade composition from Ague (1991). A
356 small adjustment to the CaO content was made to account for the likely presence of apatite
357 and the $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$ ratio was arbitrarily set at 0.077. For Fig. 7, the MnO
358 content (0.284 mol. %) is higher than that used in the preceding diagrams (0.1) so that
359 most of the diagram is garnet-bearing. Garnet-absent assemblages are restricted to a small
360 window in the bottom left of the diagram and a second at low pressure at $T > 500$ °C. The
361 garnet-in lines for bulk MnO contents of 0.15 and 0.05 mol. % are additionally shown on
362 the diagram. These two garnet-in lines are similar in shape and position to the equivalent
363 ones in Fig. 5. Topologically, the disposition of the main AFM ferromagnesian assemblages
364 in Fig. 7 is similar to that in Fig. 5, with the exception of the extent of garnet stability
365 and, due to the more magnesian composition for Fig. 7, the appearance of kyanite-bearing
366 fields in Fig. 7. As with the NCKFMASHTO calculations presented in White *et al.* (2014),
367 the large number of potential phases stable in these diagrams allows for the possibility of
368 univariant reactions to be stable. In Fig. 7 short segments of two univariant reactions are
369 seen at conditions close to 6 kbar and 540–580 °C and are linked by narrow divariant fields.
370 Each of these univariant reactions involve nine phases (excluding in-excess phases) and are
371 dominated by large reaction coefficients for the micas and plagioclase and relatively small
372 coefficients for the ferromagnesian phases and the oxide phases, with the exception of
373 biotite. For example the higher temperature reaction of the two at 5.6 kbar is,



374 Given the issues outlined in White *et al.* (2014) regarding margarite stability it is possible
375 that the presence of these two univariants in the pseudosection is anomalous, though they
376 may be stable in a grid.

377 A P - T pseudosection for the amphibolite-facies metapelite composition from Ague
378 (1991) is shown in Fig. 8. Here, the $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$ ratio was set at 0.081 but the
379 CaO content was not reduced. The MnO content ($\text{MnO} = 0.175$) is lower than that for
380 Fig. 7, resulting in a more restricted field for garnet stability. The two univariant reactions
381 present in Fig. 7 are also seen in this bulk composition and both diagrams are topologically
382 very similar in terms of the main assemblage fields. As with many of the other

383 pseudosections, a small garnet-absent field occurs within the larger area of garnet presence.
384 Garnet-in lines are additionally shown for bulk MnO contents of 0, 0.05, 0.1 and 0.15 mol.
385 %. As with the diagrams presented earlier, the addition of MnO drives the garnet-in line
386 down T under greenschist facies conditions and down P under amphibolite facies
387 conditions, with a wedge-shaped pressure minima for garnet at approximately 2 kbar and
388 520 °C involving the assemblage g-and-chl-bi-pl-ilm-mt. In the MnO free system the
389 stability of garnet-bearing assemblages is restricted to pressures above about 7.5 kbar (see
390 White *et al.* (2014, fig. 11) for the corresponding NCKFMASHTO pseudosection).

391 The effect of MnO at higher metamorphic grades is shown on a P - T pseudosection
392 (Fig. 9) calculated for the amphibolite-facies metapelite composition from Ague (1991).
393 Under amphibolite-facies conditions MnO exerts a significant effect on the stability of
394 garnet-bearing assemblages. At temperatures below the muscovite breakdown reaction, the
395 addition of 0.175 mol. % MnO shifts the garnet in line down approximately 3 kbar relative
396 to the MnO-absent system. Between the muscovite breakdown reaction and the first
397 appearance of cordierite, the garnet-in line is steep and displaced close to 80 °C down T
398 relative to the manganese-free system. Overall this greatly expands the P - T range of
399 g-sill-bi-bearing assemblages relative to that in the MnO-free system. At temperatures
400 above the appearance of cordierite the effect of adding MnO is less profound, with, for
401 example, the garnet in line now located less than 1 kbar lower than for the MnO-free
402 system at 850 °C.

403 The effect of considering MnO in calculations can be further addressed via T - x_{MnO}
404 and P - x_{MnO} pseudosections such as Fig. 10, based on the greenschist-facies composition
405 from Ague (1991). Figure 10a is a T - x_{MnO} pseudosection constructed for a pressure of 6
406 kbar to illustrate the down-temperature shift of the garnet-in line as a function of MnO
407 content. The x axis varies from MnO = 0 to MnO = 0.3 mol %. At low MnO contents
408 ($x < 0.15$) garnet is absent from the assemblages over the whole temperature range
409 considered. The garnet-in line generally trends to lower T with increasing MnO, but with
410 several switch-backs, especially at temperatures above 590 °C, a feature that can also be
411 seen in the garnet-in line for MnO = 0.05 in Fig. 7.

412 A P - x_{MnO} pseudosection calculated for a temperature of 580 °C for the same
413 composition range is shown in Fig. 10b and shows the down-pressure shift of the garnet-in
414 line as a function of bulk rock MnO content. In the MnO-free system, garnet-bearing

415 assemblages are restricted to pressures of above 8.5 kbar for this composition but get as
416 low as 1.5 kbar for MnO contents above 0.27 mol %. A switch-back in the garnet-in line
417 occurs at close to 4 kbar related to the up pressure consumption of garnet through the
418 higher-variance equivalent of reaction 8. In both the $T-x_{\text{MnO}}$ and $P-x_{\text{MnO}}$ pseudosections
419 the P and T conditions for the main assemblages are little influenced by the consideration
420 of MnO with most assemblages forming near horizontal bands across each diagram.

421 The pseudosections in Fig. 10 are also contoured for garnet mode. The garnet mode
422 contours in both diagrams broadly parallel the garnet-in boundary reflecting the variable
423 consumption or production of garnet as P or T conditions evolve. For Fig. 10a garnet is
424 not stable for low MnO contents, such that the garnet-bearing assemblages in the diagram
425 are a direct consequence of the addition of MnO. Despite the large increase in the overall
426 stability of garnet-bearing assemblages, the addition of MnO results in only small
427 proportions of garnet being stable ($< 3\%$) for the highest bulk MnO contents considered
428 here. The maximum garnet contents are achieved at temperatures just below 590 °C at the
429 low- T boundary (st-out) of the assemblage g-st-bi-pl-ilm-mt. For temperatures
430 below this, relatively little garnet is produced for close to 50–100 °C above the garnet-in
431 line. For example, at $x = 0.5$ garnet proportions only reach 1% approximately 100 °C
432 above the initial appearance of garnet.

433 For the $P-x_{\text{MnO}}$ pseudosection Fig. 10b the garnet mode contours are similarly sub
434 parallel to the garnet-in line. However, unlike the $T-x_{\text{MnO}}$ pseudosection garnet does
435 become stable in the MnO-free system at about 8.5 kbar. As with the $T-x_{\text{MnO}}$ diagram,
436 the mode of garnet remains low for a considerable pressure above the garnet in line. For
437 example at $x = 0.7$ the calculations predict less than 1% garnet for 3 kbar above the initial
438 appearance of garnet. However, at higher MnO contents garnet modes above 4% are
439 possible. In general, the mode of garnet increases with increasing pressure with the
440 exception of the narrow field (g-sill-st-bi-pl-ilm-mt) across which garnet is consumed. A
441 notable increase in the mode of garnet occurs across the narrow set of divariant fields and
442 the section of univariant equilibria (at $x < 0.75$) close to 5.6 kbar.

DISCUSSION AND CONCLUSIONS

The extension of the NCKFMASHTO $a-x$ relations presented in White *et al.* (2014) to include MnO provides a chemical system for phase diagram calculations (MnNCKFMASHTO) that closely matches that of natural metapelites and metapsammites. Importantly, the $a-x$ relations in both MnO-bearing and MnO-absent systems are thermodynamically consistent, with the Mn-end-member properties calibrated in concert with the $a-x$ relations presented in White *et al.* (2014). This contrasts with many previous sets of MnO-bearing $a-x$ relations in which the Mn-end-member properties (DQF adjustments) from Mahar *et al.* (1997) were coupled with the extant version of the Holland & Powell end-member dataset and NCKFMASHTO $a-x$ relations of the time. This resulted in inherent inconsistencies within the models, with such inconsistencies becoming more problematic as the NCKFMASHTO $a-x$ relations evolved. The thermodynamic descriptions of the Mn-bearing minerals are built on the $a-x$ development approach referred to as micro- ϕ of Powell *et al.* (2014), as detailed in the body of the paper and in Appendix 1. This approach is designed for situations where little is known about the $a-x$ relations, which is true for Mn incorporation in the the minerals being considered here, apart from garnet and ilmenite. Once the $a-x$ relations were established the enthalpy modifications to the dataset properties of Holland & Powell (2011) were derived from a large database of natural coexisting minerals in metapelites (see Appendix 2–3).

The components of the MnNCKFMASHTO system commonly account for more than 98% of the mass of common metapelitic to metapsammitic rocks. Despite being a relatively minor component of metapelites, MnO exerts an important influence on the $P-T$ stability of garnet-bearing assemblages. Other than the stabilisation of garnet, the presence of MnO has little effect on the $P-T$ conditions of common assemblages. At higher grades, the effect of MnO on the $P-T$ extent of garnet-bearing assemblages is less profound, as most metapelite compositions will be garnet-bearing regardless at such conditions. Thus, for many high- T studies, inclusion of MnO is likely to have little effect on the resulting estimates of $P-T$ conditions, unless the appearance or absence of garnet is of central importance. However, for modelling of transitional amphibolite to granulite facies assemblages or high-grade metamorphism at low pressures, consideration of MnO may strongly influence the interpretation of $P-T$ conditions.

474 Although MnO greatly expands garnet stability to lower P - T conditions, the resulting
475 mode of garnet commonly remains low until higher variance equivalents to
476 garnet-producing KFMASH reactions are crossed. This can be seen in Fig. 10 which is
477 contoured for garnet mode. Thus, garnet-rich rocks metamorphosed at P - T conditions
478 outside the MnO-free stability field of garnet are likely to be rather rich in MnO compared
479 to typical metapelites.

