



	Experiment title: The fate and behaviour of volatiles during subduction of oceanic crustal material towards greater mantle depths	Experiment number: ES-240
Beamline: ID21-	Date of experiment: from: 21/01/2015 to: 27/01/2015	Date of report: 10.09.2016
Shifts: 21	Local contact(s): Dr. Marine Cotte, Dr. Camille Rivard	<i>Received at ESRF:</i>
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Report:

Fluxes of volatiles between the Earth's interior and exosphere remain highly controversial, despite being critical for the development of the atmosphere, the establishment of climatic cycles, for geochemical differentiation of the Earth through the profound influence of volatiles on mantle melting, and for life on Earth¹⁻³. The chief means to replenish the Earth's interior with volatiles over geological time is subduction (the transport of near-surface material into the deep interior) and the amounts of volatiles resorbed into the mantle will vary with the pressure, temperature and oxygen fugacity (fO_2) at the location where this resorption occurs, as well as on the bulk composition of subducted material¹⁻⁵ (Fig. 1). The latter includes former oceanic crust, which transforms to a rock called eclogite at depths greater than about 30 km, and this eclogite will contain H₂O. This study aims, to determine various oxidation states of oceanic crustal material (that is eclogite) during subduction, and their impact on the mobility of H₂O during subduction by using multi anvil apparatuses as well as synchrotron Fourier-transform infrared (FTIR) and Micro-X-ray absorption near edge structure (XANES) at the Fe K-edge at ID21, ESRF.

Outcomes will allow constraints to be placed on the conditions at which oxidised eclogite+H₂O will transform to reduced diamond-bearing eclogite+fluid during subduction. It will indicate the extent to which eclogite +H₂O will melt during subduction and later upwelling, and how this affects the stability of diamond in residual eclogite that has lost a melt fraction.

Preliminary results: We use average oceanic basalt (GA1, representative of recycled oceanic crust⁶) with H₂O up to 7 wt.%), doped with Ir which acts as a redox sensor^{4,5}. We conducted experiments using GA1 at different pressures (6-10 GPa; i.e. up to ~330 km Earth's mantle depth), temperatures (850-1500°C) and bulk %H₂O using multi anvil apparatuses. We analysed major, minor and trace elements of phase compositions by electron microprobe analyses. Synchrotron FTIR were employed to determine small amounts of H₂O and related substitution mechanism of H₂O incorporation in eclogitic NAMs. Fe³⁺ were determined in eclogitic garnets, using Micro-XANES at the Fe K-edge. Experiments on GA1+H₂O yield well-crystallised assemblages of garnet ± clinopyroxene ± coesite/stishovite ± rutile ± phengite ± melt ± vapour, with average grain sizes of 10 to 20 µm (Fig. 1), big enough for analysis by synchrotron FTIR microscopy, and Micro-XANES. Similar to previous studies⁷⁻¹¹, the stability of phengite varies as a function of pressure, temperature, buffering mineral paragenesis and bulk H₂O concentration. Runs at 6 GPa and up to ~900°C, runs at 8 GPa and up to ~1000°C, and runs at 9 GPa and up to ~1050°C are subsolidus, while towards higher temperatures

small melt fractions appear. At 6 GPa, at 950°C and 1050°C, phengite co-exists with small melt fractions for bulk H₂O contents of 0.4-1.0 wt% before it disappears completely towards higher temperatures. Phengite breaks down above 9 GPa (~300 km depth).

Figure 1. Scanning electron microscope images of representative run products of *GA1+H₂O* at 6 GPa. grt, garnet; cpx, clinopyroxene; coe, coesite.

Eclogitic NAMs and phengite also break down at subsolidus conditions in the presence of excess hydrous fluids (Fig. 2).

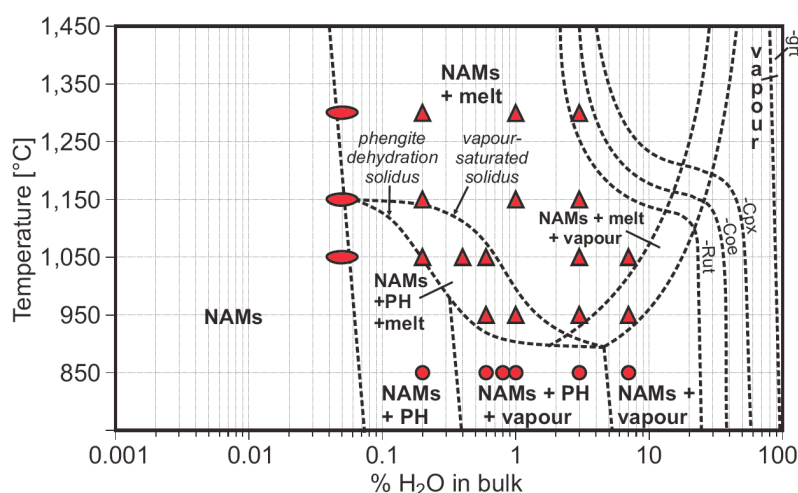
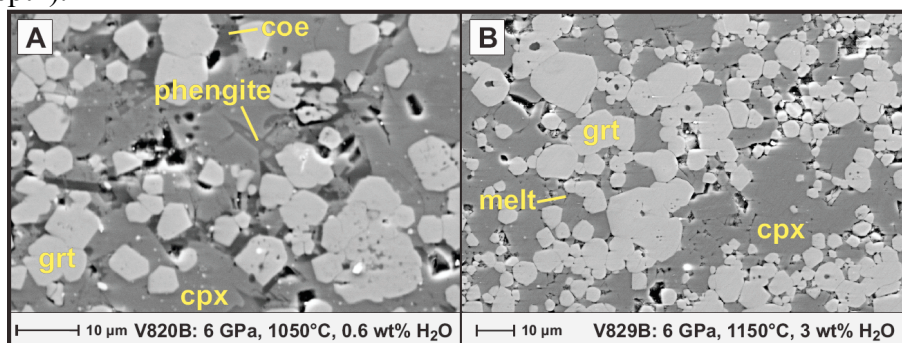


