Garnet growth as a proxy for progressive subduction zone dehydration

Ethan F. Baxter[1] and Mark J. Caddick[2]
[1]Department of Earth & Environment, Boston University, 675 Commonwealth Avenue, Boston, Massachusetts 02215, USA
[2]Department of Geosciences, Virginia Tech, 5060 Derring Hall, Blacksburg, Virginia 24061, USA

ABSTRACT

The release of volatiles from subducting lithologies is a crucial triggering process for arc magmatism, seismicity, the growth and maturation of continents, and the global geological water-CO_2 cycle. While models exist to predict slab volatile release from hydrous phases, it is challenging to reconstruct and test these fluid fluxes in nature. Here we show that the growth of garnet may be used as a proxy for devolatilization at blueschist to lower eclogite facies conditions in subduction zones. Using thermodynamic analysis including the effects of garnet fractionation and fluid removal, we show the proportional relationship between garnet and water production in two end-member crustal lithologies (pelitic sediment and hydrated mid-oceanic-ridge basalt [MORB]) in three representative subduction geotherms. Dehydrating minerals such as lawsonite, chlorite, amphibole, and epidote contribute to garnet growth, especially between ~1.4 and 3.0 GPa where geophysical models and observations predict dehydration. The average production ratio for altered MORB compositions is 0.52 (wt% water as fluid per vol% garnet) in cooler geotherms (Honshu [Japan] and Nicaragua) and 0.27 in hotter geotherms (Cascadia [North America]), whereas for pelite the production ratios are about half (0.24 and 0.13, respectively). Garnet growth correlates with production of 3.3–5.9 wt% water in hydrated MORB and 1.8–3.1 wt% water in pelite, representing 42%–100% of the water lost between 0.5 and 6.5 GPa from a fully saturated starting material. Garnet abundance, its pressure-temperature growth span, and its growth chronology may be used to recognize, reconstruct, and test models for progressive subduction zone dehydration.

INTRODUCTION

The progressive dehydration of subducted lithologies represents a fundamental part of the global geologic water cycle. This dehydration influences myriad earth processes and properties including (1) the return of volatiles into the mantle (e.g., Bebout, 1995; Rupke et al., 2004), (2) arc magma genesis (e.g., Tatsumi, 1989), (3) subduction zone seismicity (e.g., Hacker et al., 2003b), (4) the physical properties of the subducting slab and overlying wedge (e.g., Hacker et al., 2003a; Hyndman and Peacock, 2003), and (5) the chemical signatures and effects of fluids (e.g., Zack and John, 2007; John et al., 2012). Precise knowledge of where, when, and how rapidly these fluids are released from downgoing lithologies is fundamental to any quantitative understanding of the above processes and properties.

Numerous models for subduction zone metamorphism and dehydration have been developed (e.g., Schmidt and Poli, 1998; Kerrick and Connolly, 2001; Rupke et al., 2004). However, it has been challenging to test these models in either modern or ancient subduction zones because the production of water is difficult to detect or reconstruct in nature. Geophysical approaches provide information related to the changing physical properties of the downgoing slab and its surroundings that might relate to dehydration (e.g., Rondenay et al., 2008). In exhumed high-pressure/ultrahigh-pressure (HP/UHP) terranes, evidence of subduction-related fluid flow is abundant (e.g., Zack and John, 2007), but the source and release of that water is difficult to pinpoint without a marker in the dehydrated rock residue that can be linked to the primary fluid production. Thus while most previous study has concentrated on the mineral sources

for water, our focus is on a co-product phase that witnesses many significant dehydration reactions: garnet. Hacker et al. (2003a) compiled mineral modal proportions in subducted (and exhumed) lithologies and calculated bulk water contents, confirming that more deeply subducted assemblages generally retain less water than shallower equivalents. Dragovic et al. (2012) recognized that garnet could be linked to dehydration and used thermodynamics and zoned garnet geochronology to bracket the amount and rate of dehydration during garnet growth in a blueschist from Sifnos, Greece. Here, we present new thermodynamic modeling evidence that the growth of garnet is a robust—and useful—proxy for dehydration during subduction zone metamorphism of the crust in general.

