INTRODUCTION

By

J. Brian Balta

Part 1: Experimental investigation of hydrous melting of the Earth's upper mantle

It is now well established that volatile elements including carbon and water strongly influence the melting of rocks on Earth. The presence of either component in an upwelling rock will cause it to begin melting at greater pressures and lower temperatures than it would if it were volatile-free. A number of experiments and analyses of natural rocks have built a basic understanding of how these components interact with natural minerals. In the mantle, a small amount of water can be hosted within the structure of most nominally anhydrous minerals (e.g., Bell and Rossman, 1992; Mosenfelder et al., 2006). Beneath a mid-ocean ridge, mantle peridotite upwells to fill the space created as the oceanic plates spread apart. When it crosses its solidus pressure and temperature, this material begins to melt, producing the liquids that eventually are erupted as mid-ocean ridge basalts. As a volatile component, water partitions strongly into the liquid phase during melting (e.g., Michael, 1995; Hirth and Kohlstedt, 1996; Danyushevsky et al., 2000). Consequently, the presence of water is also able to suppress the solidus of peridotite, such that peridotites with higher water contents will melt at greater depths (Hirth and Kohlstedt, 1996). Anhydrous peridotites would typically be expected to begin melting at ~60 km depth (Hirschmann et al., 2009), and the presence of water could increase this depth by several 10's of km depending on the exact amount of water present and its relationship to the solids.

Understanding the effects of water on melting under mid-ocean ridges therefore requires experiments equilibrating solids and liquids with compositions that are representative of the upper mantle, conducted under pressure and temperature conditions that approximate those that are found on Earth. However, a number of experimental difficulties have thus far prevented a full analysis of hydrous melting under these

conditions. These issues include: the difficulty in quenching liquids from high pressure to unaltered glass that can be analyzed at low pressure, interaction of samples with the capsule materials encasing them, and contamination of experiments by carbon during heating (Liu et al., 2006).

We have performed experiments that have successfully equilibrated hydrous liquids with natural solids at the pressures and temperatures of interest after overcoming these difficulties. The results of these experiments make up Part 1 of this thesis. We were able to successfully quench hydrous liquids to analyzable glasses from 3 GPa pressure and 1375°C. To quench these liquids, we adapted the technique of Putirka et al. (1996) which was effective at producing a glass in our piston-cylinder. Preventing significant interaction of the samples with the capsules was more complicated. To contain water during the experiments, we chose to use capsules composed of an alloy of $Au_{75}Pd_{25}$, which is commonly used as a capsule material for water-bearing experiments (e.g., Kawamoto and Hirose, 1994). However, capsules composed of Au/Pd alloys will take up small amounts of several elements at high temperature, including Fe, which is a major element in natural rocks. Avoiding significant Fe loss to our capsules motivated the work in Chapter 4 of this thesis. We performed experiments to calibrate the equilibrium iron concentration in this alloy as a function of iron activity, such that we gained the ability to pre-saturate capsules with an appropriate amount of iron before use in high-pressure experiments. Thus, we were able to precondition our capsules with enough iron to avoid significant iron loss or gain to the capsules during the run. Finally, to control carbon contamination during experiments, we applied a version of the double-capsule design of Kägi et al. (2005), which was originally designed to control oxygen fugacity during

hydrous experiments. By creating a large outer capsule filled with the same contents as the inner capsule, the concentration of carbon in the final liquids only increased slightly during the experiments, allowing us to examine low-carbon, hydrous melts that have not previously been sampled.

The liquids we produced and the solids that they have equilibrated with appear to have significant implications for the understanding of natural peridotite melting on earth. The basic effect of water on the composition of silicate liquids has been understood as increasing the silica content of the liquid at the expense of other oxides such as magnesium and iron (e.g., Kushiro, 1968; Gaetani and Grove, 1998; Liu et al., 2006). Because these oxides are the main components of olivine, the ratio of silica to iron and magnesium can be understood as reflecting increasing or decreasing amounts of olivine in the melt. However, a number of variables other than simply water content affect this ratio by affecting the stability of olivine. For example, increasing carbon content appears to oppose the effect of increasing water. Compared to hydrous melting at lower temperatures and lower pressures (e.g., Gaetani and Grove, 1998), our liquid shows higher magnesium and iron contents and lower silica, while compared to anhydrous melts from the same pressure and higher temperature (e.g., Walter, 1998) our liquid shows higher silica and lower magnesium and iron. Our experiments show the magnitude of this effect under plausible conditions for the production of natural hydrous melts and likely closely reflect the actual composition of natural liquids.

