

## SUPPLEMENTAL MATERIAL

### Calculation method

The evolving mineralogy and bulk water content of each lithology was calculated along each of three example geotherms (after Syracuse et al., 2010), starting at 0.5 GPa and terminating at 6.5 GPa (at corresponding temperatures, see inset panels of Fig. 1). Calculations utilized Gibbs' energy minimization with *Perple\_X* version 6.6.7 (Connolly, 2005). Each geotherm was discretized into approximately 2000 *P-T* points, with free energy minimizations (calculation of mineral assemblage, abundances and compositions) undertaken at each point. For calculations in Figure 1 of the paper (also shown below as bold curves in DR-2 and as panel 'a' of DR-3), the composition of any garnet and/or fluid produced at a *P-T* point was extracted from the bulk rock composition before proceeding to the next point.

Fluid was considered as a H<sub>2</sub>O–CO<sub>2</sub> binary solution (Holland and Powell, 1991, 1998) but in practice was always strongly H<sub>2</sub>O dominated. Solubility of additional components was not considered. End-member thermodynamic data was from Holland & Powell (2004 'ds5.5' update to the 1998 dataset). In addition to end-member phases (e.g. rutile, quartz and coesite), several mineral solution models were considered: ideal clinozoisite–epidote (Holland et al., 1998); a regular clinochlore–amesite–daphnite–Al-free-chlorite–Mn-chlorite solution (Holland and Powell, 1998); a tremolite–ferro-tremolite–pargasite–tschermakite–glaucophane–riebeckite amphibole solution (Dale et al., 2000; Dale et al., 2005); an asymmetric (Van Laar) calcite–magnesite–dolomite solution (Holland and Powell, 2003); an asymmetric diopside–jadeite–hedenbergite–acmite solution (Green et al., 2007); regular grossular–almandine–pyrope–spessartine–khoharite mixing in garnet (White et al., 2005); asymmetric muscovite–paragonite–margarite–celadonite–ferro-celadonite–ferro-muscovite and symmetric Fe–Mg–Mn–Fe<sup>3+</sup>–Al chloritoid and carpholite solutions (all after Smye et al., 2010). Incorporation of stilpnomelane followed Massonne and Willner (2008).

Our calculations included the effects of garnet and water fractionation from the bulk rock system. Figure DR-2 shows an example of these effects. If garnet chemistry is not progressively removed, the proportions and compositions of predicted phases can be substantially modified (e.g. Dragovic et al., 2012; Gaidies et al., 2008; Konrad-Schmolke et al., 2005; Marmo et al., 2002). Specifically, the *apparent* amount of garnet growth at higher *P-T* increases, thereby changing the predicted water:garnet production ratio (figure DR-2). Garnet fractionation can also lead to increased stability and growth of key phases such as lawsonite (e.g. Dragovic et al., 2012), which will significantly modify the rock's subsequent H<sub>2</sub>O budget (Clarke et al., 2006). A subtle but important consequence of progressively sequestering garnet's components is that, because the Fe<sup>3+</sup> content of this garnet is low, the residual Fe<sup>2+</sup>:Fe<sup>3+</sup> ratio decreases dramatically with garnet growth (bottom panel of Figure DR-2). Calculations suggest that unless components from garnet are allowed to re-enter the reactive volume (e.g. by garnet resorption), high *P-T* phases must grow from an almost Fe<sup>2+</sup>-free environment (excluding effects of redox reactions).

Figure DR-2 highlights another key difference between this and earlier studies, in which free water was not removed from the system as it is produced. In models where such ‘pore fluids’ are retained (e.g. the fine curves in Figure DR-2), this H<sub>2</sub>O is available for reaction when the system reaches ‘2<sup>nd</sup> growth’ lawsonite (which occurs because the subduction path  $dP/dT$  is steeper than that of lawsonite stability above  $\sim 2.5$  GPa). The free water is consumed by lawsonite at this point, also at the expense of garnet (which contributes CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>). If water were re-introduced into the system at those conditions (e.g. from other dehydrating assemblages) then such lawsonite growth would indeed be possible and the rock would effectively be partially ‘re-fertilized’. A better general model will include progressive removal of the locally-produced fluids, as we do here. This reduces the abundance of ‘2<sup>nd</sup> growth’ lawsonite, which is limited instead by breakdown of the scant remaining unstable hydrous phases (e.g. epidote; Figure DR-3).