WHY GARNET?

The growth of garnet, a common mineral in diverse lithologies, typically heralds the major dehydration of subducting lithologies. For example, examination of the compilation by Hacker et al. (2003a) reveals that the largest changes (decreases) in bulk water content also correlate with the introduction of garnet. This is because most garnet-forming reactions involve the consumption of hydrous phases and the consequent release of water as free fluid. Other minerals, like omphacite, can also grow in these same reactions but they are a less useful proxy than garnet. Garnet thermodynamics are well understood, which permits reconstruction of its pressure-temperature (P-T) growth history from its chemical zonation (e.g., Spear and Selverstone, 1983; Caddick and Thompson, 2008). Garnet growth in blueschist and eclogite facies rocks can be dated at high (<±1 m.y.) precision with the Lu-Hf or Sm-Nd systems (e.g., Lagos et al., 2007; Dragovic et al., 2012), including the potential for constraining growth duration via integrated Sm-Nd and Lu-Hf analysis of bulk crystals (e.g., Skora et al., 2009) or concentric age analyses in larger crystals (e.g., Pollington and Baxter, 2011). Chemical diffusivities in garnet are such that many prograde features (i.e., P-T-t [time]) of garnet growth will be retained up to temperatures of ~650–750 °C, depending on heating-cooling rates (e.g., Florence and Spear, 1991; Tirone et al., 2005; Caddick et al., 2010). Garnet also has distinct physical properties (e.g., isotropic, high density, and high bulk modulus) that might allow its abundance to be inferred from geophysical techniques in modern subduction zones.

METHODS

We modeled two dominant end-member crustal subduction-zone input lithologies, an average hydrated mid-oceanic-ridge basalt (MORB) and an average pelitic sediment (modified after Staudigel et al. [1996] and Shaw [1956]; see the GSA Data Repository[1] for compositions) along three subduction geotherms from Syracuse et al. (2010) appropriate for the top of the descending oceanic crust in the Cascadia (North America; hot), Nicaragua (medium), and Honshu (Japan; cold) subduction zones (see insets, Fig. 1). The evolving mineralogy and bulk water content of each lithology was calculated along each geotherm from 0.5 to 6.5 GPa using the program Perple_X (Connolly, 2005) in the system
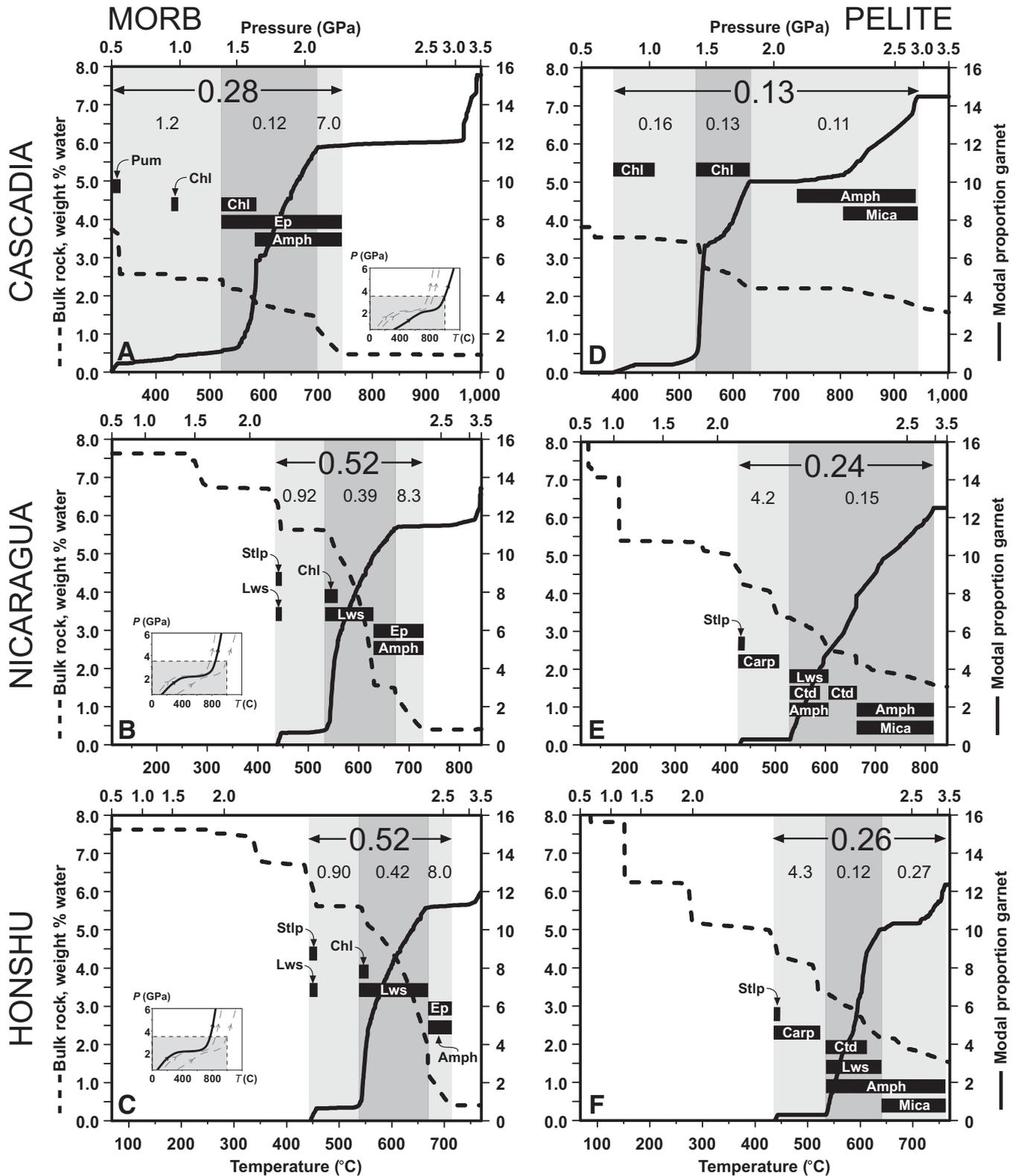