The hydrous melting experiments also show important changes in the composition of the co-existing clinopyroxenes. Previously, virtually every experiment produced at 3 GPa pressure shows clinopyroxenes with a substantial amount of aluminum in their

structure (e.g. Walter, 1998; Longhi, 2002). Indeed, our starting solid material was synthesized without water present and also shows high aluminum contents in the clinopyroxenes. However, when these clinopyroxenes are exposed to a hydrous melt, there is a substantial shift in their composition to lower aluminum contents. These experiments show clinopyroxenes with lower aluminum contents than any previous set of experiments at this pressure, including our own synthesis work, suggesting that the presence of water must be responsible for the change in clinopyroxene composition. Clinopyroxene aluminum contents have been proposed to be particularly important for the partitioning of a number of elements during melting due to coupled substitutions between trace elements and aluminum in the clinopyroxene structure (e.g., Blundy et al., 1998). Most notably, water itself has been proposed to enter the pyroxene structure by this mechanism (e.g., Aubaud et al., 2004; Hirschmann et al., 2009). Our experiments suggest that the presence of water in fact causes a decrease in the partition coefficient (= concentration in solid/concentration in liquid) for water during melting and therefore can produce hydrous melts with higher water contents than were previously expected.

A final set of results from these experiments is presented in Chapter 3, which discusses the measured partition coefficients between garnet and hydrous melts for iron and manganese. Anhydrous melting would only be expected to produce melts in the presence of significant quantities of garnet if the melting happened at particularly high temperatures (Robinson and Wood, 1998). Hydrous melts however are produced at greater pressures and lower temperatures than anhydrous melts, and thus could be produced in the garnet field. Manganese contents and the iron/manganese ratio of magmatic rocks have recently assumed a key role in a number of petrologic debates, as

new high-precision measurements of manganese contents have allowed for the quantification of small variations (e.g., Sobolev et al., 2007; Qin and Humayun, 2008). Our experiments show manganese to have a surprisingly large partition coefficient in garnet during hydrous melting, such that changing the modal abundance of garnet in a melting source by changes in composition or pressure could produce measurable changes in the iron/manganese ratio of the resulting melt. We explore the resulting liquid compositions for the partition coefficients we measure and compare them with the liquids produced via natural melting.

Part 2: Olivine abundances and compositions in Hawaiian lavas

The final chapter of this thesis moves from examination of the melting process to examining the details of the processes of crystallization and mixing within Hawaiian magma chambers. The main compositional difference seen in basalts produced from the main stage of activity at a Hawaiian volcano reflects the addition of significant quantities of olivine to a basaltic liquid (e.g., Wright, 1971). This olivine is formed by crystallization of liquids after they enter the volcano's plumbing system. The compositional variation between different Hawaiian units is caused by the entrainment of varying amounts of this olivine during eruption. Using data collected from a number of sources including the recent Hawaiian drill cores (e.g., Garcia et al., 2007; Haskins and Garcia, 2004; Quane et al., 2000) we have analyzed the amounts and compositions of olivines through time at the different volcanoes. Several trends seem apparent. Overall, Mauna Kea appears to erupt substantially more olivine than other volcanoes, while Kilauea appears to erupt less. Mauna Kea shows an increase in olivine output with time, which suggests changing eruptive conditions with time, possibly due to an elevated

overall magma flux compared with other Hawaiian volcanoes. Mauna Kea's olivines also show a surprising enrichment in calcium compared with other Hawaiian volcanoes, likely expressing the same phenomenon. Using calibrations developed in recent years (e.g., Toplis, 2005; Wang and Gaetani, 2008) for the composition of olivine produced by crystallizing a liquid of known composition, we have also mathematically reversed the process of olivine crystallization to calculate average parental liquids feeding the best-sampled Hawaiian volcanoes.

REFERENCES

Aubaud, C., Hauri, E. H., and Hirschmann, M. M. (2004) Hydrogen partition coefficients between nominally anhydrous minerals and basaltic melts. *Geophys. Res. Lett.* **31**, *L20611*.

Blundy, J. D., Robinson, J. A. C., and Wood, B. J. (1998) Heavy REE are compatible in clinopyroxene on the spinel lherzolite solidus. *Earth Planet Sc. Lett.* **160**, 493-504.