### Bulk rock compositions

	Hydrated MORB	Average Pelite
SiO <sub>2</sub>	43.47	58.94
TiO <sub>2</sub>	1.06	0.74
Al <sub>2</sub> O <sub>3</sub>	14.74	16.32
Fe <sub>2</sub> O <sub>3</sub>	5.32	1.27
Na <sub>2</sub> O	1.96	1.70
K <sub>2</sub> O	0.53	3.48
FeO	3.78	5.15
MgO	6.32	2.58
CaO	12.22	1.07
MnO	0.16	0.10
H <sub>2</sub> O	7.63	8.63
CO <sub>2</sub>	2.80	-

**Table DR1.** Initial bulk rock compositions used for calculations presented in manuscript (wt %). Hydrated MORB after Staudigel et al. (1996), with additional H<sub>2</sub>O included to ensure fluid saturation at the 0.5 GPa initiation of the model. Pelite after Shaw (1956), with modifications from Mahar et al. (1997) and Caddick & Thompson (2008). Compositions used for figure 1 (and supplementary figure DR-3a) progressively deviate from these tabulations as garnet and/or fluid are produced and extracted.

### Starting bulk water content

One of the assumptions of our modeling was that the system passed through 0.5 GPa in a water saturated state. If the rock were not initially saturated, there would be less total dehydration flux. In fact, with much lower initial water, several early hydrous phases would be unstable and thermodynamic modeling predicts that garnet growth, marked by a distinctive Ca-Mn rich composition, could begin at much lower  $P$ - $T$ , before significant fluid production. On the other hand, such dry low- $T$  conditions could also lead to the persistence of metastable assemblages (e.g., Baxter 2003; Clarke et al. 2006), including overstepping and delay of this predicted low- $T$  garnet

growth until kinetic barriers were overcome when water saturated conditions were met either by internally derived dehydration (i.e., where initial bulk water content intersects dashed curve in Fig. 1) or by external fluid infiltration. The data compilation by Hacker et al. (2003a) provides valuable context for the question of initial bulk water content. Their analysis shows that low grade zeolite, prehnite-pumpellyite-actinolite, and lawsonite-jadeite facies rocks contain high water contents, averaging between 4.4 and 5.8 wt% H<sub>2</sub>O. These values are near water saturation for rocks entering the span of garnet growth in Figure 1 (where dashed curves effectively denote the fluid saturation surface). While the existence of very low  $P$ - $T$ , high Mn–Ca garnet appears to be limited in nature (Hacker et al. 2003a), its rare occurrence (e.g., Pabst et al. 2012 report such garnets in ~350 °C blueschist clasts in serpentinite mud volcanoes), could be used to infer starting water content and dehydration timing.

### Closed system assumption

In our model, we allow for the escape of a binary H<sub>2</sub>O–CO<sub>2</sub> fluid produced at each model increment, and we treat the local fractionating effect of garnet growth on the surrounding reactive matrix. Otherwise, for simplicity, we assume that the bulk rock chemistry remains fixed throughout the model. However in natural systems, especially given the copious evidence (including our own modelling) for fluid production and metasomatism, some amount of open system chemical exchange is inevitable. Numerous studies have shown the potential for loss (or gain) of major elements (like Si, K, Na, Ca) trace elements (like Li, B) and their isotopes by interactions with these metasomatising fluids (e.g. Bebout, 1995; Breeding et al., 2003; John et al., 2012; Manning, 2004; Marschall et al., 2009; Zack and John, 2007). Furthermore, it has been shown that certain redox reactions (for example lawsonite breakdown) can produce free oxygen and an oxidizing fluid which leaves the residual rock system in a progressively more reduced (lower  $fO_2$ ) state as that fluid is removed (e.g. Groppo and Castelli, 2010). Sensitivity analysis of such open system chemical exchange on the garnet:water production correlations we determine here will be worth exploring in future study. For now, we note the remarkable similarity between total water:garnet production ratios (well within a factor of ~4; see Figure 1) spanning extremely compositionally diverse end-members (MORB and pelite). This suggests that more subtle compositional variations due to open system metasomatism or initial protolith compositions will generally create only second order effects. The most significant of these effects would be those that permit stabilization (or destabilization) of a particularly hydrous phase (e.g. addition of more K<sub>2</sub>O to the MORB will permit both enhanced stilpnomelane stability at low  $P$ - $T$  and enhanced phengite stability at high  $P$ - $T$ ).

### Mineral abbreviations, and compositions of hydrous phases

Anhydrous phase abbreviations: Calcite-dolomite (Cc), Coesite (Coe), Garnet (Gt), Kyanite (Ky), Omphacite (Omph), Quartz (Qtz), Rutile (Rut), Titanite (Sph). The purpose of the following list is to clarify the molar water contents of each phase considered in our calculations, so phases calculated as solid solutions are represented here by a single end-member.