480 The phase diagrams presented here reproduce the main assemblages seen in common
481 metapelites, at least for typical MnO contents $\text{MnO} < 0.3 \text{ wt } \%$ (e.g. Ague 1991; Atherton
482 and Brotherton, 1982). Furthermore, using the amphibolite facies average metapelite
483 composition from Ague (1991) as an example (Fig. 8), key features such as the garnet,
484 staurolite, kyanite and silimanite isograds occur in the correct order along typical
485 metamorphic field gradients inferred for barrovian metamorphism, with the biotite isograd
486 occurring off the diagram at $T = 400\text{--}450 \text{ }^\circ\text{C}$. For higher MnO contents, such as in Fig. 7,
487 the garnet and biotite isograds could potentially swap positions but the other isograds
488 would be unaffected.

489 In application, these models may be less reliable for bulk rock compositions much
490 richer in MnO. Furthermore, as Mn can occur in several oxidation states in rocks,
491 compositions rich in Mn_2O_3 for example are not suitable for calculations with these
492 models. As with Fe, it is likely that all rocks contain some mixture of MnO and Mn_2O_3 ,
493 and successful modelling of many rocks may require that small adjustments be made to the
494 bulk rock composition. Such adjustments should be petrographically and geochemically
495 justified, via identification of Mn in phases in which it is likely to be in the Mn^{3+} state (e.g.
496 Mn^{3+} in andalusite, epidote/piedmontite) where possible.

497 Additionally, MnO is not considered in several key high T phases (e.g. melt,
498 sapphirine, osumilite) nor has the veracity of the Mn-end-member and mixing properties
499 been tested at these conditions. Calculated phase equilibria at higher T conditions could
500 be erroneous, at least until Mn is incorporated in the thermodynamic descriptions of these
501 phases.

502 Despite the considerable progress in the development of a - x relations for complex
503 multi-component minerals over the last ten years (e.g. White *et al.*, 2007; Green *et al.*,
504 2007; Diener *et al.* 2007; Tajčmanová, et al., 2009; Diener & Powell, 2012) there remain
505 considerable challenges and inconsistencies. As discussed in White *et al.* (2014) the

506 persistence of margarite-bearing fields in common metapelite compositions represents one
507 such challenge, and it would appear at this stage that an appraisal of how the
508 Na₂O–CaO–K₂O-bearing phases (mica feldspar and epidote) are interacting in the large
509 systems is required. In addition to uncertainties associated with the *a*–*x* relations
510 themselves, there are considerable uncertainties regarding oxidation state of several key
511 elements including Mn. To these may be added many geologically-based sources of
512 uncertainty such as in relation to equilibrium volume, including fractionation of
513 components into porphyroblast cores, composition of co-existing fluids and open system
514 behaviour. Given these caveats interpretations that use the results literally, such as to
515 interpret the degree of overstep of reactions based on intersecting compositional isopleths
516 are unlikely to be defensible. Thus, the *a*–*x* relations presented here and phase diagrams
517 produced from their use are better thought of as a thermodynamic framework in which to
518 interpret metamorphic features rather than a literal and absolute solution. However, these
519 limitations should not prevent the quantitative assessment of metamorphic conditions, but
520 rather should prompt an appropriate degree of uncertainty to be attached to such results.

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781 **APPENDIX 1: Interaction energies**

782 Following the adoption of micro- ϕ for the incorporation of the Mn-end-members in the
 783 minerals, as discussed in the text, along with the interaction energies from White *et al.*
 784 (2014), the interaction energies W_{ij} in matrix form are:

g	py	gr	kho	spss
alm	2.5	5	22.6	2
py		31	5.4	2
gr			-15.3	0
kho				29.4

chl	afchl	ames	daph	ochl1	ochl4	f3clin	mnchl
clin	17	17	20	30	21	2	15
afchl		16	37	20	4	15	32
ames			30	29	13	19	26
daph				18	33	22	10
ochl1					24	28.6	25
ochl4						19	31
f3clin							17

bi	ann	obi	east	tbi	fbi	mn
phl	12	4	10	30	8	9
ann		8	15	32	13.6	6.3
obi			7	24	5.6	8.1
east				40	1	13
tbi					40	30
fbi						11.6

st	fst	mnst	msto	mstt
mst	16	12	2	20
fst		8	18	36
mnst			14	32
msto				30

ctd	fctd	mnctd	ctdo
mctd	4	3	1
fctd		3	5
mnctd			4

cd	ferd	herd	mncrd
crd	8	0	6
ferd		9	4
herd			6

opx	fs	fm	mgts	fopx	mnopx	odi
en	7	4	$13 - 0.15P$	$11 - 0.15P$	5	$32.2 + 0.12P$
fs		4	$13 - 0.15P$	$11.6 - 0.15P$	4.2	$25.54 + 0.084P$
fm			$17 - 0.15P$	$15 - 0.15P$	5.1	$22.54 + 0.084P$
mgts				1	$12 - 0.15P$	$75.4 - 0.94P$
fopx					$10.6 - 0.15P$	$73.4 - 0.94P$
mnopx						$24.54 + 0.084P$

ilm	dilm	hem	geik	pnt
oilm	15.6	26.6	4	2
dilm		11	4	2
hem			36	25
geik				4

APPENDIX 2: Natural assemblage data

A natural assemblage database has been assembled with the focus on mineral assemblages from rocks with a range of MnO content (see Supplementary material). The analyses given in the supplementary material were taken from the following: 1, Grew (1981) — rutile present; 2, Hauzenberger *et al.* (2001); 3, Sevigny & Ghent (1989); 4, Redler (2011); 5, Kunz (2011); 6, Fraser *et al.* (2000); 7, Bickle & Archibald (1984); 8, Bosse *et al.* (2002); 9, Blümel & Schreyer (1977); 10, Droop & Moazzen (2007); 11, Álvarez-Valero *et al.* (2007) — El Hoyazo locality; 12, Fletcher & Greenwood (1979); 13, Ghent & De Vries (1972); 14, Greenfield (1997); 15, Grew (1981)— rutile absent; 16, Guidotti (1974) — supp. data; 17, Guidotti (1974); 18, Harris (1976); 19, Hodges & Spear (1982); 20, Kamineni (1975); 21, Kawakami *et al.* (2007); 22, Likhanov *et al.* (2001); 23, Lui (2004); 24, Mather (1970); 25, Álvarez-Valero *et al.* (2007) — Mazarrón locality; 26, Mposkos (1989); 27, Novak & Holdaway (1981); 28, Otamendi *et al.* (1999); 29, Pomroy (2004); 30, Pattison & Vogl (2005); 31, Tiddy (2002); 32, Johnson *et al.* (2004); 33, Vilà *et al.* (2007); 34, West *et al.* (2008); 35, Williams & Grambling, (1990); 36, White (1997); 37, Waters & Whales (1984); 38, Stewart (1942); 39, Thompson *et al.* (1977); 40, Atherton (1968); 41, Heald (1940); 42, Green (1963); 43, Leake (1958); 44, Chinner (1960); 45, Miyashiro (1953); 46, Engel & Engel (1960); 47, Phinney (1963); 48, Albee (1965); 49, Hietanen (1956) 50, Chinner (1967); 51, Reinhardt (1968); 52, Davidson & Matheson (1974); 53, Kays & Medaris (1976); 54, Chinner (1962); 55, Herman *et al.* (1978); 56, Patiño Douce & Beard (1995); 57, Patiño Douce & Beard (1996); 58, Patiño Douce *et al.* (1993); 59, Vielzeuf & Montel (1997).

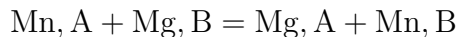
A proportion of the data involved wet chemical analyses, with analysed FeO and Fe₂O₃. The data for the remainder of the analyses involve all-Fe-as-FeO. Given the large uncertainties in calculated ferrous-ferric that arise from charge balance calculations (e.g. Powell & Holland, 2008), with the added difficulty of the reliability of stoichiometric constraints for hydrous minerals, the approach followed for analyses involving all-Fe-as-FeO is to adopt heuristics for conversion of FeO to Fe₂O₃: as proportions, $cd = 0$; $ctd = 0.02$; $g = 0.03$; $opx = 0.05$; $chl = 0.1$; $st = 0.1$; and $bi = 0.15$ (see also the Appendix in White *et al.*, 2014). Given that Mg–Mn exchange reactions are used in the data analysis, the precise values used for the conversion are not important, but it is appropriate to have them in what is considered to be a petrologically consistent order. Charge balance is used to

816 recalculate the ilmenite analyses.

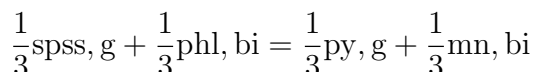
817 Processing of the analyses involves mineral calculation in the commonly-used way, on a
818 specified number of oxygens, and assuming the full complement of hydroxyls for the
819 hydrous minerals (except for biotite as a consequence of the oxy-substitution used for Ti).
820 The cations are then used to calculate the composition parameters as defined in the
821 Appendix of White *et al.* (2014). The order parameters, Q , for the Fe–Mg order-disorder
822 in the minerals (and the Mg–Al order-disorder in chlorite) are calculated by solving the
823 appropriate internal equilibria in each mineral using the a - x relations given in Appendix 1,
824 and the ΔH of the internal equilibria given in the Appendix of White *et al.* (2014).

APPENDIX 3: Processing the natural assemblage data

The Mg-Mn exchange reactions can be written in a standard form, involving one cation exchange between minerals A and B, with A-B for Mg-Mn meaning



or as an example, g-bi for Mg-Mn meaning that we are considering the equilibrium involving



The thermodynamics, in the form $\Delta h = \Delta G^\circ + RT \ln K$, are evaluated for each such reaction for each appropriate natural assemblage mineral pair. In this, ΔG° is calculated using Holland & Powell (2011), and K is calculated from the compositional and order parameters calculated from the mineral compositions as outlined in Appendix 2. Δh can be thought of as a ΔDQF on a one cation exchange basis. Given that the enthalpies of the magnesian end-members are taken to be well-known, Δh relates just to the manganese end-members, e.g. for the above example.

$$\Delta h_{\text{g,bi}} = -\frac{1}{3}\text{DQF}_{\text{spss,g}} + \frac{1}{3}\text{DQF}_{\text{mn,bi}}$$

As noted above, the properties of the pyrophanite and spessartine end-members in the Holland & Powell (2011) dataset are not based on Mahar *et al.* (1997). Therefore, in principle, this means that

$$\Delta h_{\text{g,ilm}} = -\frac{1}{3}\text{DQF}_{\text{spss,g}} + \text{DQF}_{\text{pnt,ilm}} = 0$$

This can be assessed with the database here, and Fig. A3-1a,b shows that this is the case within error (49 data points). In Fig. A3-2, a selection of Δh plots show the nature of the data, the dotted line being the median of the data, the band representing its uncertainty (see below), and the solid line the result of the least squares analysis of all of the data below.