Figure 1. Growth of garnet (in vol%) and production of water (in wt%) along three subduction geotherms labeled Cascadia (North America), Nicaragua, and Honshu (Japan). Pressure-temperature (*P-T*) paths (after Syracuse et al., 2010) shown as insets in A–C. Each figure spans 0.5–3.5 GPa (*P* at top axis) but for a different temperature span (*T* at lower axis) corresponding to each geotherm. A–C are for an average hydrated mid-oceanic-ridge basalt (MORB) composition. Panels D–F are for an average pelitic sediment. Labeled black bars (vertical placement for clarity only) indicate the *P-T* span over which hydrous phases are breaking down and contributing significantly to the release of water. Amph—amphibole; Carp—carpholite; Chl—chlorite; Ctd—chloritoid; Ep—epidote; Lws—lawsonite; Mica—white mica; Pum—pumpellyite; Stlp—stilpnomelane. Gray bands indicate spans of coupled water:garnet production; darker-gray band indicates the span of strongest coupling. Numbers in each gray band are the average water:garnet production ratio over that span (units of wt% water produced per vol% garnet grown).

SiO_2-TiO_2-Al_2O_3-Fe_2O_3-FeO-MgO-CaO-MnO-K_2O-Na_2O-H_2O-CO_2. Models were initiated at water-saturated conditions, a reasonable assumption for rocks entering into garnet growth conditions; water undersaturation would lower the total dehydration flux and permit some garnet growth before dehydration (see the Data Repository for discussion). The free fluid evolved at each model increment was progressively removed from the system (i.e., H_2O and CO_2 were only carried to higher *P-T* conditions if structurally bound in hydrous minerals). Likewise, the reacting bulk composition was modified after each garnet-bearing model increment to account for the fractionating effects of zoned garnet growth (e.g., Marmo et al., 2002; Konrad-Schmolke et al., 2005; Gaidies et al., 2008). Neglecting the effects of garnet and water fractionation in thermodynamic calculations can overpredict garnet abundance and Fe^{2+}/Fe^{3+} in the evolving bulk composition, and misrepresent stability and abundance of key phases (such as lawsonite) leading to inaccurate results (e.g., see Figs. DR2 and DR3 in the Data Repository). No melt is included in our model, nor would it be expected except above ~750 °C in the pelite in the hottest (Cascadia) geotherm (e.g., Hermann and Spandler, 2008), after most of the garnet has already formed. For simplicity, we model a closed chemical system with constant oxygen fugacity (f_{O_2}) (i.e., we do not include redox reactions) and permit no loss (nor gain) of major elements from the bulk rock system (other than the H_2O-CO_2 binary fluid). Especially given the liberation of fluids at high *P*, this closed-system assumption for elements including Si, K, Na, and O_2 may not hold in nature (see the Data Repository for discussion). Last, our models assume equilibrium. Slower reaction kinetics, which may characterize cooler, drier systems, could lead to the persistence of metastable assemblages (e.g., Baxter, 2003; Clarke et al., 2006; Pattison et al., 2011), including overstepping and delay of predicted garnet growth and dehydration until kinetic barriers are overcome.

RESULTS