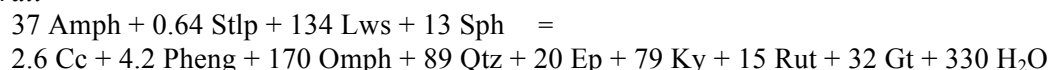
Amphibole	(Amph):	$\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$
Carpholite	(Car):	$\text{FeAl}_2\text{Si}_2\text{O}_6(\text{OH})_4$
Chlorite	(Chl):	$\text{Mg}_4\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_8$
Chloritoid	(Ctd):	$\text{FeAl}_2\text{SiO}_5(\text{OH})_2$
Epidote	(Ep):	$\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})$
Lawsonite	(Law):	$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$
Paragonite	(Parag):	$\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
Phengite	(Phen):	$\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2$
Stilpnomelane	(Stlp):	$\text{K}_5\text{Fe}_{48}\text{Al}_5\text{Si}_{67}\text{O}_{168}(\text{OH})_{48} \cdot (\text{H}_2\text{O})_{36}$

### Example reaction stoichiometries for Nicaragua geotherm

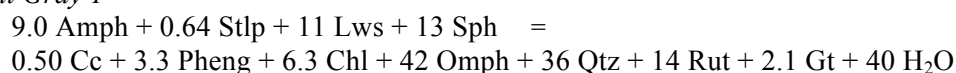
Below we show an example of the garnet forming dehydration reactions for MORB and pelite in the Nicaragua geotherm. Reactions are listed in units of moles consumed/produced per 100 kilograms of rock. Note that the molar water:garnet stoichiometric production ratios evident in the equations below can be re-cast (by considering rock and mineral molecular weights and densities) into the wt% water per vol% garnet units, as shown in Figure 1. These are the sum of all successive *changes* in phase assemblage in the garnet-growth interval, and do not directly reflect absolute phase abundance at the start or end of garnet growth (abundances are shown in Figure DR-3). “Overall” reactions correspond to the full garnet growth interval as shown in Figure 1. “Light gray” and “Dark Gray” correspond to discrete spans of garnet growth as shown in Figure 1.

#### Nicaragua MORB

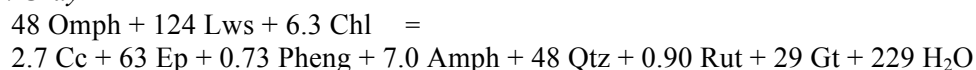
##### Overall



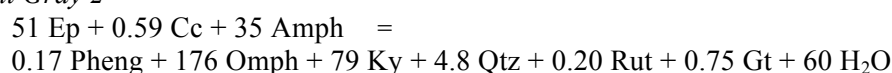
##### Light Gray 1



##### Dark Gray



##### Light Gray 2



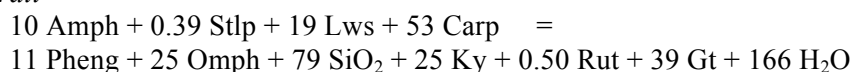
Since the ‘overall’ reaction is cumulative for a significant *P-T* span of garnet growth, phases that grow and then dissolve within this range (e.g. chlorite) may appear to be under represented. Table 2 summarizes the progressive storage and production of water for the Nicaragua MORB, cast in units of moles of water released or consumed by each phase per 100 kilograms of rock. This table thus excludes anhydrous phases, excepting garnet, which is shown for reference.

	<i>Stlp</i>	<i>Chl</i>	<i>Lws</i>	<i>Amph</i>	<i>Ep</i>	<i>Pheng</i>	<i>Water</i>	<i>Garnet</i>
<b>Overall</b>	<b>39</b>	<b>x</b>	<b>268</b>	<b>37</b>	<b>-10</b>	<b>-4</b>	<b>330</b>	<b>32</b>
<i>Lt Gray 1</i>	39	-25	21	9	x	-3	40	2.1
<i>Dk Gray</i>	x	25	247	-7	-32	-1	229	29
<i>Lt Gray 2</i>	x	x	x	35	25	-<1	60	0.75

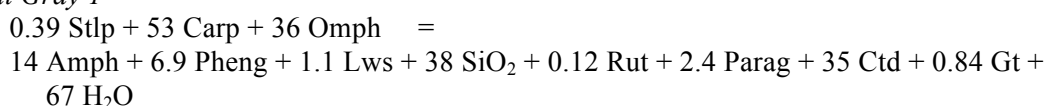
**Table DR2.** Water balance summary for Nicaragua MORB, presented as moles of water released (+) or consumed (-) by each phase per 100 kg of rock. Moles of garnet per 100 kg also shown for reference