In the following table, n is the number of mineral pairs involved. Δh is the median of the natural assemblage values; $\sigma_{\Delta h}^{\text{distr}}$ is an estimate of the standard deviation on this value using the normalised median absolute deviation, nMAD (e.g. Powell *et al.*, 2002). Medians are used to try and downplay the effect of the scatter and outliers in the data. Treating

849 $\sigma_{\Delta h}^{\text{distr}}$ now as a Gaussian estimate of standard deviation on the distribution of the data, this
850 divided by the square root of the number of data gives an estimate of the standard
851 deviation on the mean of Δh . This is what would then used to represent the data in the
852 next stage of the data, if the data are homoscedastic, in other words if they are all
853 uncorrelated. But the data are most likely correlated given that they are not individually
854 from separate studies. As a gross approximation to account for this, we use $\sigma_{\Delta h} = 2\sigma_{\Delta h}^{\text{mean}}$,
855 the last column of the following table. That this is appropriate is established *a posteriori*
856 below. the uncertainty bands in Figs A3-1, A3-2 are for $2\sigma_{\Delta h}$

A	B	n	Δh	$\sigma_{\Delta h}^{\text{distr}}$	$2\sigma_{\Delta h}^{\text{mean}}$
g	bi	149	2.623	3.821	0.626
g	chl	22	3.585	6.595	2.812
g	cd	27	4.815	9.239	3.556
g	ctd	25	1.298	4.340	1.736
g	st	47	-0.325	1.661	0.484
g	opx	23	-0.964	4.814	2.008
bi	chl	29	0.490	2.803	1.041
bi	cd	64	-1.639	3.132	0.783
bi	st	43	-1.087	3.308	1.009
bi	opx	52	-6.338	5.661	1.570
chl	cd	8	0.765	1.476	1.044
chl	ctd	13	-5.632	2.628	1.685
chl	st	11	-2.448	1.084	0.654
cd	opx	13	-8.310	4.593	2.548
ctd	st	14	0.180	3.181	1.701

857 Determining the “best” Δh values from this table is a weighted least squares problem.
858 Assuming that there is no enthalpy modification needed for spessartine, the analysis gives
859 the enthalpy modifications for the individual manganese end-members, on a one cation

860 basis

	bi	chl	cd	ctd	st	opx
h	-2.63	-2.61	-2.10	0.66	-0.04	3.34

861

862 Multiplied by the number of Mn in the end-member formulae, this gives the DQF of the
 863 manganese end-members

	bi	chl	cd	ctd	st	opx
DQF	-7.89	-13.03	-4.21	0.66	-0.17	6.68

864

865 The σ_{fit} of the least squares is 1.24, reflecting that the σ_h used were not inappropriate. The
 866 correlation coefficient matrix of the DQF is:

ρ	bi	chl	cd	ctd	st	opx
bi	1	0.429	0.526	0.131	0.337	0.275
chl	0.429	1	0.445	0.267	0.508	0.144
cd	0.526	0.445	1	0.126	0.275	0.232
ctd	0.131	0.267	0.126	1	0.237	0.043
st	0.337	0.508	0.275	0.237	1	0.105
opx	0.275	0.144	0.232	0.043	0.105	1

Casting the least squares result in the original form, we get:

A	B	Δh^{obs}	$2\sigma_{h^{\text{obs}}}$	Δh^{calc}	$2\sigma_{h^{\text{calc}}}$	e	e^*
g	bi	2.62	1.25	2.63	1.45	0.01	0.01
g	chl	3.58	5.62	2.61	1.76	-0.98	-0.35
g	cd	4.82	7.11	2.10	2.19	-2.71	-0.76
g	ctd	1.30	3.47	-0.66	3.05	-1.96	-1.13
g	st	-0.32	0.97	0.04	1.24	0.37	0.76
g	opx	-0.96	4.02	-3.34	3.44	-2.38	-1.18
bi	chl	0.49	2.08	-0.02	1.74	-0.51	-0.49
bi	cd	-1.64	1.57	-0.53	1.88	1.11	1.42
bi	st	-1.09	2.02	-2.59	1.56	-1.50	-1.49
bi	opx	-6.34	3.14	-5.97	3.35	0.37	0.23
chl	cd	0.76	2.09	-0.50	2.11	-1.27	-1.21
chl	ctd	-5.63	3.37	-3.27	3.09	2.36	1.40
chl	st	-2.45	1.31	-2.56	1.56	-0.12	-0.18
cd	opx	-8.31	5.10	-5.45	3.63	2.86	1.12
ctd	st	0.18	3.40	0.71	3.01	0.53	0.31

868 This shows that the fit of the data is good, with $e = \Delta h^{\text{calc}} - \Delta h^{\text{obs}}$ the residuals, and e^*

869 the residuals normalised to the original specified uncertainties on the data, $\sigma_{h^{\text{obs}}}$.

Figure captions

Fig. 1: Petrogenetic grids in the MnKFMASH system for subsolidus and suprasolidus conditions. The square inset shows the in-excess phases used in the different parts of the diagram. The horizontal ticks on select univariants give the value of $m(g)$ of garnet along the reaction. The set of open triangles at 4.5 kbar indicate the P - T conditions for the AFM compatibility triangles in Fig. 2. The filled triangles at 12 and 6 kbar show the conditions for the MnO-FeO-MgO compatibility triangles in Fig. 3

Fig. 2: Al_2O_3 -FeO-MgO (AFM) compatibility triangles for a sequence of temperatures at 4.5 kbar. The MnKFMASH system is reduced to AFM by taking garnet, muscovite, quartz and H_2O to be in excess. The diagrams show the changing divariant to trivariant phase relationships on crossing reactions 3 to 6 (see text for details). The P - T conditions for each compatibility triangle are given on the figure and additionally shown as a series of open triangles in Fig. 1.

Fig. 3: MnO-FeO-MgO compatibility triangles for conditions either side of reaction 3 at 12 kbar (Fig. 3a, b) and 6 kbar (Fig. 3c, d). The MnKFMASH system is reduced to MnO-FeO-MgO by taking kyanite, muscovite, quartz and H_2O to be in excess and is thus only applicable to aluminous metapelites. The P - T conditions for each compatibility triangle are given on the figure and additionally shown as a series of filled triangles in Fig. 1.

Fig. 4: MnKFMASH pseudosections constructed for three different bulk compositions in terms of the A/AFM and x_{Fe} proportions, which are given on each pseudosection. Each of the pseudosections is calculated for a MnO content of 0.1 mol % and additional garnet-in lines are shown for an MnO content of 0.05 mol % (red dashed line) and for the MnO-free system (solid red line labelled MnO = 0). (a) P - T pseudosection from 0.4 to 12 kbar and 450-950 °C. For the subsolidus calculations, H_2O was taken to be in excess, the H_2O content for the suprasolidus calculations was set such that the assemblage at the solidus was just saturated in H_2O (see Table 1). The bulk rock composition is that from fig. 4 in White *et al.* (2014). (b). P - T pseudosection from 0.4 to 12 kbar and 450-700 °C for a more magnesian composition

900 than (Fig. 4a) but with the same Al_2O_3 content. (c). P - T pseudosection for a more
901 aluminouse composition but with the same x_{Fe} as Fig. 4b

902 **Fig. 5:** MnNCKFMASHTO P - T pseudosection for subsolidus conditions based on the
903 synthetic metapelite composition from fig. 5b in White et al. (2014) but with 0.1
904 mol% MnO. The garnet-in boundary is shown as a thick red line. Garnet-in
905 boundaries for bulk MnO contents of 0 mol% (thin red line), 0.05 mol % (thin dashed
906 red line) and 0.15 mol % (thin dotted red line) are additionally shown. Several zero
907 mode boundaries are highlighted in colour (see legend for explanation).

908 **Fig. 6:** MnNCKFMASHTO P - T pseudosection for subsolidus conditions for a synthetic
909 aluminous metapelite composition. The bulk composition used is that from fig. 7 in
910 White et al. (2014) with 0.1 mol % added. The garnet-in boundary is shown as a
911 thick red line. Garnet-in boundaries for bulk MnO contents of 0 mol% (thin red line),
912 0.05 mol % (thin dashed red line) and 0.15 mol % (thin dotted red line) are
913 additionally shown. Several zero mode boundaries are highlighted in colour (see
914 legend for explanation).

915 **Fig. 7:** MnNCKFMASHTO P - T pseudosection for subsolidus conditions calculated for
916 the average greenschist facies metapelite composition from Ague (1991). The CaO
917 content was reduced slightly to account for the likely presence of apatite in most
918 metapelites. The value for O, representing the Fe_2O_3 component was set at 0.498
919 mol. % to give a $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$ value of 0.077. The bulk composition used has
920 0.284 mol % MnO and garnet is stable throughout much of the diagram. Garnet-in
921 lines are also shown for bulk MnO contents of 0.05 and 0.15 mol %. Several zero
922 mode boundaries are highlighted in colour (see legend for explanation).

923 **Fig. 8:** MnNCKFMASHTO P - T pseudosection for subsolidus conditions calculated for
924 the average amphibolite facies metapelite composition from Ague (1991). The value
925 for O, representing the Fe_2O_3 component was set at 0.602 mol. % to give a
926 $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$ value of 0.081. The bulk composition used has 0.175 mol %
927 MnO and garnet has a smaller stability range than for Fig. 7. Garnet-in lines are
928 also shown for bulk MnO contents of 0.05 and 0.15 mol %. Several zero mode
929 boundaries are highlighted in colour (see legend for explanation).

