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Sulfide melts and long-term low seismic wavespeeds in lithospheric and asthenospheric mantle

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[1] Some studies of lithospheric and asthenospheric seismic structure, report mantle velocities as low as ~4% below the reference models used. While these low wavespeeds may be attributed to thermal effects in tectonically young or actively volcanic regions, in older, tectonically stable regions low velocity anomalies apparently persist even past the decay time of any thermal perturbation, rendering such a mechanism implausible. Low volume melts can also reduce wavespeeds, but their buoyancy should drain them upward away from source regions, preventing significant accumulation if they are able to segregate. Sulfide, ubiquitous as inclusions in lithospheric mantle xenoliths, forms dense, non-segregating melts at temperatures and volatile fugacities characteristic of even old lithospheric mantle. We show that 1-5 volume percent sulfide melts can act to permanently create reductions up to 5.5% in seismic wavespeeds in areas of the lithosphere and the asthenosphere disturbed by prior melting events that carry and concentrate sulfide. Citation: Helffrich, G., J.-M. Kendall, J. O. S. Hammond, and M. R. Carroll (2011), Sulfide melts and long-term low seismic wavespeeds in lithospheric and asthenospheric mantle, Geophys. Res. Lett., 38, L11301, doi:10.1029/ 2011GL047126.

1. Introduction

[2] Low shear wave speeds arise in a variety of old tectonic environments. In the British Isles, the main phase of tectonic activity was ~400 Ma when the proto-Atlantic Ocean closed. In the later stages of Atlantic rifting at ~60 Ma, volcanic centers on the western coast of Britain created an extensive intrusive dike network in northern England and Scotland that extends across to the North Sea [Craig, 1991]. Arrowsmith et al. [2005] found shear wave speed decreases of 1.5%, corresponding to ~200 K hotter temperatures, that extended to 150 km depth under the British Isles. Tomographically determined shear wave speeds in Brazil's Saõ Francisco craton [Schimmel et al., 2003] are 1% slower than the IASP91 reference velocity model [Kennett and Engdahl, 1991] in a columnar structure extending from about 100 km to 400 km depth beneath the Paraná Basin. The structure is attributed to activity of the Tristan de Cunha plume, active at ~130 Ma, which modified the pre-existing, 250 km deep, cratonic structure. While the anomalies discussed above all affect the lithosphere and asthenosphere under continents, oceanic

regions show anomalies of similar magnitude. The Iceland hot spot has 4.2% slower shear wave speeds extending to depths of at least 400 km [Wolfe et al., 1997]. The Cape Verde Islands in the equatorial Atlantic feature shear velocities below all islands 2.4% slower than average [Lodge and Helffrich, 2006]. Ekström and Dziewonski [1998] observe an unusual pattern of surface wave anisotropy in the mid-Pacific around Hawaii, where, at 200 km depth, vertically polarized shear waves (SV) are 7% slower than horizontally polarized ones (SH) elsewhere in either the Pacific basin or other oceans. A straightforward explanation for anomalies near hot spots is to attribute it to some influence of melt or chemical buoyancy that promotes melting, and that sustains volcanism.

2. Persistence of Low Wavespeeds

[3] The principal problem with long-term persistence of low seismic wavespeeds in lithospheric or asthenospheric mantle is the requirement of maintaining high temperatures or retaining melt at depth. Thermal anomalies of a few tens of km breadth will diffuse away in about 10 Ma in a linear, one-dimensional geometry; and in cylindrical geometry radial diffusion away from a pipe will be about twice as fast [Carslaw and Jaeger, 1959]. Thus, for long-term reduction of wavespeeds, a steady hot material flux is usually invoked to maintain temperatures high enough [Arrowsmith et al., 2005] or to sustain melt supply [Bastow et al., 2008]. Melt is effective at reducing shear wave speeds but is difficult to retain for long in a matrix when it wets grain boundaries and can migrate buoyantly. Spence and Turcotte [1990] found that fracture-driven basaltic melt ascent times are on the order of meters per second through the top 50 km of the mantle, implying residence times of a few hours. If buoyant rise is governed by porous flow, melts will reach the surface in 7–10 kyr from 50 km depth [McKenzie, 1984; Rose and Brenan, 2001], necessitating constant replenishment to maintain low wavespeeds.