### Nicaragua pelite

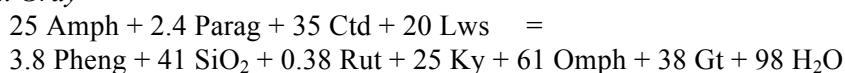
#### Overall



#### Light Gray 1

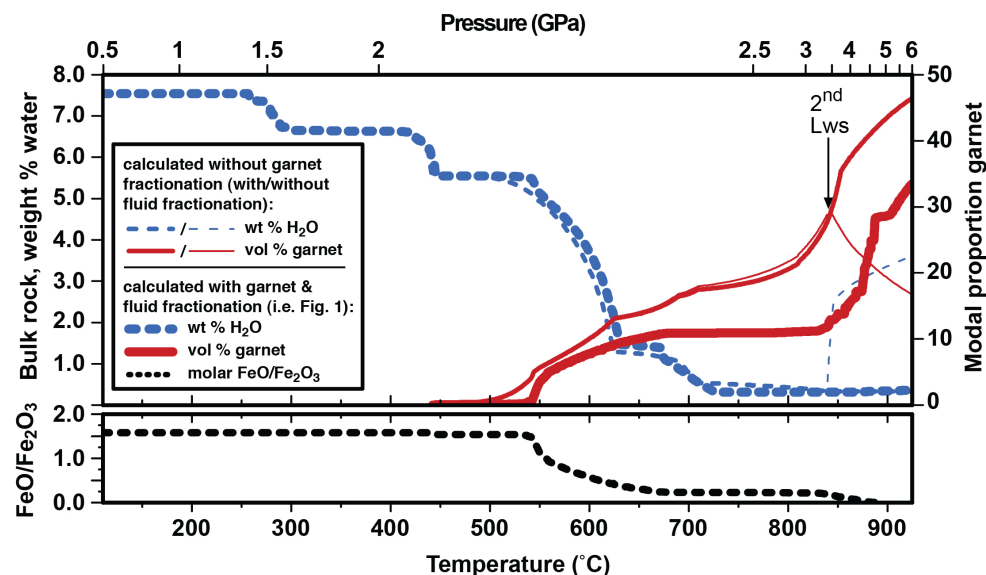


#### Dark Gray

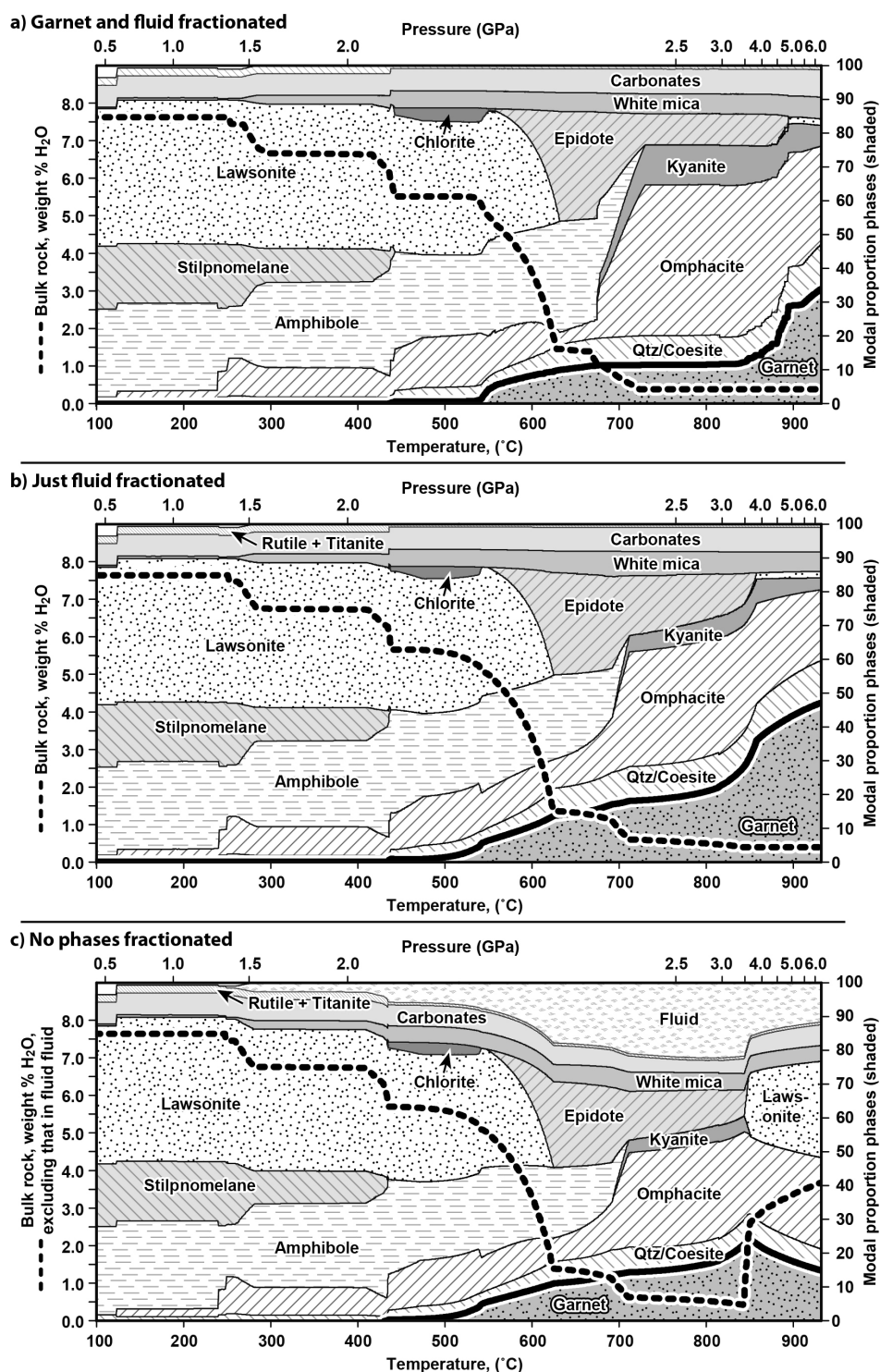


	<i>Stlp</i>	<i>Carp</i>	<i>Amph</i>	<i>Lws</i>	<i>Ctd</i>	<i>Parag</i>	<i>Pheng</i>	<i>Water</i>	<i>Garnet</i>
<b>Overall</b>	<b>23</b>	<b>105</b>	<b>10</b>	<b>38</b>	<b>x</b>	<b>x</b>	<b>-11</b>	<b>166</b>	<b>39</b>
<i>Lt Gray 1</i>	23	105	-15	-2	-35	-2	-7	67	0.84
<i>Dk Gray</i>	x	x	25	40	35	2	-4	98	38

**Table DR3.** Water balance summary for Nicaragua pelite, presented as moles of water released (+) or consumed (-) by each phase per 100 kg of rock. Moles of garnet per 100 kg also shown for reference



**Data repository Figure DRI.** Diagram showing importance of garnet and water fractionation. Top panel shows progressive growth of garnet (in vol %) and production of water (in wt %) for hydrated MORB along the Nicaragua geotherm with garnet and water fractionation (bold lines, as in Figure 1), ignoring garnet fractionation (thinner lines), and ignoring both garnet and water fractionation (thinnest lines). Location of the apparent water increase at the second lawsonite-in reaction at ~3.5 GPa for the non-water fractionating model is indicated with an arrow. Note significant differences between the properly fractionated result and the other two. Lower panel shows the effect of garnet fractionation on the residual molar ferrous/ferric iron ratio.



**Figure DR2.