Reply to comment by R. Bousquet et al. on "Subduction factory: 1. Theoretical mineralogy, densities, seismic wave speeds and H₂O contents"

Bradley R. Hacker,[1] Geoffrey A. Abers,[2] Simon M. Peacock,[3] and Scott Johnston[1]

[1] Steady increases in the mineral physical property database, new methods of calculating the physical properties of rocks, and the growing understanding of ultrahigh-pressure rocks [e.g., *Liou et al.*, 2000] has stimulated considerable effort in recent years to calculate rock physical properties at high to ultrahigh pressure. One approach [e.g., *Hacker et al.*, 2003] is to use the mineral abundances and mineral compositions of natural rocks determined in the field and in experiments. Another approach [e.g., *Kerrick and Connolly*, 2001] uses the thermodynamic properties of minerals to calculate mineral abundances and mineral compositions. Both approaches have strengths and weaknesses [*Hacker et al.*, 2003]: the former is grounded in the reality that the mineral abundances and mineral compositions actually exist in natural rocks, the latter has the internal consistency and elegance that comes from a purely theoretical approach. Between these two end-member methodologies lie a range of approaches, including that presented by *Bousquet et al.* [1997]. *Hacker et al.* [2003] and *Bousquet et al.* [1997] both used metamorphic facies determined from a combination of natural and experimental studies; the boundaries of the facies fields are relatively similar but differ in key areas where temperatures are low (and thus equilibrium is often not attained) or pressures are unusually high (an area of active research). *Hacker et al.* [2003] used natural mineral abundances and compositions to calculate rock physical properties from a mineral equation of state that uses a third-order finite strain approximation with full consideration of the effects of changes in pressure and temperature. *Bousquet et al.* [1997] calculated mineral abundances from assumed mineral compositions and calculated rock densities at 1 bar and 25°C [*Goffé et al.*, 2003] using an unspecified procedure. Because the thermal expansivities and compressibilities of key minerals such as feldspar translate into density changes of 15% over the 800°C to 3 GPa pressure range of interest [*Hacker and Abers*, 2004], the differences in these approaches will necessarily lead to different calculated densities.

[2] Our calculated densities do not violate thermodynamics as implied by *Bousquet et al.* [2005]. With increasing temperature, thermodynamics requires the entropy of a system to increase whereas the density of the system may increase or decrease. With increasing pressure, thermodynamics requires the density of a system to increase, but we and *Bousquet et al.* [1997, 2005] present calculated densities for the solid minerals, not the whole system which includes H₂O in addition to the solid minerals. The specific example cited, of a temperature-dependent increase in density at 800°C and 1.0–1.5 GPa, is caused by the dehydration of amphibole. Our new results "contradict" our previous results [*Hacker*, 1996] because our new calculations explicitly consider the effect of Fe.

[3] We are perplexed by *Bousquet et al.*'s [2005] suggestion that our density calculations contradict densities of natural rocks measured by *Austrheim* [1987]. *Austrheim* [1987] measured granulite facies anorthositic rocks with densities of 2.79–3.21 g/cm³ and mafic eclogites of 3.5–3.6 g/cm³ but did not specify mineral abundances or compositions, precluding a direct comparison. If, however, we use mineral compositions from *Austrheim and Griffin* [1985] and assume mineral abundances typical for granulites (50% plagioclase, 25% garnet, and 25% pyroxene) and eclogites (50% garnet and 50% pyroxene), we calculate STP densities of 3.20 and 3.61 g/cm³, in agreement with those measured by Austrheim, who noted that the presence of microcracks and alteration in his rocks would lower the density measurements. It is even more difficult to make comparisons between our calculated densities and the other papers cited by *Bousquet et al.* [2005]. *Green and Ringwood* [1967] did not measure the densities of their experimental rocks. *Ito and Kennedy* [1971] did not measure garnet compositions and reported only a single pyroxene composition. *Bousquet et al.* [2005] are correct to note that within individual facies fields our calculated densities depend only on the formula weight, molar volume, expansivity α, $\partial\alpha/\partial T$, isothermal bulk modulus K_T, $\partial K_T/\partial P$, shear modulus μ, $\partial\mu/\partial P$, $\Gamma = (\partial\ln\mu/\partial\ln\rho)_P$, Grüneisen parameter γ_{th}, and the second Grüneisen parameter $\delta_T = (\partial\ln K_T/\partial\ln\rho)_P$; we do not model the changes in mineral composition and abundance within those individual fields.