Results are shown in Figure 1. The models for both MORB and pelite predict some low-temperature, low-pressure dehydration before the start of garnet growth, amounting to <17% and <58% of the total water loss between 0.5 and 6.5 GPa from MORB and pelite, respectively (for these well-hydrated protoliths). Garnet growth starts earliest (at lowest pressure) along the hotter Cascadia geotherm. For all geotherms, both lithologies show an episode of early garnet growth and dehydration (first light-gray bands in Fig. 1) related to the breakdown of low-*T* hydrous phases followed by a major growth event, beginning at ~540 °C and spanning ~100–300 °C, in which garnet growth and dehydration are most strongly correlated (dark-gray bands in Fig. 1). The pressure span of this strongly correlated water:garnet production ratio varies for each geotherm but in general is focused between 1.4 and 3.0 GPa (equivalent to 53 and 113 km depth). The major hydrous phases contributing to this dehydration include lawsonite, chlorite, amphibole, chloritoid, epidote, and paragonitic white mica. Variably correlated garnet and fluid production follows the major pulse (second light-gray bands in Fig. 1) to pressures as high as 3.3 GPa (shallower in the MORB). Dehydration ceases by 3.5 GPa (shallower in the MORB), with 0.4 wt% (MORB) and 1.5 wt% (pelite) water still retained at 6.5 GPa. Most of this deeply subducted water is stored in phengitic white mica, the abundance of which is primarily controlled by bulk K_2O content. In MORB, additional water is stored in epidote which converts to second-generation lawsonite above ~4 GPa. Breakdown of phengite and this second-growth lawsonite occurs at depths beyond our modeling. In the MORB, a second phase of major garnet growth begins at *P* > 3 GPa (e.g., Fig. DR2) but without correlated water loss.

The data in Figure 1 permit quantification of average water:garnet production ratios which may be cast in convenient units of weight percent water (as fluid) produced per volume percent garnet produced (shown in Fig. 1). Nicaragua and Honshu paths yield similar results, whereas the Cascadia path yields water:garnet production ratios about half those for the cooler geotherms. The dehydrating capacity for well-hydrated MORB

(3.3–5.9 wt%) is about twice that of pelite (1.8–3.1 wt%) over the span of garnet growth. The garnet-forming dehydration reaction(s) and the related water:garnet production ratios vary across the entire span of garnet growth with hydrous phases variably contributing to the storage and/or release of water (for example, see the reaction stoichiometries for the Nicaragua geotherm in the Data Repository). In cooler geotherms, lawsonite plays the dominant role in the release of water during the major phase of garnet growth in MORB and pelite, while other phases (e.g., chlorite, chloritoid, epidote) can grow (to consume water) and break down (to release water) all within the garnet-growth span (e.g., Tables DR2 and DR3, and Fig. DR3). Interestingly, the difference between average water:garnet production ratios along any calculated geotherm for compositions as diverse as MORB and pelite are remarkably small (generally less than a factor of 4). This indicates that reasonable variations in bulk chemistry are of second-order importance, and water:garnet production ratios can be generalized across a moderately large compositional range for sediment and hydrated basalt, respectively.