** Phase abundances calculated for a hydrated MORB on the Nicaragua geotherm. Calculations involve different assumptions: (a) garnet and fluid are progressively fractionated from the bulk rock composition as they form, (b) fluid is fractionated but garnet is not, (c) no phases are fractionated. Bold curves highlight garnet abundance (right-hand axis), bold dashed curves denote amount of bulk rock H<sub>2</sub>O (excluding in fluid). Option (a) as in Figure 1c. Note that in (c) the persistence of a fluid phase could also lead to wet-melting

(Hermann and Green, 2001; Schmidt and Poli, 1998; Vielzeuf and Schmidt, 2001), which is not depicted here. Melt fraction would be proportional to  $H_2O$  content. Thermodynamic data for many of the lower temperature ( $<400^\circ C$ ) phases includes greater uncertainties, though the first-order phase petrology should still be accurate for the bulk composition modeled. For example, the dominance of stilpnomelane over chlorite at lower  $P$ - $T$  is due to the presence of a small amount of potassium, which stabilizes stilpnomelane (sequestering 96 moles of  $FeO$  +  $MgO$ , 134 moles of  $SiO_2$  and 120 moles of  $H_2O$  per 5 moles of  $K_2O$ , and destabilizing chlorite accordingly). Low  $T$  stability of amphibole and pyroxene is partly also a consequence of this, and dominance of the thermodynamics of the diopside end-member. Fortunately, these uncertainties manifest themselves most strongly at temperatures below the bulk of garnet growth and are thus less relevant to the aims and key conclusions of this study.

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