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[1]Department of Geological Sciences, University of California, Santa Barbara, California, USA.
[2]Department of Earth Sciences, Boston University, Boston, Massachusetts, USA.
[3]Department of Geological Sciences, Arizona State University, Tempe, Arizona, USA.

[4] It is true that chloritoid occurs in metamafic rocks, particularly in Mg-rich metagabbros of non-mid-ocean ridge basalt (MORB) composition [*Droop et al.*, 1990]. However, we remain unaware of documented occurrences of chloritoid in naturally metamorphosed rocks of MORB composition, the papers cited by *Bousquet et al.* [2005] notwithstanding. For example, *Schliestedt* [1986] gives the bulk compositions for nine rocks; one contains chloritoid, and it differs from MORB in having low CaO. As all of Schliestedt's rocks were metamorphosed at the same P-T conditions, the presence of chloritoid in only one requires bulk compositional control; *Schliestedt* [1986] even notes that chloritoid + omphacite is unstable in these rocks, a prerequisite for stability of a chloritoid eclogite. *Miller* [1986] reports no bulk compositions. *Bearth* [1973] and *Messiga et al.* [1995] give no bulk compositions for their chloritoid-bearing rocks, although *Messiga et al.* [1995] do show that unusually low-Ca bulk compositions are required.

[5] It is worth repeating that the (quite valuable) experiments of *Schmidt and Poli* [1998] are unreversed synthesis experiments on glassy starting materials; the presence of a phase in such experiments cannot be taken as proof that such a mineral would exist under equilibrium conditions. The presence of chloritoid in experimental products does not ensure that it is a stable phase. *Liu et al.* [1996] showed with reversal experiments that chloritoid is metastable in MORB at similar PT conditions.

[6] *Bousquet et al.* [2005] correctly note that glaucophane and ferro-glaucophane are unstable in MORB at $600-800°C$ and $0.8-1.2$ GPa; our choice of these end-members resulted from the fact that the physical properties of rather few amphiboles are well measured. A better choice from a petrological perspective is pargasite, but note that this changes the calculated density by <0.3%.

[7] Finally, the elegant paper by *Kerrick and Connolly* [2001] based on Perple_x does indeed show different calculated H_2O contents than our Figure 1 because of two main differences: (1) Kerrick and Connolly fixed the maximum H_2O content at 2.5 wt %, whereas we imposed no constraint; and (2) their model rock is an altered MORB that is, for example, enriched in Al, Ca, and Mg. Their lawsonite stability field, in particular, extends $\sim200°C$ beyond ours. Using Perple_x for our MORB composition also results in a similar, extended calculated stability field for lawsonite, but we disregard this calculated result because natural rocks that were apparently metamorphosed at these conditions lack lawsonite (our recalculations of the PT results of *Feininger* [1980], *Heinrich* [1986], and *Okay et al.* [1985]).

References

Austrheim, H. (1987), Eclogitization of lower crustal granulites by fluid migration through shear zones, *Earth Planet. Sci. Lett.*, *81*, 221–232.

Austrheim, H., and W. L. Griffin (1985), Shear deformation and eclogite formation within granulite-facies anorthosites of the Bergen Arcs, western Norway, *Chem. Geol.*, *50*, 267–281.

Bearth, P. (1973), Gesteins- und Mineralparagenesen aus den Ophiolithen von Zermatt. Rock and mineral paragenesis of the ophiolites of Zermatt, Switzerland, *Schweiz. Mineral. Petrogr. Mitt.*, *53*, 299–334.

Bousquet, R., B. Goffe, P. Henry, X. Le Pichon, and C. Chopin (1997), Kinematic, thermal and petrological model of the central Alps: Lepontine metamorphism in the upper crust and eclogitisation of the lower crust, *Tectonophysics*, *273*, 105–127.

Bousquet, R., B. Goffé, X. Le Pichon, C. de Capitani, C. Chopin, and P. Henry (2005), Comment on "Subduction factory: 1. Theoretical mineralogy, densities, seismic wave speeds and H_2O contents" by Bradley R. Hacker, Geoffrey A. Abers, and Simon M. Peacock, *J. Geophys. Res.*, *110*, B02206, doi:10.1029/2004JB003450.