DISCUSSION

Our modeling constrains the primary dehydration flux from subducting crustal materials, and links that water directly to the production of garnet in the crust. Subduction-zone dehydration is the primary driver of arc magmatism. However, our modeling shows that most of the garnet-related dehydration occurs at fore-arc depths (<100 km). Thus, in the absence of any lateral component of fluid transport upon production, these fluids would not be immediately responsible for generating mantle-wedge melts. However, if these fore-arc fluids infiltrate and hydrate the overlying mantle wedge (e.g., Hyndman and Peacock, 2003), corner flow can then drag that water into the melting region (e.g., Tatsumi, 1989). Similarly, dehydration of primary mantle serpentinites, which we have not addressed in our modeling, could also impart a significant water flux into the sub-arc region if they can find a pathway through the overlying slab crust (e.g., Rupke et al., 2004; John et al., 2012).

The water:garnet correlation exists most strongly at 1.4–3.0 GPa depths within which some geodynamic models predict onset of slab-mantle coupling and/or focusing of dehydration (e.g., Wada and Wang, 2009; van Keken et al., 2011). For example, Rondenay et al. (2008) showed a dipping low-velocity layer in subducting crust in Cascadia with a termination at >45 km depth and related this to metamorphic dehydration. Coincident with dehydration, our models for MORB and pelite predict the most dramatic growth of garnet in Cascadia between 1.4 and 1.7 GPa (~53–64 km depth), just below where Rondenay et al. (2008) observed termination of the low-velocity layer. It may be that dehydration-related garnet growth, rather than dehydration per se, is what permits recognition of this important process via geophysical or petrological means.

CONCLUSION

Garnet growth and water production (totaling 1.8–5.9 wt% H_2O released as fluid) are strongly coupled in tight spans between 1.4 and 3.0 GPa during subduction of two end-member crustal lithologies. Early lower-temperature water release does not have concomitant garnet growth, and late eclogite facies (>~3 GPa) garnet growth does not have concomitant water production, but these scenarios are recognizable via garnet chemistry and can be quantified to put the garnet-related dehydration flux into context. The average water:garnet production ratios in all examined geotherms and compositions range from 0.13 to 0.52 wt% fluid produced per vol% garnet grown, remarkably consistent given the range of conditions. These equilibrium thermodynamic predictions would shift if sluggish reaction kinetics allow metastable assemblages to persist to greater depths or if severely water-undersaturated conditions dominate. Garnet abundance (recognized by geophysical or petrological observations), its growth chronology (via Sm-Nd or Lu-Hf methods), and the *P-T* span of its growth (via thermodynamic analysis) can be used by petrologists and

geophysicists as a powerful proxy to monitor progressive dehydration in subduction zones, and test model predictions of the flux, rate, and depth(s) at which dehydration occurs, including models requiring spatially/temporally continuous versus focused pulses of primary fluid generation. For example, Dragovic et al. (2012) linked zoned garnet geochronology to thermodynamic dehydration analysis of a blueschist from Sifnos, Greece, revealing a rapid burst of fluid and heating spanning just hundreds of thousands of years.

REFERENCES CITED

Baxter, E.F., 2003, Natural constraints on metamorphic reaction rates, *in* Vance, D., Muller, W., and Villa, I.M., eds., Geochronology—Linking the Isotopic Record with Petrology and Textures: Geological Society of London Special Publication 220, p. 183–202, doi:10.1144/GSL.SP.2003.220.01.11.

Bebout, G.E., 1995, The impact of subduction-zone metamorphism on mantle-ocean chemical cycling: Chemical Geology, v. 126, p. 191–218, doi:10.1016/0009-2541(95)00118-5.

Caddick, M.J., and Thompson, A.B., 2008, Quantifying the tectono-metamorphic evolution of pelitic rocks from a wide range of tectonic settings: Mineral compositions in equilibrium: Contributions to Mineralogy and Petrology, v. 156, p. 177–195, doi:10.1007/s00410-008-0280-6.