930 **Fig. 9:** MnNCKFMASHTO P - T pseudosection for suprasolidus conditions calculated for
931 the same composition as Fig. 8. The H_2O content was set such that the solidus was
932 just fluid saturated at close to 9 kbar. The garnet-in line for the MnO-free system is
933 also shown as a thin red line labelled MnO = 0. Several zero mode boundaries are
934 highlighted in colour (see legend for explanation).

935 **Fig. 10:** A T - x_{MnO} (Fig. 10a) and P - x_{MnO} (Fig. 10b) pseudosection based on the
936 greenschist facies metapelite composition presented in Ague (1991). For both
937 diagrams the x axis ranges from MnO = 0 mol % at $x = 0$ to MnO = 0.3 mol % at
938 $x = 1$. In both diagrams the garnet in line is shown as a thick red line and contours of
939 garnet mode are shown as thin red lines. (a). A T - x_{MnO} pseudosection from 400°C to
940 the wet solidus calculated for a pressure of 6 kbar. (b). A P - x_{MnO} pseudosection for
941 0.4–10 kbar, calculated for a temperature of 580 °C.

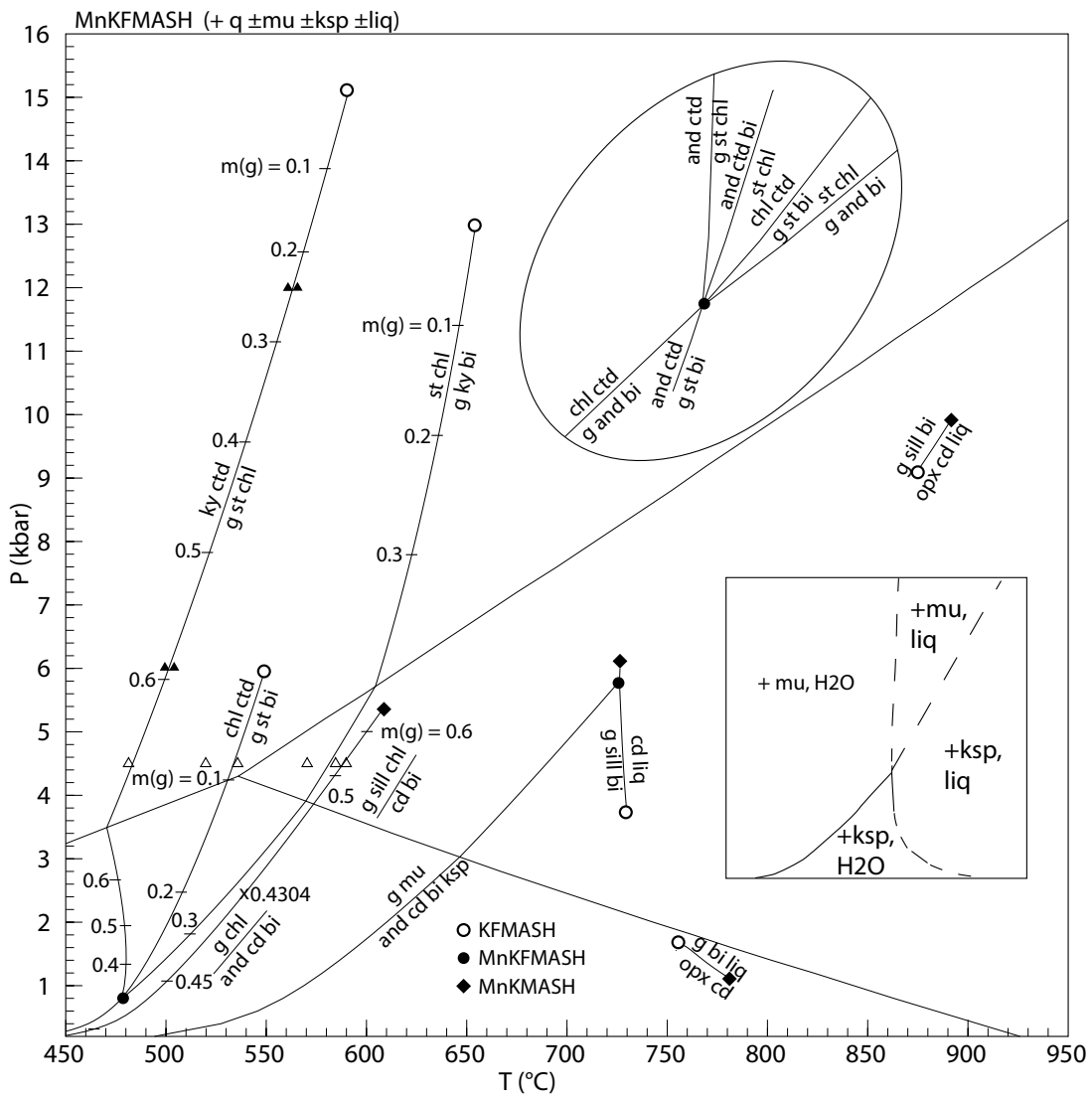
942 **Fig. A3-1 :** Plots of Δh versus manganese compositional parameters (m) for
943 garnet–ilmenite pairs. Natural assemblage data, ferric iron not analysed (circles);
944 natural assemblage data, wet chemistry (squares); experimental data, ferric iron not
945 analysed (diamonds). (see text).

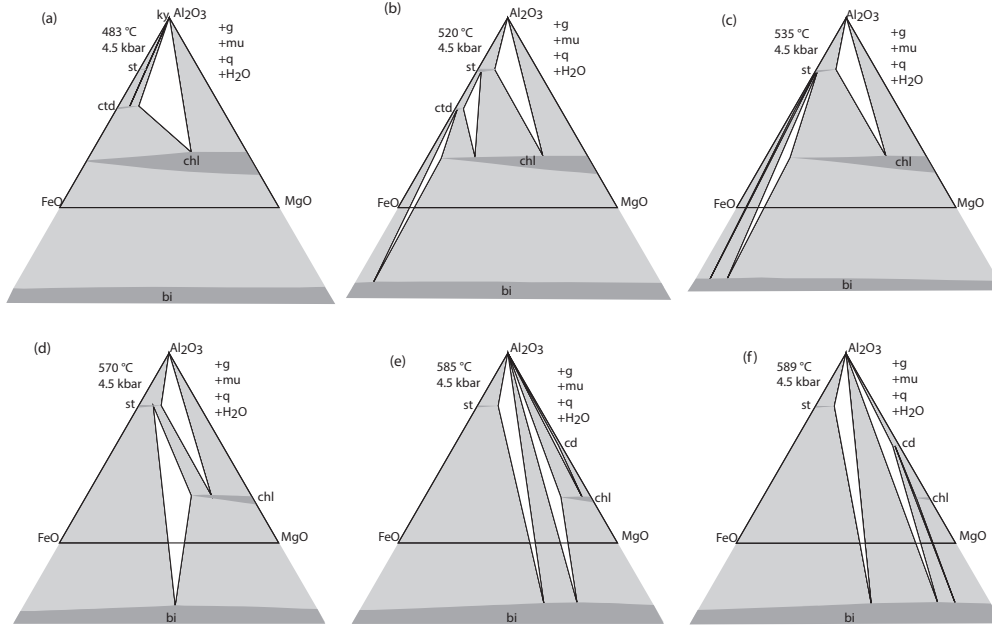
946 **Fig. A3-2 :** Plots of Δh versus manganese compositional parameters (m). (a–f) select
947 mineral pairs involving garnet with biotite, chloritoid and staurolite. (g–l) select
948 mineral pairs involving biotite with chlorite, cordierite and orthopyroxene. Natural
949 assemblage data, ferric not analysed (circles); natural assemblage data, wet chemistry
950 (squares); experimental data, ferric not analysed (diamonds). (see text).

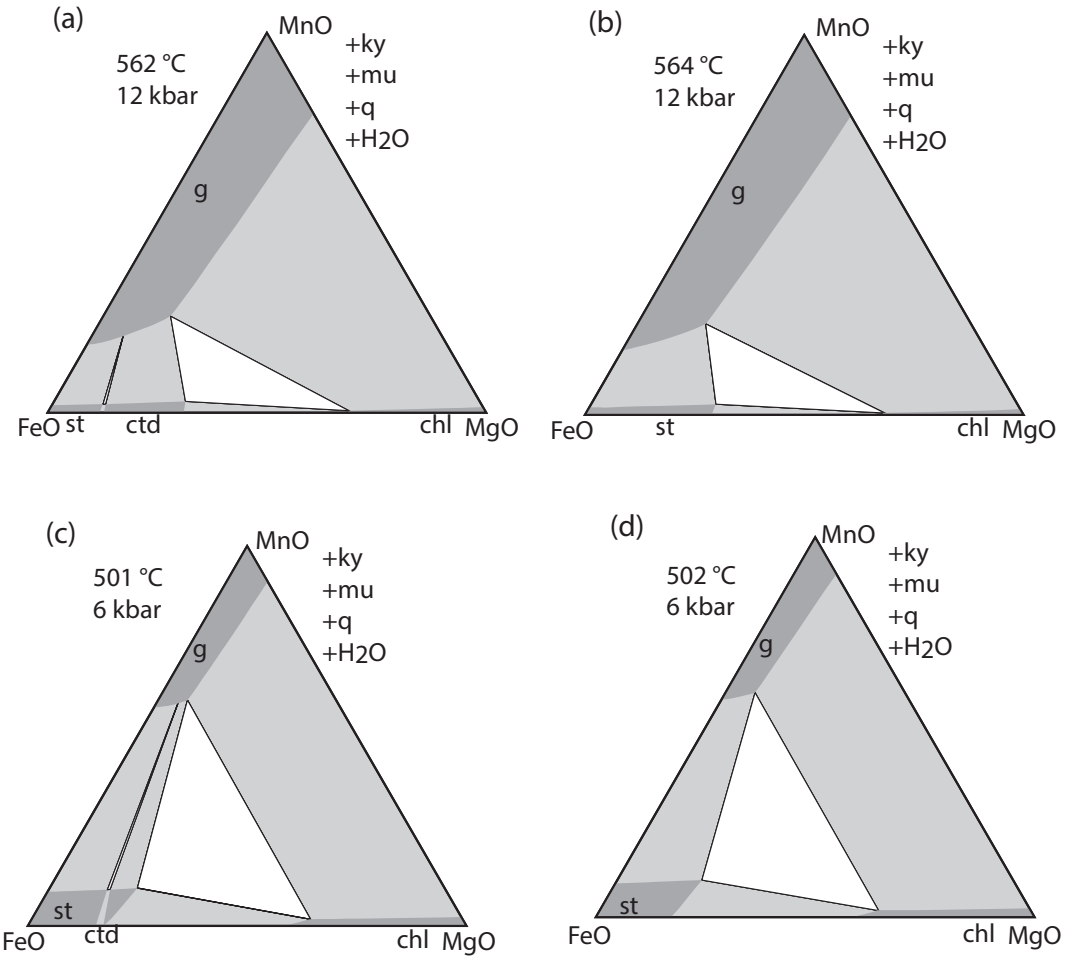
Table 1: Bulk rock compositions used in the construction of pseudosections