3. Sulfide Melt Properties and Retention

[4] Silicate or carbonate melts are not the only types possible in the mantle. Fe-Ni-Cu-S inclusions are common in mantle samples, mid-ocean ridge basalts and Alpine peridotites [*Roy-Barman et al.*, 1998; *Ryabchikov et al.*, 1995; *Lorand*, 1987]. Sulfur is an abundant volatile constituent of the mantle that is readily replenished in the upper mantle by subduction [*McDonough and Sun*, 1995; *Ryabchikov et al.*, 1995]. Magmatic processes concentrate sulfide from the low abundances in the shallow mantle to form deposits of economic importance [*Naldrett*, 1989]. Sulfide in MORB typically has the composition of monosulfide solid solution

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Figure 1. Composition of sulfide inclusions and velocity and density of mantle and molten sulfide. (a) Sulfide inclusion compositions in MORB (· [Roy-Barman et al., 1998]) and OIB (× [Ryabchikov et al., 1995]) and composition of stoichiometric MSS (FeS; red circle). MSS compositions more S-rich than the Fe-FeS eutectic (E) incongruently melt at 988° C and are completely melted at 1188° C at 1 bar and the 1 bar ternary eutectic melting temperature in the Fe-O-S system is 920° C (TE) [Hilty and Crafts, 1952]. (b) Depth profiles of velocity and density of molten sulfide along adiabatic profiles initiated at 95 km depth with temperatures of 1250°C, 1350° and 1450°C (the curves virtually overlie one another; see Helffrich and Kaneshima [2010] for properties calculation). Mantle velocities and densities are AK135 and PREM, respectively [Kennett et al., 1995; Dziewonski and Anderson, 1981].

(MSS; approximately pyrrhotite if (Fe, Ni, Cu)S \approx FeS; Figure 1). This becomes completely molten at 1180° C, a temperature that in cratonic regions is reached at 100–125 km [*Mareschal et al.*, 2004], and in old oceanic lithosphere, at depths of ~60 km [*Stein and Stein*, 1992] or shallower if under younger lithosphere.

[5] Sulfide melts are dense and do not rise in the mantle. Using methods described elsewhere to calculate wavespeeds and densities [*Helffrich and Kaneshima*, 2010], along an adiabat fixed at 1450° C at 95 km depth [*Stein and Stein*, 1992] densities at 100 km depth for pyrrhotite compositions are 4512 kg m⁻³ as compared to the mantle's density of 3373 kg m⁻³ [*Dziewonski and Anderson*, 1981]. Unlike silicate and carbonate melts, however, which wet mantle silicates [*Yoshino et al.*, 2009], anion-poor sulfide melt connectivity in solid silicate depends on the oxygen content of the melt, with more oxidizing conditions leading to lower wetting angles and efficient segregation, while reducing conditions lead to high wetting angles and melt isolation [*Gaetani and Grove*, 1999; *Rose and Brenan*, 2001]. Mantle

sulfides are generally more sulfur rich (Figure 1) but orogenic peridotites do not show evidence of sulfur depletion that would occur if sulfide melt connected and drained from host silicate [*Eggler and Lorand*, 1993].

[6] Under conditions of mechanical equilibrium, *von* Bargen and Waff [1986] showed that the capacity of rock to retain non-draining melts is limited by the solid-liquid interfacial angles. The isolation of non-draining melt pockets is overcome when the melt fraction grows to a critical capacity that reconnects the pockets. As the angle decreases towards 60°, the capacity to retain a non-draining melt also decreases; melt migrates for lower angles. The possible reductions in wavespeeds for different amounts of sulfide melt are shown in Figure 2. Significant wavespeed reductions result at any wetting angle preventing draining (>60°), and can range up to 4.5–5% decreases at low f_{O_2} . Under typical upper mantle conditions, approximately 1 log unit below the fayalite-quartz-magnetite buffer (FMQ), sulfide melts drain. At lower f_{O} , however, sulfide could be retained, trapping melt at shallow lithospheric or mantle levels and causing persistent velocity reductions due to the low melting temperature.