Droop, G. T. R., B. Lombardo, and U. Pognante (1990), Formation and distribution of eclogite facies rocks in the Alps, in *Eclogite Facies Rocks*, edited by D. A. Carswell, pp. 225–259, Blackie Acad. and Prof., New York.

Feininger, T. (1980), Eclogite and related high-pressure regional metamorphic rocks from the Andes of Ecuador, *J. Petrol.*, *21*, 107–140.

Goffé, B., R. Bousquet, P. Henry, and X. Le Pichon (2003), Effect of the chemical composition of the crust on the metamorphic evolution of orogenic wedges, *J. Metamorph. Geol.*, *21*, 123–141.

Green, D. H., and A. E. Ringwood (1967), An experimental investigation of the gabbro-eclogite transformation and its petrological implications, *Geochim. Cosmochim. Acta*, *31*, 767–833.

Hacker, B. R. (1996), Eclogite formation and the rheology, buoyancy, seismicity, and H_2O content of oceanic crust, in *Subduction: Top to Bottom*, *Geophys. Monogr. Ser.*, vol. 96, edited by G. E. Bebout et al., pp. 337–346, AGU, Washington, D. C.

Hacker, B. R., and G. A. Abers (2004), Subduction Factory 3: An Excel worksheet and macro for calculating the densities, seismic wave speeds, and H2O contents of minerals and rocks at pressure and temperature, *Geochem. Geophys. Geosyst.*, *5*, Q01005, doi:10.1029/2003GC000614.

Hacker, B. R., G. A. Abers, and S. M. Peacock (2003), Subduction factory: 1. Theoretical mineralogy, density, seismic wave speeds, and H_2O content, *J. Geophys. Res.*, *108*(B1), 2029, doi:10.1029/2001JB001127.

Heinrich, C. A. (1986), Eclogite facies regional metamorphism of hydrous mafic rocks in the central alpine Adula Nappe, *J. Petrol.*, *27*, 123–154.

Ito, K., and G. C. Kennedy (1971), An experimental study of the basalt-garnet granulite-eclogite transition, in *The Structure and Physical Properties of the Earth's Crust*, *Geophys. Monogr. Ser.*, vol. 14, edited by J. G. Heacock, pp. 303–314, AGU, Washington, D. C.

Kerrick, D. M., and J. A. D. Connolly (2001), Metamorphic devolatilization of subducted oceanic metabasalts: Implications for seismicity, arc magmatism and volatile recycling, *Earth Planet. Sci. Lett.*, *189*, 19–29.

Liou, J. G., B. R. Hacker, and R. Y. Zhang (2000), Ultrahigh-pressure (UHP) metamorphism in the forbidden zone, *Science*, *287*, 1215–1216.

Liu, J., S. R. Bohlen, and W. G. Ernst (1996), Stability of hydrous phases in subducting oceanic crust, *Earth Planet. Sci. Lett.*, *143*, 161–171.

Messiga, B., M. Scambelluri, and G. B. Piccardo (1995), Chloritoid-bearing assemblages in mafic systems and eclogite-facies hydration of alpine Mg-Al metagabbros (Erro-Tobbio Unit, Ligurian western Alps), *Eur. J. Mineral.*, *7*, 1149–1167.

Miller, C. (1986), Alpine high-pressure metamorphism in the eastern Alps, *Schweiz. Mineral. Petrogr. Mitt.*, *66*, 139–144.

Okay, A. I., M. B. Arman, and M. C. Goncuoglu (1985), Petrology and phase relations of the kyanite-eclogites from eastern Turkey, *Contrib. Mineral. Petrol.*, *91*, 196–204.

Schliestedt, M. (1986), Eclogite-blueschist relationships as evidenced by mineral equilibria in the high-pressure metabasic rocks of Sifnos (Cycladic Islands), Greece, *J. Petrol.*, *27*, 1437–1459.

Schmidt, M. W., and S. Poli (1998), Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation, *Earth Planet. Sci. Lett.*, *163*, 361–379.

G. A. Abers, Department of Earth Sciences, Boston University, Boston, MA 02215, USA. (abers@bu.edu)

B. R. Hacker and S. Johnston, Department of Geological Sciences, University of California, Santa Barbara, CA 93106-9630, USA. (hacker@geology.ucsb.edu)

S. M. Peacock, Department of Geological Sciences, Arizona State University, Tempe, AZ 85287-1404, USA. (peacock@asu.edu)