Figure 2. Schematic phase diagram (based on [10 & 11]) at ~6 GPa showing the phase stabilities of eclogitic NAMs and phengite (hydrous phase) as a function of H₂O [wt%] and T. If the H₂O storage of phengite and the eclogitic NAMs is exceeded at subsolidus conditions, vapour will form in association with phengite and NAMs. Strikingly, runs with 7 wt.% H₂O are phengite-free. Towards higher temperatures instead, melt in association with phengite will appear at the phengite dehydration solidus until phengite is completely exhausted at the vapoursaturated solidus of *GA1+H₂O*. Ph, phengite.

For instance, K₂O in phengite and clinopyroxene decreases with increasing bulk H₂O content at subsolidus conditions at given pressure and temperature, suggesting a leaching role of K₂O by a vapour-rich fluid. At 9 GPa, 1400°C, residual eclogitic clinopyroxene (34%) and garnet (43%) incorporate 1280±192 and 33±10 ppm H₂O, respectively (Fig. 3), suggesting that near-solidus residual eclogite may only able to accommodate ~0.045 wt% H₂O at these mantle conditions. Towards deeper mantle levels, at 10 GPa,

1400°C, residual eclogitic clinopyroxene (30%) and garnet (44%) take up even less H₂O, i.e. 256±77 and 29±9 ppm H₂O, respectively, prompting into the incorporation of only ~0.009 wt% H₂O into residual eclogite at these conditions.

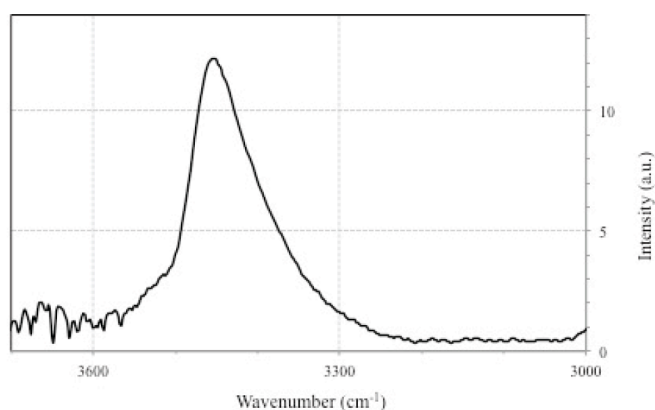


Figure 3. Synchrotron-FTIR spectra for clinopyroxene of run H3840B (9 GPa, 1400°C, 7 wt.% H₂O in bulk). The absorbance peak at 3460 cm⁻¹ is attributed to O-H stretching mode of H-substitution in clinopyroxene. The average unpolarized spectra is normalised to 1 cm thickness.

Conclusions and further work: Obtained data will be compared with earlier studies, which concentrated on the direct measurement of H₂O in single mineral phases only, which were not in equilibration with the bulk phase assemblage (i.e. subducted crustal material). Considering the strong influence of volatiles on mantle melting processes, including redox melting, obtained data will then be also used to understand the behaviour of volatiles in subducted material along subduction zones, and subsequent recycling and mantle melting processes. The data obtained during ES240 are currently being written up as a manuscript for publications.

References: [1] Dasgupta & Hirschmann (2010). *Earth Planet Sci Lett* 298, 1-13. [2] Hirschmann & Dasgupta (2009). *Chem Geol* 262, 4-16. [3] Rosenthal et al. (2015). *Earth Planet Sci Lett* 412, 77-87. [4] Stagno & Frost (2010) *Earth Planet Sci Lett* 300, 72-84. [5] Stagno et al. (2013) *Nature* 493, 84-88. [6] Yaxley & Green *Earth Planet Sci Lett* 128, 313-325 (1994). [7] Hermann & Green. *Earth Planet Sci Lett* 188, 149-168 (2001). [8] Hermann & Spandler, *J Petrol* 49, 717-740 (2008). [9] Schmidt *Science* 272, 1927-1930 (1996). [10] Schmidt & Poli *Earth Planet Sci Lett* 163, 361-379 (1998). [11] Schmidt et al. *Earth Planet Sci Lett* 228, 65-84 (2004).