Gaetani, G. A. and Grove, T. L. (1998) The influence of water on melting of mantle peridotite. *Contrib. Mineral. Petr.* **131**, 323-346.

Garcia, M. O., Haskins, E. H., Stolper, E. M., and Baker, M. (2007) Stratigraphy of the Hawai'i Scientific Drilling Project core (HSDP2): anatomy of a Hawaiian shield volcano. *Geochem. Geophys. Geosyst.* **8**.

Haskins, E. H. and Garcia, M. O. (2004) Scientific drilling reveals geochemical heterogeneity within the Ko'olau shield, Hawai'i. *Contrib. Mineral. Petr.*, 162-188.

Hirschmann, M. M., Tenner, T., Aubaud, C., and Withers, A. C. (2009) Dehydration melting of nominally anhydrous mantle: the primacy of partitioning. *Phys. Earth Planet In.* **176**, 54-68.

Kägi, R., Muntener, O., Ulmer, P., and Ottolini, L. (2005) Piston-cylinder experiments on H_2O undersaturated Fe-bearing systems: An experimental setup approaching $f(O_2)$ conditions of natural calc-alkaline magmas. *Am. Mineral.* **90**, 708-717.

Kawamoto, T. and Hirose, K. (1994) Au-Pd sample containers for melting experiments on iron and water bearing systems. *Eur. J. Mineral.* **6**, 381-385.

Kushiro, I. (1968) Compositions of magmas formed by partial melting of the Earth's upper mantle. *J. Geophys. Res.* **73**, 619-634.

Liu, X., O'Neill, H. S. C., and Berry, A. J. (2006) The effects of small amounts of H_2O, CO_2 and Na_2O on the partial melting of spinel lherzolite in the system CaO-MgO-Al_2O_3-SiO_2 +/- H_2O +/- CO_2 +/- Na_2O at 1.1 GPa. *J. Petrol.* **47**, 409-434.

Longhi, J. (2002) Some phase equilibrium systematics of lherzolite melting: I. *Geochem. Geophys. Geosyst.* **3**, 1020.

Putirka, K., Johnson, M., Kinzler, R., Longhi, J., and Walker, D. (1996) Thermobarometry of mafic igneous rocks based on clinopyroxene-liquid equilibria, 0–30 kbar. *Contrib. Mineral. Petr.* **123**, 92-108.

Qin, L. and Humayun, M. (2008) The Fe/Mn ratio in MORB and OIB determined by ICP-MS. *Geochim. Cosmochim. Ac.* **72**, 1660-1677.

Quane, S. L., Garcia, M. O., Guillou, H., and Hulsebosch, T. P. (2000) Magmatic history of the east rift zone of Kilauea Volcano, Hawai'i, based on drill core SOH-1. *J. Volcanol. Geoth. Res.* **102**, 319-388.

Robinson, J. A. C. and Wood, B. J. (1998) The depth of the spinel to garnet transition at the peridotite solidus. *Earth Planet Sc. Lett.* **164**, 277-284.

Sobolev, A. V., Hofmann, A. W., Kuzmin, D. V., Yaxley, G. M., Arndt, N. T., Chung, S.-L., Danyushevsky, L. V., Elliott, T., Frey, F. A., Garcia, M. O., Gurenko, A. A., Kamenetsky, V. S., Kerr, A. C., Krivolutskaya, N. A., Matvienkov, V. V., Nikogosian, I. K., Rocholl, A., Sigurdsson, I. A., Sushchevskaya, N. M., and Teklay, M. (2007) The amount of recycled crust in sources of mantle-derived melts. *Science* **316**, 412-417.

Toplis, M. J. (2005) The thermodynamics of iron and magnesium partitioning between olivine and liquid: criteria for assessing and predicting equilibrium in natural and experimental systems. *Contrib. Mineral. Petr.* **149**, 22-39.

Walter, M. J. (1998) Melting of garnet peridotite and the origin of komatiite and depleted lithosphere. *J. Petrol.* **39**, 29-60.

Wang, Z. and Gaetani, G. A. (2008) Partitioning of Ni between olivine and siliceous eclogite partial melt: experimental constraints on the mantle source of Hawaiian basalts. *Contrib. Mineral. Petr.* **156**, 661-678.

Wright, T. L. (1971) Chemistry of Kilauea and Mauna Loa lava in space and time. *U.S. Geological Survey Professional Paper* **735**, 1-40.