Caddick, M.J., Konopásek, J., and Thompson, A.B., 2010, Preservation of garnet growth zoning and the duration of prograde metamorphism: Journal of Petrology, v. 51, p. 2327–2347, doi:10.1093/petrology/egq059.

Clarke, G.L., Powell, R., and Fitzherbert, J.A., 2006, The lawsonite paradox: A comparison of field evidence and mineral equilibria modeling: Journal of Metamorphic Geology, v. 24, p. 715–725, doi:10.1111/j.1525-1314.2006.00664.x.

Connolly, J.A.D., 2005, Computation of phase equilibria by linear programming: A tool for geodynamic modeling and its application to subduction zone decarbonation: Earth and Planetary Science Letters, v. 236, p. 524–541, doi:10.1016/j.epsl.2005.04.033.

Dragovic, B., Samanta, L.M., Baxter, E.F., and Selverstone, J., 2012, Using garnet to constrain the duration and rate of water-releasing metamorphic reactions during subduction: An example from Sifnos, Greece: Chemical Geology, v. 314–317, p. 9–22, doi:10.1016/j.chemgeo.2012.04.016.

Florence, F.P., and Spear, F.S., 1991, Effects of diffusional modification of garnet growth zoning on *P-T* path calculations: Contributions to Mineralogy and Petrology, v. 107, p. 487–500, doi:10.1007/BF00310683.

Gaidies, F., De Capitani, C., and Abart, R., 2008, THERIA_G: A software program to numerically model prograde garnet growth: Contributions to Mineralogy and Petrology, v. 155, p. 657–671, doi:10.1007/s00410-007-0263-z.

Hacker, B.R., Abers, G.A., and Peacock, S.M., 2003a, Subduction factory 1. Theoretical mineralogy, densities, seismic wave speeds, and H_2O contents: Journal of Geophysical Research, v. 108, 2029, doi:10.1029/2001JB001127.

Hacker, B.R., Peacock, S.M., Abers, G.A., and Holloway, S.D., 2003b, Subduction factory 2. Are intermediate-depth earthquakes in subducting slabs linked to metamorphic dehydration reactions?: Journal of Geophysical Research, v. 108, 2030, doi:10.1029/2001JB001129.

Hermann, J., and Spandler, C.J., 2008, Sediment melts at sub-arc depths: An experimental study: Journal of Petrology, v. 49, p. 717–740, doi:10.1093/petrology/egm073.

Hyndman, R.D., and Peacock, S.M., 2003, Serpentinization of the forearc mantle: Earth and Planetary Science Letters, v. 212, p. 417–432.

John, T., Gussone, N., Podladchikov, Y.Y., Bebout, G.E., Dohmen, R., Halama, R., Klemd, R., Magna, T., and Seitz, H.-M., 2012, Volcanic arcs fed by rapid pulsed fluid flow through subducting slabs: Nature Geoscience, v. 5, p. 489–492, doi:10.1038/ngeo1482.

Kerrick, D.M., and Connolly, J.A.D., 2001, Metamorphic devolatilization of subducted oceanic metabasalts: Implications for seismicity, arc magmatism and volatile recycling: Earth and Planetary Science Letters, v. 189, p. 19–29, doi:10.1016/S0012-821X(01)00347-8.

Konrad-Schmolke, M., Handy, M.R., Babist, J., and O'Brien, P.J., 2005, Thermodynamic modelling of diffusion-controlled garnet growth: Contributions to Mineralogy and Petrology, v. 149, p. 181–195, doi:10.1007/s00410-004-0643-6.

Lagos, M., Scherer, E.E., Tomaschek, F., Munker, C., Keiter, M., Berndt, J., and Ballhaus, C., 2007, High precision Lu–Hf geochronology of Eocene eclogite-facies rocks from Syros, Cyclades, Greece: Chemical Geology, v. 243, p. 16–35, doi:10.1016/j.chemgeo.2007.04.008.

Marmo, B.A., Clarke, G.L., and Powell, R., 2002, Fractionation of bulk rock composition due to porphyroblast growth: Effects on eclogite facies mineral equilibria, Pam Peninsula, New Caledonia: Journal of Metamorphic Geology, v. 20, p. 151–165, doi:10.1046/j.0263-4929.2001.00346.x.

