

High-P-T fluids in diamond trap experiments analyzed frozen with LA-ICPMS: The technique

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Diamond trap experiments are used to explore the chemical composition of the liquid phase (aqueous fluid and hydrous melt alike) coexisting with eclogite at 4-6 GPa and 800-1200 °C. Uncontrolled loss of dissolved constituents with fluid emanating upon piercing have severely limited the reliability of chemical data on high-P fluids so far.

Our novel freezing approach eliminates these problems (Kessel et al. 2004): After the experiments, capsules are first frozen, then cut open, and mounted in a custom-built ablation chamber to be analyzed by LA-ICPMS (193 nm ArF Excimer laser with homogenized energy beam profile interfaced with an Elan6100 ICP-QMS) while maintained frozen. The fluid (mixture of 20 µm diamonds of the trap with ice and interstitial quenched solute) was analyzed at several spots with a large pit (≥60 µm). Cesium, doped in the synthetic basalt starting material, is used as an internal standard for quantification of fluid composition, assuming that all Cs resides in the fluid phase coexisting with K- and mica-free eclogite. Minerals are analyzed by EMP. Agreement between fluid compositions obtained by internal standardization on Cs and derived through mass balance validates the freezing approach. Analytical uncertainties for element concentrations in the fluid are 5-20 % 1 SD for a given capsule.

Comparison of data obtained by the freezing approach with results from conventional diamond trap LA-ICPMS analysis ("evaporated" fluids; i.e., capsule pierced, oven-dried, embedded in epoxy, polished to expose the diamond layer for analysis) agree with each other, except for Cs. The Cs/element signal ratios from frozen capsules is about one order of magnitude higher than that of evaporated capsules at identical P and T, demonstrating that >70 % of the Cs was lost upon piercing the capsule.

The freezing approach now allows reliable quantification of high-P fluid compositions including alkali and alkali earth metals, by LA-ICPMS analysis of the diamond trap only.

Reference

Kessel R., Ulmer P., Pettke T., Schmidt M. W., and Thompson A. B. (2004a) *American Mineralogist* 89(7), 1078-1086.

Fluid and melt compositions coexisting with eclogite at high pressure and temperature

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Fluids and melts emanating from dehydrating subducting slabs cause mantle metasomatism and are an essential ingredient for melting in the mantle wedge. However, the composition of such liquids has not been investigated in detail due to experimental and analytical difficulties. Kessel et al. (2004) developed a new analytical technique, the "freezing" approach, by which frozen fluids are directly ablated and, for the first time, completely analyzed in diamond-trap experiments. We used this technique to characterize the fluid/melt phase coexisting with K-free eclogite at 4 and 6 GPa, 700-1200°C, and determined the partitioning of a suite of key trace elements between eclogite minerals and the fluid/melt phase.

Our results indicate that at 4 GPa a fluid with ~80 wt% H₂O coexists with eclogite up to 850°C while a hydrous melt is stable above 900°C, indicating a solidus between 850 and 900°C. The solidus is between 1000 and 1050°C at 5 GPa, but ends at a second critical endpoint between 5 and 6 GPa. A supercritical liquid that changes its chemistry continuously with temperature coexists with gar+cpx at 6 GPa.

The 4 GPa trace element pattern confirms the dichotomy of dehydration vs. melting at relatively low pressures, e.g., contrasting mobilities of U/Th, Sr, Ba and Li, for an aqueous fluid vs. a hydrous melt. However, our results show a distinct change when moving from 4 GPa to a supercritical liquid at 6 GPa. The supercritical liquids are characterized by a high mobility of Be, B, Rb, Cs, Sr, Ba, and Pb, by $D^{Th} > D^U$, and by a strong fractionation of LREE from HREE (resulting in a strong garnet signature) at all investigated temperatures (800-1200°C). The high mobility of Th and Be in supercritical liquids at relatively low T relaxes the necessity of classical melting and thus any "temperature requirement". Secondly, the 6 GPa pattern is not dissimilar to an "adakite-type" signature. In both cases, supercritical liquids provide an appealing alternative origin for such geochemical features.

Reference

Kessel R., Ulmer P., Pettke T., Schmidt MW, Thompson AB (2004) *Am.Min* 89, 1078-1086.