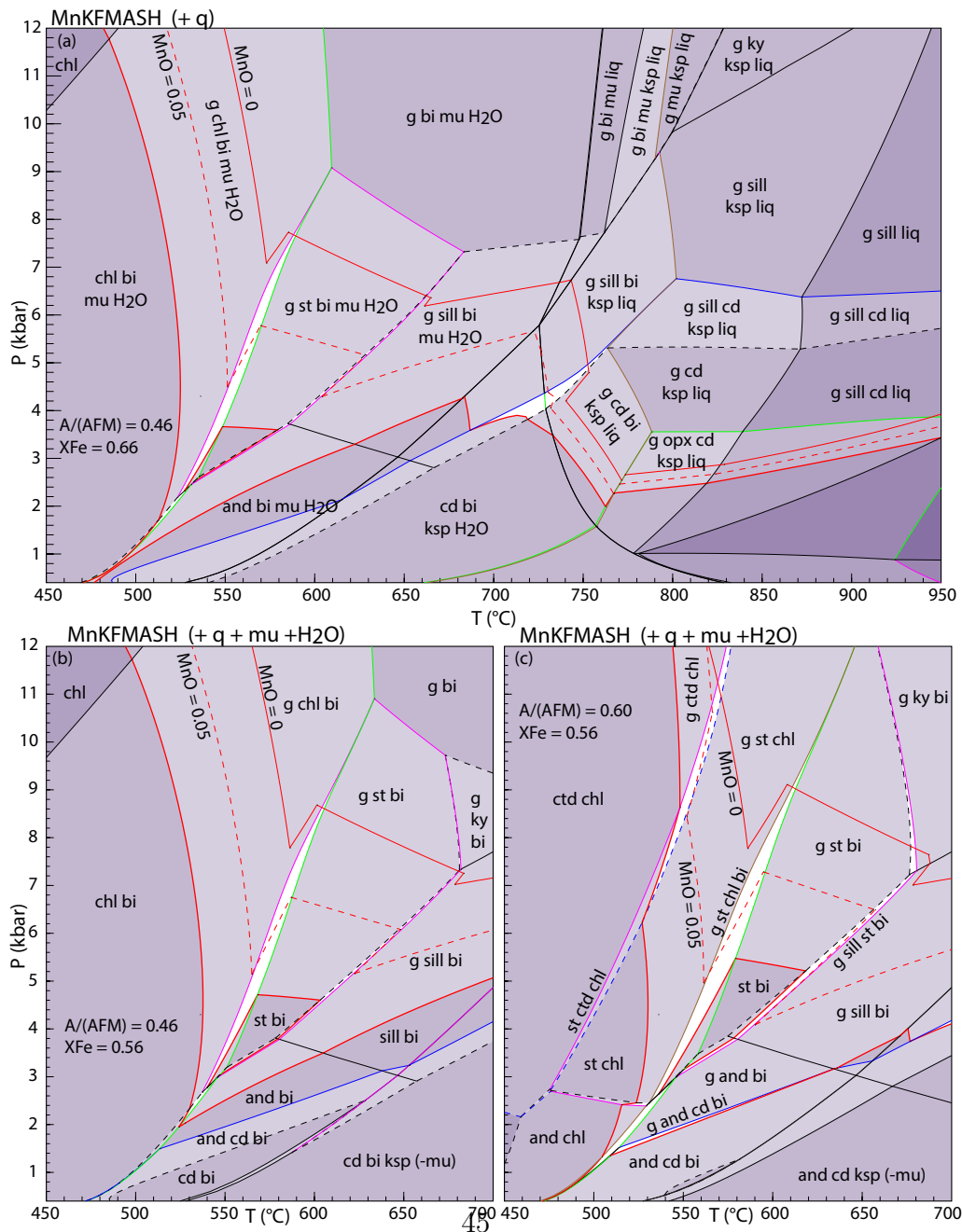
mol. %	H_2O	SiO_2	Al_2O_3	CaO	MgO	FeO	K_2O	Na_2O	TiO_2	MnO	O
Fig. 4a	6.553*	68.691	9.860	—	4.006	7.632	3.157	—	—	0.100	—
Fig. 4b	+	73.509	10.552	—	5.480	6.975	3.378	—	—	0.107	—
Fig. 4c	+	73.509	13.898	—	4.008	5.100	3.378	—	—	0.107	—
Fig. 5	+	73.943	9.442	0.295	3.840	7.522	3.028	0.601	0.658	0.105	0.564
Fig. 6	+	68.477	16.560	0.274	3.556	6.966	2.804	0.557	0.610	0.100	0.098
Fig. 7	+	67.322	12.671	1.558	5.179	7.000	2.929	1.779	0.781	0.284	0.498
Fig. 8	+	64.578	13.651	1.586	5.529	8.025	2.943	2.000	0.907	0.175	0.602
Fig. 9	6.244	60.546	12.799	1.487	5.183	7.524	2.759	1.878	0.850	0.164	0.565
Fig. 10 $x=0$	+	67.513	12.707	1.563	5.194	7.019	2.938	1.784	0.783	0.000	0.499
Fig. 10 $x=1$	+	67.311	12.669	1.558	5.178	7.000	2.929	1.779	0.781	0.300	0.497

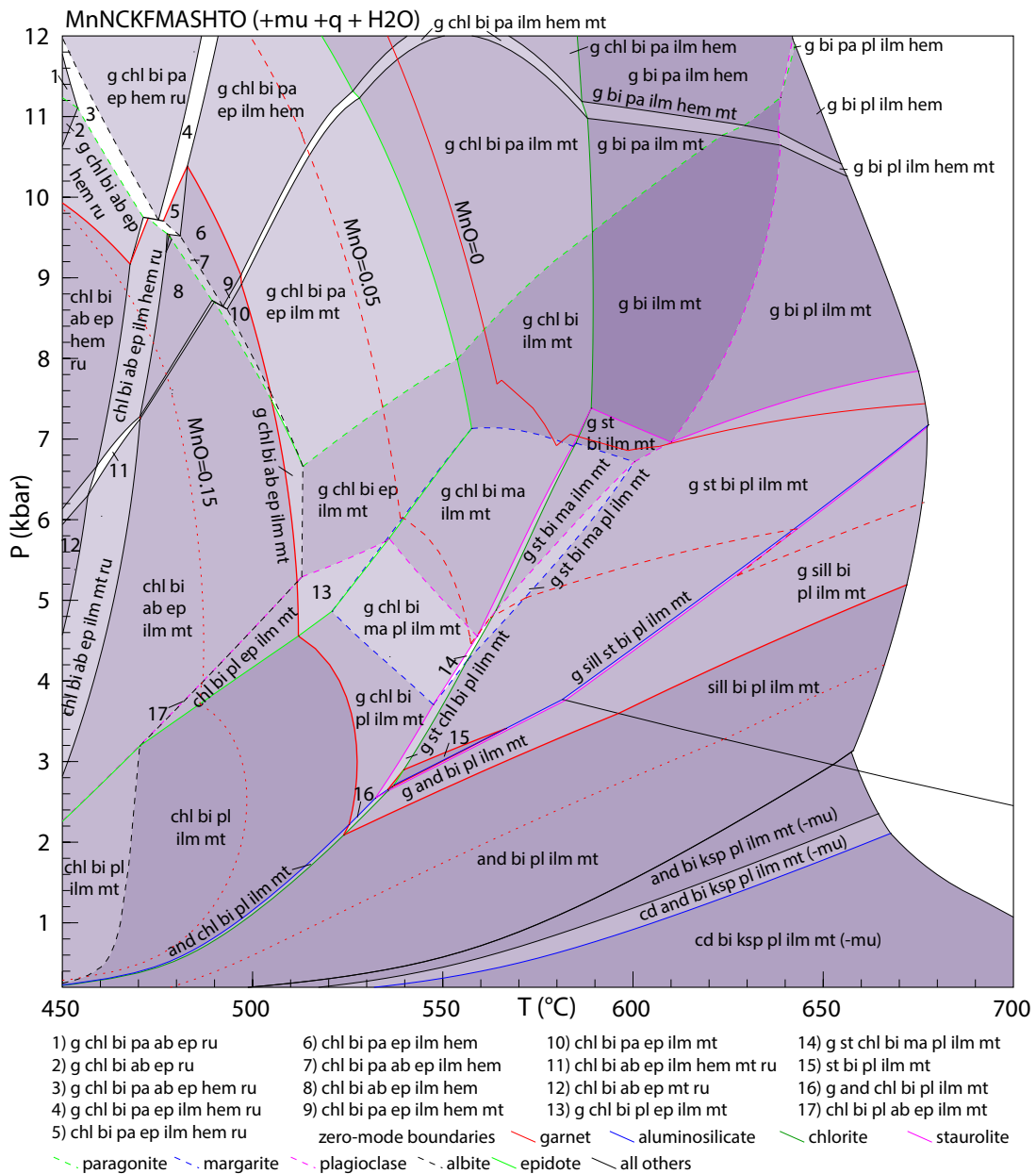
+, H_2O in excess; *, H_2O taken as in-excess for subsolidus part of diagram