Pattison, D.R.M., De Capitani, C., and Gaidies, F., 2011, Petrological consequences of variations in metamorphic reaction affinity: Journal of Metamorphic Geology, v. 29, p. 953–977, doi: 10.1111/j.1525-1314.2011.00950.x.

Pollington, A.D., and Baxter, E.F., 2011, High precision microsampling and preparation of zoned garnet porphyroblasts for Sm-Nd geochronology: Chemical Geology, v. 281, p. 270–282, doi:10.1016/j.chemgeo.2010.12.014.

Rondenay, S., Abers, G.A., and van Keken, P.E., 2008, Seismic imaging of subduction zone metamorphism: Geology, v. 36, p. 275–278, doi:10.1130/G24112A.1.

Rupke, L.H., Morgan, J.P., Hort, M., and Connolly, J.A.D., 2004, Serpentine and the subduction zone water cycle: Earth and Planetary Science Letters, v. 223, p. 17–34, doi:10.1016/j.epsl.2004.04.018.

Schmidt, M.W., and Poli, S., 1998, Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation: Earth and Planetary Science Letters, v. 163, p. 361–379, doi:10.1016/S0012-821X(98)00142-3.

Shaw, D.M., 1956, Geochemistry of pelitic rocks. Part III: Major elements and general geochemistry: Geological Society of America Bulletin, v. 67, p. 919–934, doi:10.1130/0016-7606(1956)67[919:GOPRPI]2.0.CO;2.

Skora, S., Lapen, T.J., Baumgartner, L.P., Johnson, C.M., Hellebrand, E., and Mahlen, N.J., 2009, The duration of prograde garnet crystallization in the UHP eclogites at Lago di Cignana, Italy: Earth and Planetary Science Letters, v. 287, p. 402–411, doi:10.1016/j.epsl.2009.08.024.

Spear, F.S., and Selverstone, J., 1983, Quantitative *P-T* paths from zoned minerals: Theory and tectonic applications: Contributions to Mineralogy and Petrology, v. 83, p. 348–357, doi:10.1007/BF00371203.

Staudigel, H., Plank, T., White, B., and Schmincke, H.-U., 1996, Geochemical fluxes during seafloor alteration of the basaltic upper oceanic crust: DSDP Sites 417 and 418, *in* Bebout, E., et al., eds., Subduction: Top to Bottom: American Geophysical Union Geophysical Monograph 96, p. 19–38.

Syracuse, E.M., van Keken, P.E., and Abers, G.A., 2010, The global range of subduction zone thermal models: Physics of the Earth and Planetary Interiors, v. 183, p. 73–90, doi:10.1016/j.pepi.2010.02.004.

Tatsumi, Y., 1989, Migration of fluid phases and genesis of basalt magmas in subduction zones: Journal of Geophysical Research, v. 94, p. 4697–4707, doi: 10.1029/JB094iB04p04697.

Tirone, M., Ganguly, J., Dohmen, R., Langenhorst, F., Hervig, R., and Becker, H.-W., 2005, Rare earth diffusion kinetics in garnet: Experimental studies and applications: Geochimica et Cosmochimica Acta, v. 69, p. 2385–2398, doi:10.1016/j.gca.2004.09.025.

van Keken, P.E., Hacker, B.R., Syracuse, E.M., and Abers, G.A., 2011, Subduction factory: 4. Depth-dependent flux of H_2O from subducting slabs worldwide: Journal of Geophysical Research, v. 116, B01401, doi:10.1029/2010JB007922.

Wada, I., and Wang, K., 2009, Common depth of slab-mantle decoupling: Reconciling diversity and uniformity of subduction zones: Geochemistry Geophysics Geosystems, v. 10, Q10009, doi:10.1029/2009GC002570.

Zack, T., and John, T., 2007, An evaluation of reactive fluid flow and trace element mobility in subducting slabs: Chemical Geology, v. 239, p. 199–216, doi:10.1016/j.chemgeo.2006.10.020.