4. Results

[7] For this mechanism to be viable, mantle f_{O_2} must be below approximately 1–2 log units below FMQ. f_{O_2} of natural samples vary as a function of tectonic province [*Frost* and McCammon, 2008] and indicate that under cratonic regions, f_{O_2} ranges from 1 to 4 log units below FMQ. MORB is more oxidizing (0 to 0.8 log units below FMQ) and massif peridotites and abysal peridotites range from below 3 to around 0 log units below FMQ. Sulfur fugacities appear to range from $\approx 10^{-3} - 10^{-1}$ [*Fonseca et al.*, 2007]. Though the glasses may not record source melting conditions due to fractionation and post-emplacement modification [*Fonseca et al.*, 2007], they do suggest that hotter and presumably more deeply-sourced lavas are more reduced. A diversity of physical conditions may arise in the mantle that includes both sulfide melt drainage and retention in rocks.

[8] If pyrrhotite-like sulfide melts are present in the mantle, velocity anomalies in the UK (1.5%) and Brazil (1%) could be created by 1.3 and 0.9 vol.% melt, respectively (Figure 2). A slightly higher 2.6 vol.% melt abundance is required to reduce velocities to 2.4% in Cape Verde. In neither case is there a need to invoke a thermal anomaly, though higher temperatures could further reduce wave speeds or melt volume requirements in areas of active magmatism.

[9] Non-draining sulfide melts would not cause significant resistivity and rheological anomalies. Because they are in isolated pockets, even highly conductive sulfide melt will not contribute significantly to whole-rock conductivity. *Waff* [1974] showed that isolated conductive melt pockets increase conductivity by only a few percent at the low melt fractions considered here, which would be unobservable given the range of resistivities characteristic of continental and oceanic environments [*Helffrich*, 2003]. Neither would small volume fractions of sulfide affect viscosity or plate flexure behavior. *Hustoft et al.* [2007] showed that liquid sulfide reduces peridotite viscosity by less than 10% at melt fractions in the range envisaged here. Treating the sulfide



Figure 2. Melt fraction, P and S velocity reduction as a function of wetting angle (θ), and range of $f_{O_2} - f_{S_2}$ expected in the mantle. (a) Maximum P and S wavespeed reductions at 100 km depth using relations from von Bargen and Waff [1986] and solid-melt composite properties of Tandon and Weng [1984]. See Figure 1 for sulfide melt density and Vp. Wavespeeds shown are relative to the global reference model AK135 [Kennett et al., 1995]. On same axes, solid line shows melt fraction (f) and long dashed line shows relation between wetting angle and $\frac{1}{2} \log f_{O_2} / f_{S_2}$ [Gaetani and Grove, 1999] delimiting feasible range of wetting angles. The curve is the maximum velocity reduction permitted before draining will take place; actual reductions may be lower. (b) Expected range of $f_{O_2} - f_{S_2}$ encountered in the mantle. Wetting angle is controlled by S/O ratio in sulfide melt (diagonal lines labeled with $1/2 \log(f_{O_2}/f_{S_2})$ value), but f_{O_2} and f_{S_2} are limited by rock sample data (gray box; [Fonseca et al., 2007; Frost and McCammon, 2008]). Dashed horizontal and vertical lines indicate position of reference buffers fayalite-magnetite-quartz (FMQ), ironwüstite (IW) iron-quartz-favalite (IOF) and iron-FeS (Fe-FeS). S/O ratios in gray box lead to θ variation between $< 60^{\circ}$ (highest f_{O_2}) to ~90° (lowest f_{O_2}) [Gaetani and Grove, 1999].

melt + rock as a composite medium [*Tandon and Weng*, 1984], Young's modulus reductions less than 9% would ensure at melt fractions of 5% or less, within the uncertainty of measurement [*Turcotte and Schubert*, 2002]. Attenuation of seismic waves might result due to scattering, but the high Q of metallic liquid and the small inclusion size compared

to seismic wavelengths renders the effect negligible [*Dziewonski and Anderson*, 1981; *Wu and Aki*, 1980].