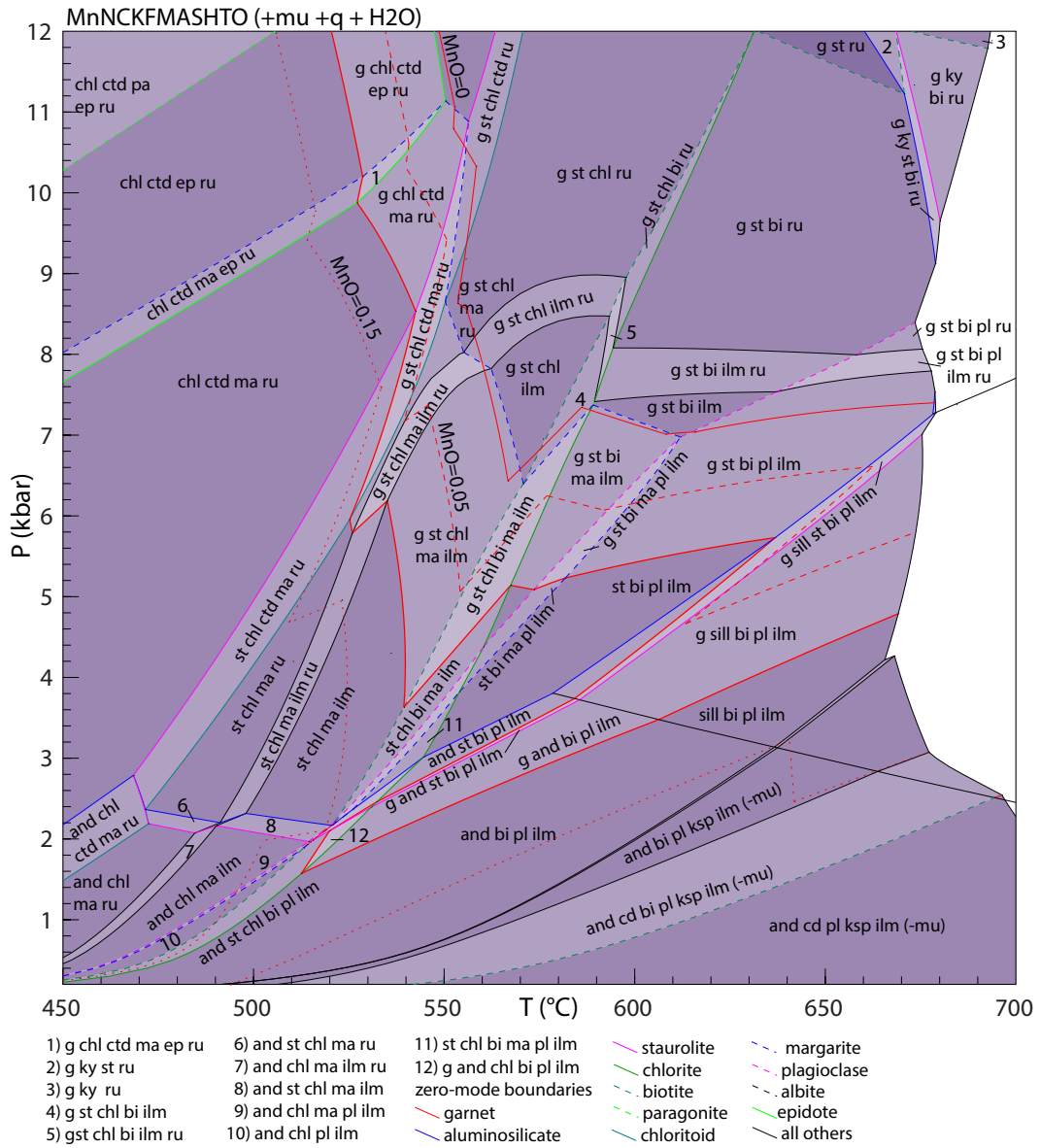
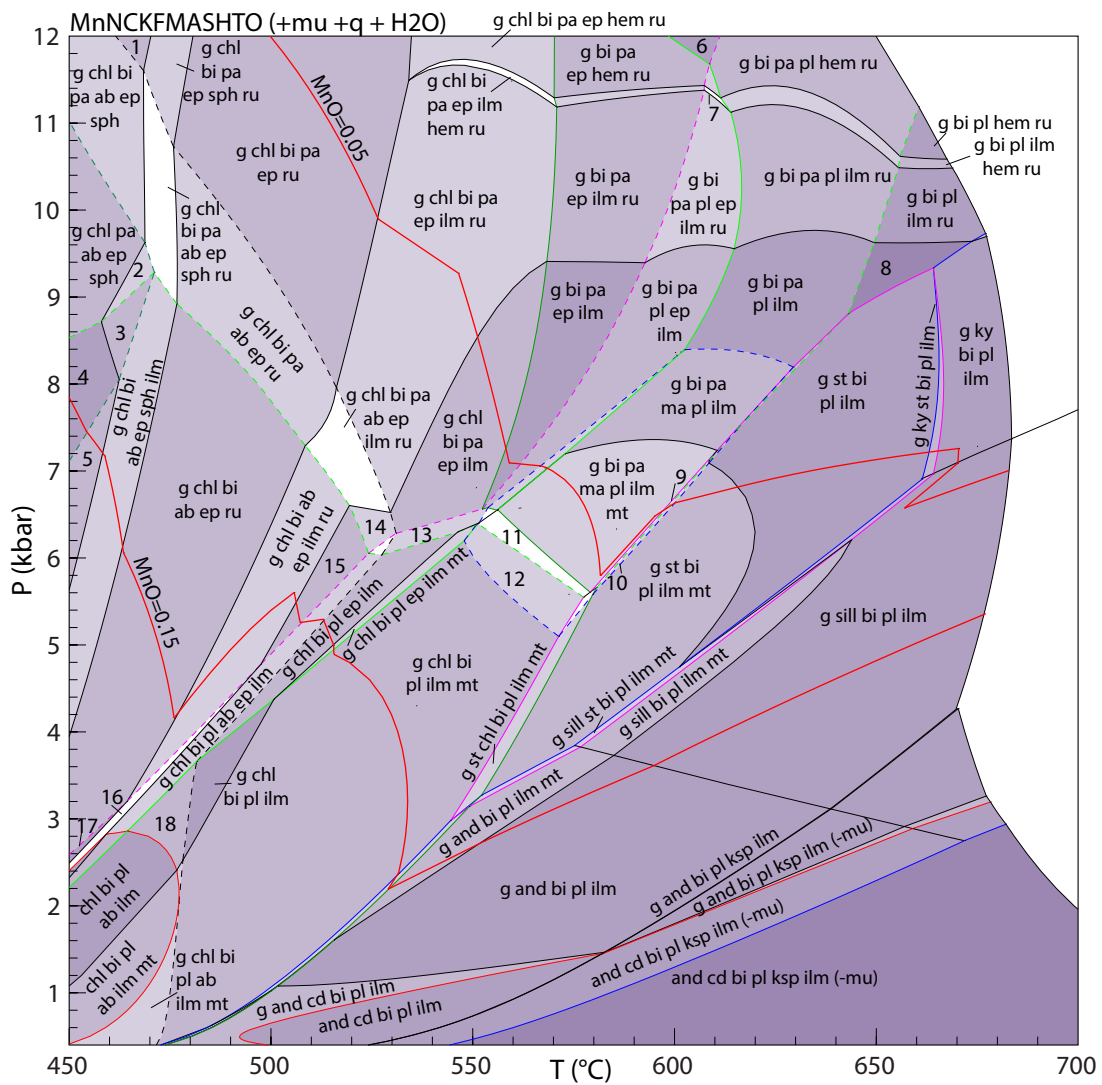
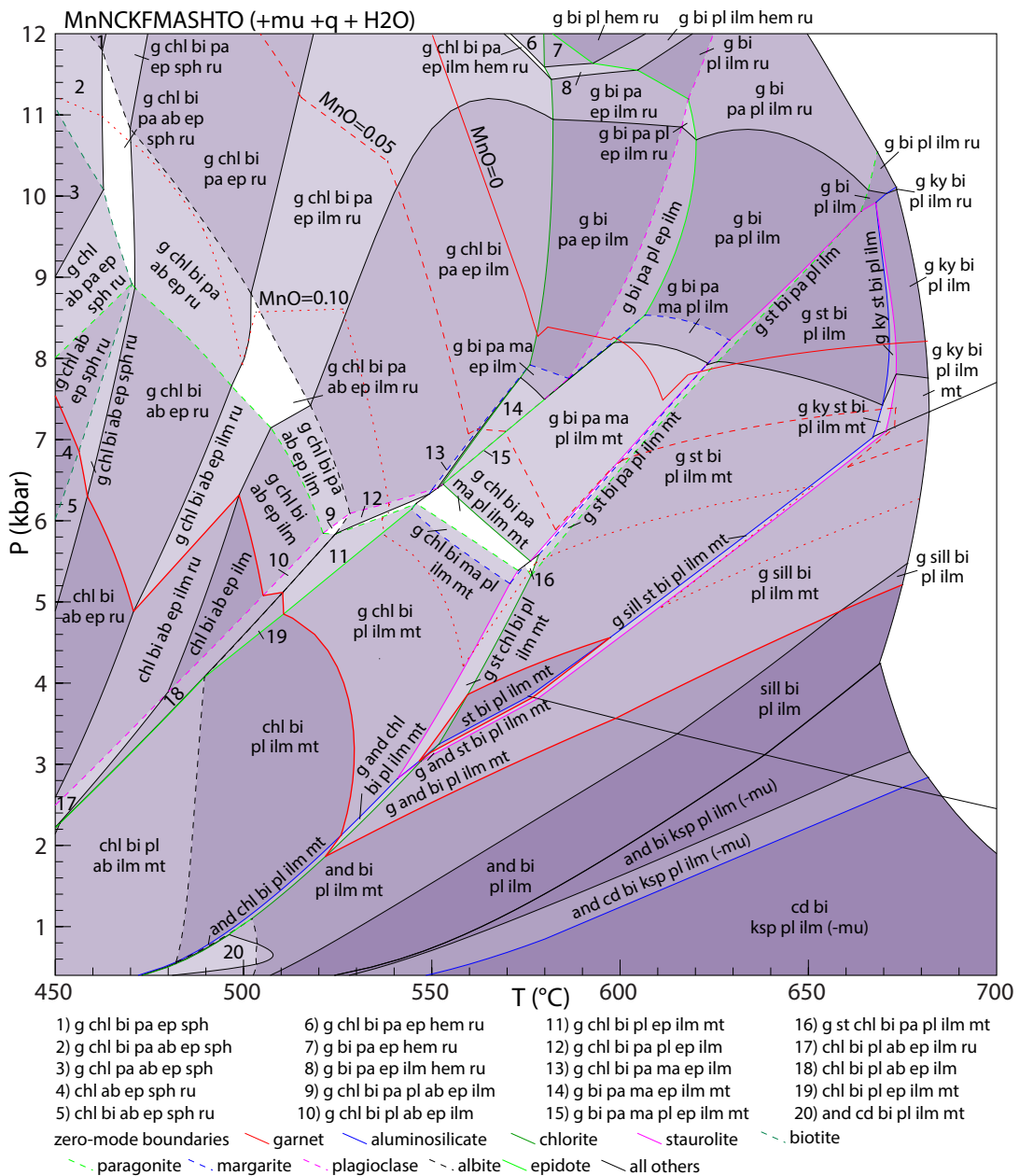
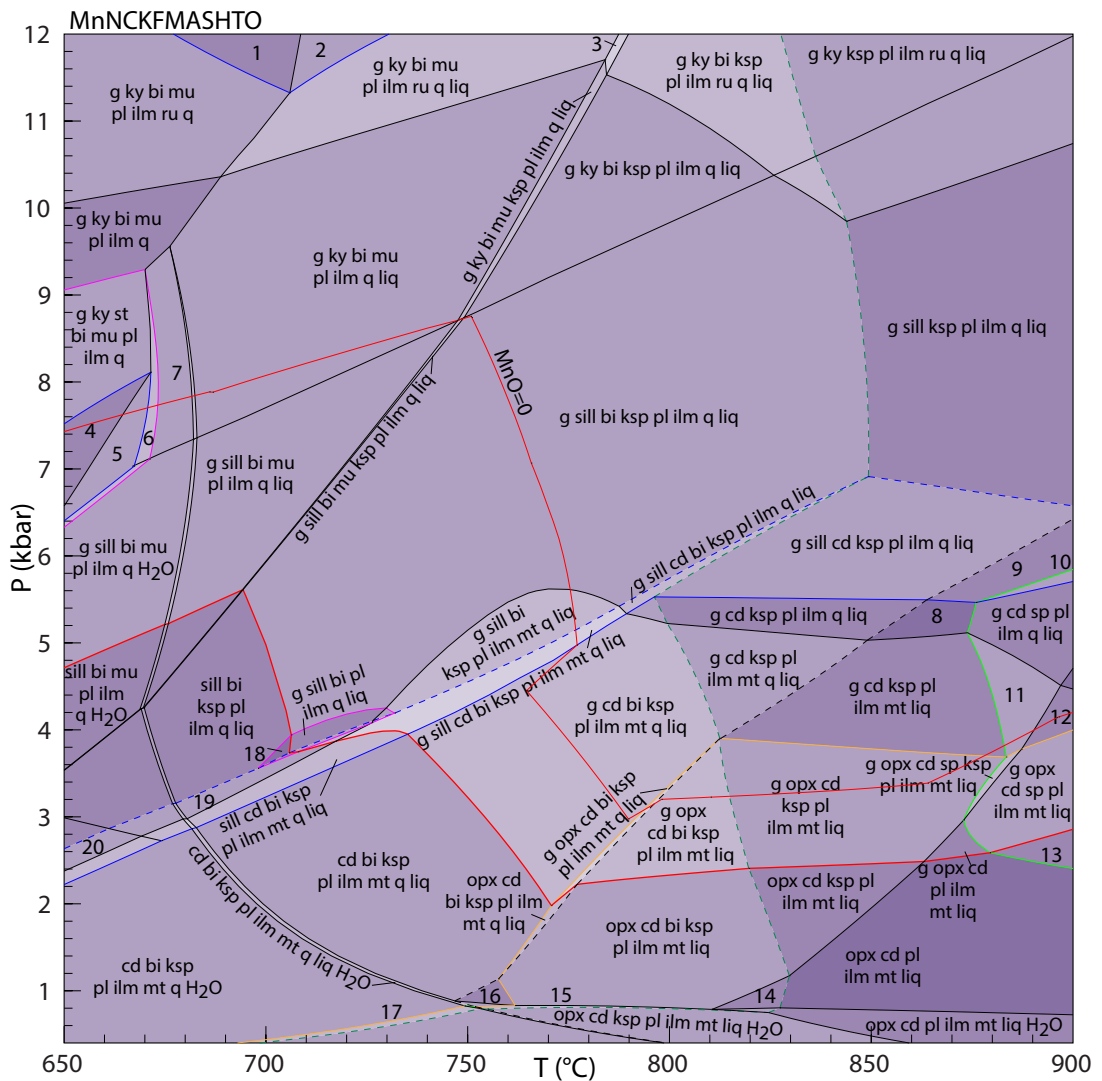