5. Discussion

[10] The sulfide melt abundances reported in continental xenolith studies range to over 1 vol.%. Spinel lherzolites generally have 0.1 vol.% sulfide, but studies report up to 1.2 vol.% in various environments [Peterson and Francis, 1977; Ducea and Park, 2000; Lorand and Grégoire, 2006; Wang et al., 2009]. Sulfide abundances in garnet peridotites are not well known, but, where reported, are higher where metasomatic textures and mineralogies are present [Lorand and Grégoire, 2006]. However, most xenolith suites are spinel lherzolites [Boyd and Meyer, 1979] and therefore not representative of deep lithospheric or asthenospheric mantle. From the existence of magmatic sulfide deposits in Siberian Trap volcanics, it is clear that a concentration mechanism operates during magmatism. Given the sampling bias and the range of sulfide content in known xenolith suites, no firm upper bound can be placed on magmatic sulfide volumes based on mantle sulfur abundance.

[11] Some limits do exist to the capacity of the mantle to retain large quantities of sulfide, however. The most restrictive is the aggregate density of the rock with added sulfide. For typical mantle viscosities $(10^{19} - 10^{21} \text{ Pa s})$, sinking rates of 0.5 mm yr⁻¹, which would lead to 50 km downward displacement in 100 Myr, arise for spherical bodies of 20 km radius at melt fractions in excess of 1% (see auxiliary material).¹ Irregular or elongate bodies will sink more slowly, limiting melt to $\sim 5\%$, similar to the range shown in Figure 2. Downward dike-like fracture due to the load of coalesced sulfide appears to be inhibited due to short column heights mediated by surface tension considerations [von Bargen and Waff, 1986]. Porous flow of sulfide is lower than sinking velocities based on experimentally determined silicate-sulfide permeabilities [Roberts et al., 2007]. Thus a few percent of retained sulfide is the maximum conceivable in the mantle unless it is continuously replenished by magmatic processes.

[12] We assume mechanical equilibrium in these calculations. *Hustoft and Kohlstedt* [2006] showed that olivine with disseminated liquid FeS deformed under shear organized its structure into bands containing 30 vol.% FeS and residual FeS of ~1% but only when bulk FeS contents were greater than 5 vol.%. These results suggest that our equilibrium analysis is valid for the two reasons that concentration only occurs at higher sulfide contents that we anticipate (Figure 2), and that the amounts retained away from the concentration zones are roughly what are required to achieve the required seismic wavespeed reductions cited earlier. Volumetrically large sulfide concentrations lead to the gravitational instabilities discussed previously.

[13] Rychert and Shearer [2009] found P-to-S converted wave arrivals under Precambrian shields and platforms at 95 ± 5 km depth and at 70 ± 4 km in oceanic regions. These depths approximately correspond to the depths at which sulfide melt would be produced along the respective geotherms. We speculate that rather than representing the lithosphere-asthenosphere boundary, this feature might demark

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GL047126.

the stabilization of non-draining sulfide liquid in the local tectonic environment. Concentration of sulfide could happen by either cryptic magmatic processes [Hirano et al., 2006] or by draining of sulfide from shallower levels at more oxidizing conditions.

6. Conclusions

[14] Sulfide melt might act to cause long-term velocity anomalies in continental and oceanic lithosphere. While sulfur concentrations are generally believed to be low in the mantle, magmatic processes can concentrate sulfide. At concentrations of percent levels by volume, it can have a significant effect on seismic wavespeeds. However, limits exist to the ability of this mechanism to reduce wavespeeds, both due to the ability of rock to retain melt, leading to draining, and due to the increased aggregate density of the rock, leading to its convective removal.