Figure 6:



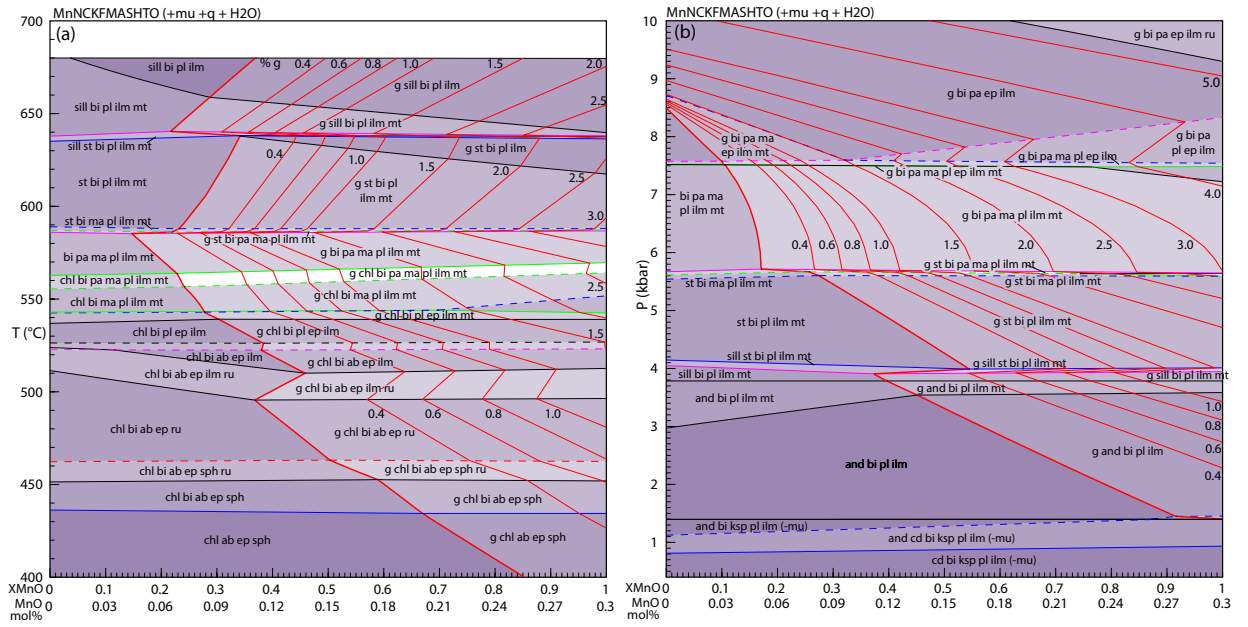
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|--------------------------|-----------------------------|------------------------------|------------------------------|
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| 2) g chl pa ab ep sph ru | 7) g bi pa pl ep ilm hem ru | 12) g chl bi ma pl ilm mt | 17) g chl bi pl ab ep ru |
| 3) g chl ab ep sph ru | 8) g bi pl ilm | 13) g chl bi pa pl ep ilm | 18) g chl bi pl ab ilm |
| 4) g chl ab ep sph | 9) g st bi pa ma pl ilm mt | 14) g chl bi pa ab ep ilm | |
| 5) g chl bi ab ep sph | 10) g st bi ma pl ilm mt | 15) g chl bi ab ep ilm | |
- zero-mode boundaries garnet aluminosilicate chlorite staurolite
 paragonite margarite plagioclase albite epidote all others

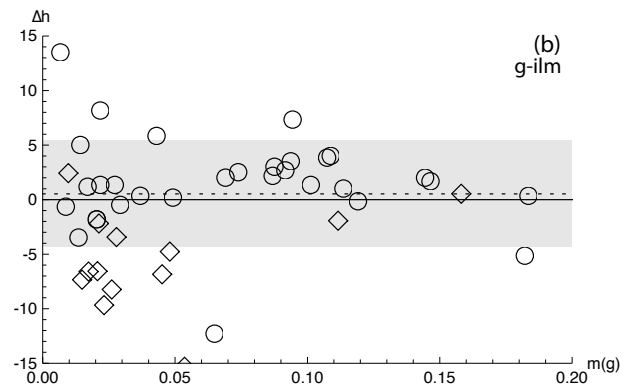
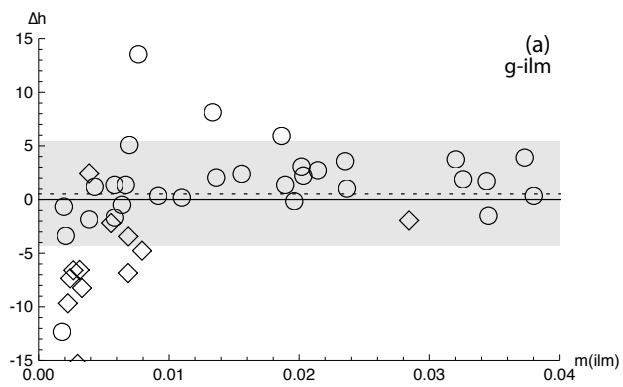