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References

- Arrowsmith, S. J., J.-M. Kendall, N. White, J. C. VanDecar, and D. Booth (2005), Seismic imaging of a hot upwelling beneath the British Isles, Geology, 33, 345-348.
- Bastow, I. D., A. A. Nyblade, G. W. Stuart, T. O. Rooney, and M. H. Benoit (2008), Upper mantle seismic structure beneath the Ethiopian hot spot: Rifting at the edge of the African low-velocity anomaly, Geochem. Geophys. Geosyst., 9, Q12022, doi:10.1029/2008GC002107.
- Boyd, F. R., and H. O. Meyer (1979), The Mantle Sample: Inclusions in Kimberlites and Other Volcanics, 424 pp., AGU, Washington, D. C.
- Carslaw, H. S., and J. C. Jaeger (1959), Heat Conduction in Solids, 510 pp., Oxford Univ. Press, Oxford, U. K.
- Craig, C. Y. (1991), The Geology of Scotland, 612 pp., Geol. Soc. London, London.
- Ducea, M. N., and S. K. Park (2000), Enhanced mantle conductivity from sulfide minerals, southern Sierra Nevada, California, Geophys. Res. Lett., 27. 2405-2408.
- Dziewonski, A., and D. Anderson (1981), Preliminary reference Earth model, Phys. Earth Planet. Inter., 25, 297-356
- Eggler, D. H., and J. P. Lorand (1993), Mantle sulfide geobarometry, Geochim. Cosmochim. Acta, 57, 2213-2222
- Ekström, G., and A. Dziewonski (1998), The unique anisotropy of the Pacific upper mantle, Nature, 394, 168-172.
- Fonseca, R. O. C., G. Mallmann, H. S. C. O'Neill, and I. H. Campbell (2007), How chalcophile is rhenium? An experimental study of the solubility of Re in sulphide mattes, Earth Planet. Sci. Lett., 260, 537-548.
- Frost, D., and C. McCammon (2008), The redox state of the Earth's mantle, Annu. Rev. Earth Planet. Sci., 36, 389-420.
- Gaetani, G. A., and T. L. Grove (1999), Wetting of mantle olivine by sulfide melt: Implications for Re-Os ratios in mantle peridotite and latestage core formation, Earth Planet. Sci. Lett., 169, 147-163.
- Helffrich, G. (2003), Basic principles of electromagnetic and seismological investigation of shallow subduction zone structure, in Inside the Subduction Factory, Geophys. Monogr. Ser., vol. 138, edited by J. Eiler, pp. 47-57, AGU, Washington, D. C.
- Helffrich, G., and S. Kaneshima (2010), Outer-core compositional stratification from observed core wave speed profiles, Nature, 468, 807-810.
- Hilty, D. C., and W. Crafts (1952), Liquidus surface of the Fe-S-O system, J. Met. Trans. AIME, 4, 1307-1312.
- Hirano, N., et al. (2006), Volcanism in response to plate flexure, Science, 313, 1426-1428
- Hustoft, J. W., and D. L. Kohlstedt (2006), Metal-silicate segregation in deforming dunitic rocks, Geochem. Geophys. Geosyst., 7, Q02001, doi:10.1029/2005GC001048
- Hustoft, J., T. Scott, and D. Kohlstedt (2007), Effect of metallic melt on the viscosity of peridotite, Earth Planet. Sci. Lett., 260, 355-360.