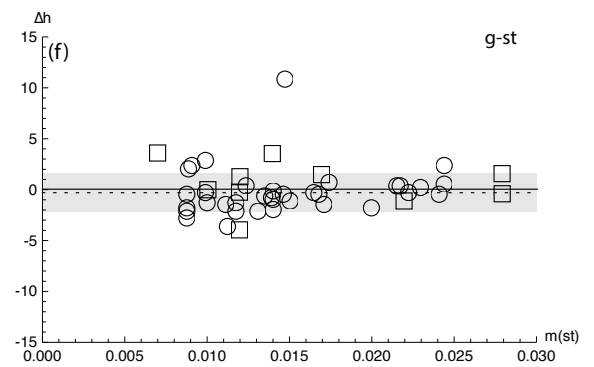
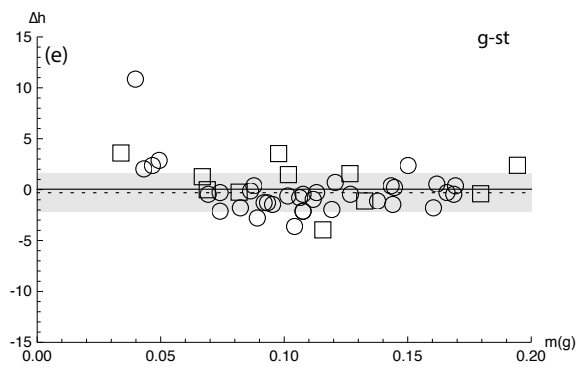
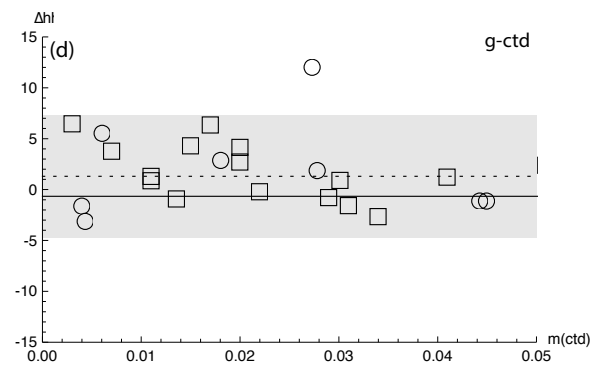
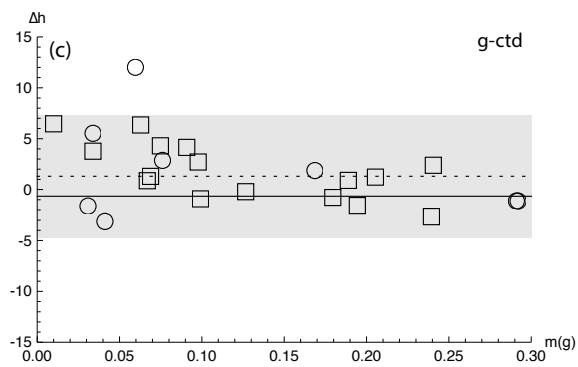
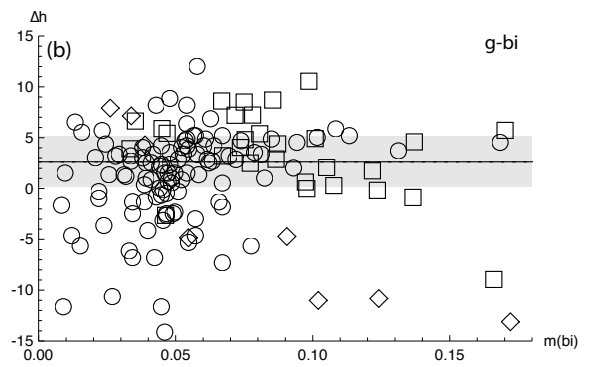
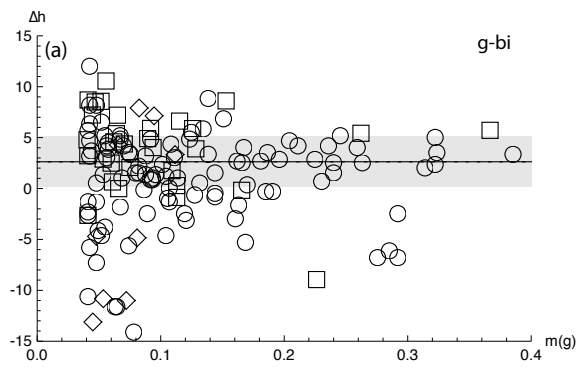
- | | | | |
|---|--|--|--|
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| 2) g bi mu pl ilm ru q liq | 7) g ky bi mu pl ilm q H ₂ O | 12) g cd sp pl ilm mt liq | 17) opx cd bi ksp pl ilm mt q H ₂ O |
| 3) g ky bi mu ksp pl ilm ru q liq | 8) g cd ksp pl ilm liq | 13) opx cd sp pl ilm mt liq | 18) sill bi pl ilm q liq |
| 4) g st bi mu pl ilm q | 9) g sill cd ksp pl ilm liq | 14) opx cd bi pl ilm mt liq | 19) sill cd bi ksp pl ilm q liq |
| 5) g st bi mu pl ilm q H ₂ O | 10) g sill cd sp ksp pl ilm liq | 15) opx cd bi ksp pl ilm mt liq H ₂ O | 20) sill cd bi ksp pl ilm q H ₂ O |

zero-mode boundaries — garnet — orthopyroxene — aluminosilicate — cordierite — spinel — staurolite
 - - - biotite - - - quartz — all others

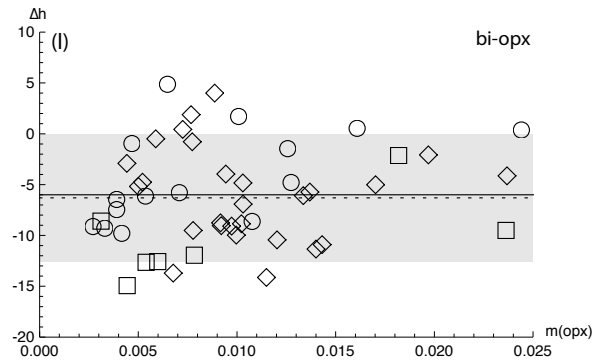
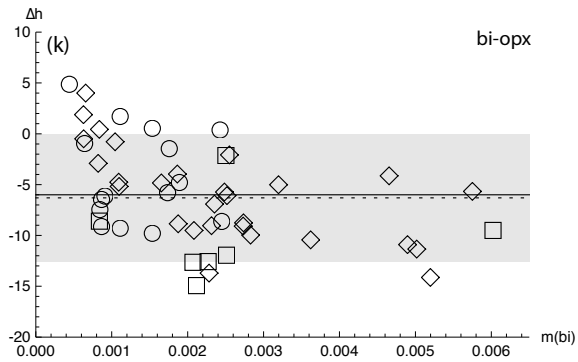
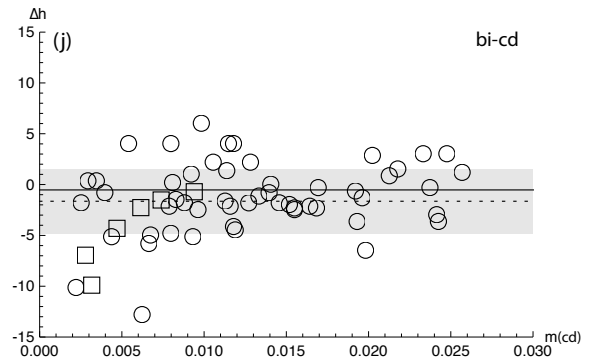
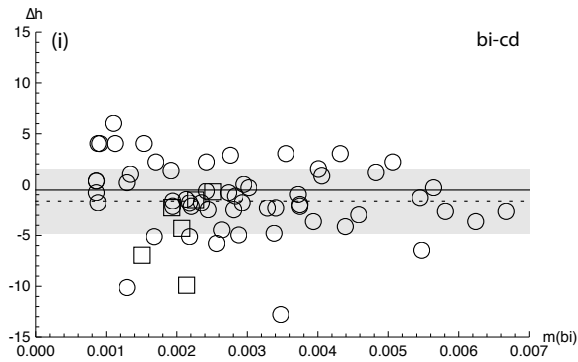
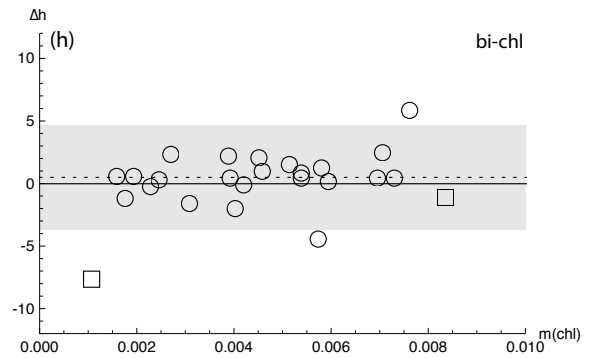
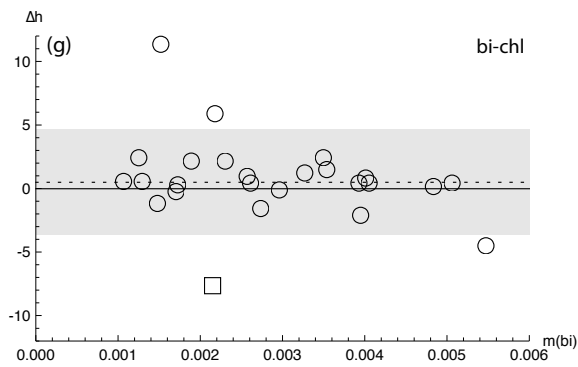




White et al fig. 3-1



White et al fig. 3-2



White et al fig. 3-2 - cont.