- Kennett, B. L. N., and E. R. Engdahl (1991), Traveltimes for global earthquake location and phase identification, Geophys. J. Int., 105, 429-465.
- Kennett, B. L. N., E. R. Engdahl, and R. Buland (1995), Constraints on seismic velocities in the Earth from traveltimes, Geophys. J. Int., 122, 108-124.
- Lodge, A., and G. Helffrich (2006), Depleted swell root beneath the Cape Verde Islands, Geology, 34, 449-452
- Lorand, J. P. (1987), Sulfide petrology of spinel and garnet pyroxenite layers from mantle-derived spinel lherzolite massifs of Arieg, Northeastern Pyrenees, France, J. Pet., 30, 987-1015.
- Lorand, J. P., and M. Grégoire (2006), Petrogenesis of base metal sulphide assemblages of some peridotites from the Kaapvaal craton (South Africa), Contrib. Mineral. Petrol., 151, 521-538.
- Mareschal, J. C., A. Nyblade, H. K. C. Perry, C. Jaupart, and G. Bienfait (2004), Heat flow and deep lithospheric thermal structure at Lac de Gras, Slave Province, Canada, Geophys. Res. Lett., 31, L12611, doi:10.1029/ 2004GL020133
- McDonough, W. F., and S. Sun (1995), The composition of the Earth,
- *Chem. Geol.*, *120*, 223–253. McKenzie, D. P. (1984), The generation and compaction of partially molten rock, J. Pet., 25, 713-765
- Naldrett, A. J. (1989), Magmatic Sulfide Deposits, 186 pp., Oxford Univ. Press, Oxford, U. K.
- Peterson, R., and D. Francis (1977), The origin of sulfide inclusions in pyroxene megacrysts, Am. Min., 62, 1049-1051.
- Roberts, J. J., J. H. Kinney, J. Siebert, and F. J. Ryerson (2007), Fe-Ni-S melt permeability in olivine: Implications for planetary core formation, Geophys. Res. Lett., 34, L14306, doi:10.1029/2007GL030497
- Rose, L. A., and J. M. Brenan (2001), Wetting properties of Fe-Ni-Co-Cu-O-S melts against olivine: Implications for sulfide melt mobility, Econ. Geol., 96, 145-157.
- Roy-Barman, M., G. J. Wasserburg, D. A. Papanastassiou, and M. Chaussidon (1998), Osmium isotope compositions and Re-Os concentrations in sulfide globules from basaltic glasses, Earth Planet. Sci. Lett., 154.331-347
- Ryabchikov, I. D., T. Ntaflos, G. Kurat, and L. N. Kogarko (1995), Glassbearing xenoliths from Cape Verde: Evidence for a hot rising mantle jet, Mineral. Petrol., 55, 217-237.
- Rychert, C. A., and P. M. Shearer (2009), A Global view of the lithosphere-asthenosphere boundary, Science, 324, 495-498.
- Schimmel, M., M. Assumpo, and J. C. VanDecar (2003), Seismic velocity anomalies beneath SE Brazil from P and S wave travel time inversions, J. Geophys. Res., 108(B4), 2191, doi:10.1029/2001JB000187.
- Spence, D. A., and D. L. Turcotte (1990), Buoyancy-driven magma fracture: A mechanism for ascent through the lithosphere and the emplacement of diamonds, J. Geophys. Res., 95, 5133-5139.
- Stein, C. A., and S. Stein (1992), A model for the global variation in oceanic depth and heat-flow with lithospheric age, Nature, 359, 123-129.
- Tandon, G. P., and G. J. Weng (1984), The effect of aspect ratio of inclusions on the elastic properties of unidirectionally aligned composites, Polym. Compos., 5, 327-333.
- Turcotte, D., and G. Schubert (2002), Geodynamics, 456 pp., Cambridge Univ. Press, Cambridge, U. K.
- von Bargen, N., and H. S. Waff (1986), Permeabilities, interfacial areas and curvatures of partially molten systems: results of numerical computations of equilibrium microstructures, J. Geophys. Res., 91, 9261-9276.
- Waff, H. (1974), Theoretical considerations of electrical conductivity in a partially molten mantle and implications for geothermometry, J. Geophys. Res., 79, 4003-4010.
- Wang, K.-L., S. O'Reilly, W. Griffin, N. Pearson, and M. Zhang (2009), Sulfides in mantle peridotites from Penghu Islands, Taiwan: Melt percolation, PGE fractionation, and lithospheric evolution of the South China Block, Geochim. Cosmochim. Acta, 73, 4531-4557.
- Wolfe, C. J., I. T. Bjarnason, J. C. VanDecar, and S. C. Solomon (1997), Seismic structure of the Iceland mantle plume, Nature, 385, 245-247.
- Wu, R., and K. Aki (1980), Elastic wave scattering by a random medium and the small-scale inhomogeneities in the lithosphere, J. Geophys. Res., 90, 10,261-10,273.
- Yoshino, T., D. Yamazaki, and K. Mibe (2009), Well-wetted olivine grain boundaries in partially molten peridotite in the asthenosphere, Earth Planet. Sci. Lett., 283, 167-173.

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