Geochemical Perspectives Letters

On the stability of acetate in subduction zone fluids

V. Szlachta, K. Vlasov, H. Keppler

Supplementary Information

The Supplementary Information includes:

- Experimental Methods
- Figures S-1 to S-4
- Supplementary Information References

Experimental Methods

Piston cylinder experiments

Piston cylinder experiments (Boyd and England, 1960) were carried out using mechanically sealed silver capsules with a length of 10 mm, an outer diameter of 5 mm and a wall thickness of 1 mm. A solution of 10 wt. % $CH_3COONa \cdot 3 H_2O$ (Merck, 99.5 %) in distilled water was loaded into the capsules together with SiO_2 powder (Chempur, 99.9%) for mechanical stabilisation. The fluid/solid ratio ranged from 0.34 to 0.9. Experiments were carried out with low-friction ½ inch NaCl-MgO assemblies containing a stepped graphite heater in an automated, end-loaded piston cylinder press (Voggenreiter GmbH, Mainleus, Germany). This device contains two spindle presses that allow a precise control of the oil pressures on the master ram and the endload, such that continuous compression and decompression profiles can be run under computer-control. Experiments were slowly pressurised and de-pressurised over 19–21 hours in order to limit bomb and piston failures at 5 GPa. Runs were heated to the target temperature of 600 °C within 30 minutes and cooled down at the end of the run again within about 30 minutes. However, the "zero time" experiment was heated more rapidly within ~10 min, maintained for ~8 min at 600 °C and cooled to room temperature in 9 minutes. Temperatures were measured by a type S (Pt-PtRh) thermocouple close to the sample and controlled by a Eurotherm controller. A constant friction correction of −0.12 GPa was applied to the nominal pressures. This correction was calibrated by the quartz–coesite transition near 3 GPa and by the density of synthetic fluid inclusions at 800 °C and 0.5–1.0 GPa.

Diamond anvil cell experiments

In situ spectroscopic experiments were carried out with a Bassett-type externally heated diamond anvil cell (Bassett *et al*., 1993) using synthetic, low-fluorescence type II-a diamond anvils with 700 µm culet. The cell was heated using molybdenum wires around the tungsten carbide seats supporting the diamonds. Temperature was monitored using K-type thermocouples (NiCr-Ni) directly attached to the diamonds. Gaskets made of Re or Ir with an initial thickness of 250 µm and a 150–180 µm drillhole were used. The 10 wt. % sodium acetate solution was loaded into the sample chamber together with a small zircon crystal (natural zircon from Sri Lanka) as a pressure sensor. The cell was flushed during experiments with a 98 % Ar–2 % H_2 gas mixture to prevent oxidation of the molybdenum heaters and the diamonds. Pressures during runs were determined based on the Raman shift of the $\nu_3(SiO_4)$ band in zircon (~1008 cm^{-1}) following the calibration of Schmidt *et al*. (2013). The objectives of the Raman spectrometer were cooled with air at high temperatures.

Raman spectroscopy

Raman spectra were measured using a Horiba/Jobin Yvon LabRam HR UV confocal Raman spectrometer in backscatter geometry. The 514 nm line of an argon laser with 75–200 mW output power was used for excitation. Spectra were measured with a 50× objective, a 1800 groves/mm grating and a Peltier-cooled CCD detector. The confocal pinhole was set to 100–1000 µm, the spectral resolution was about 3.5 cm^{-1}, and each spectrum was typically collected using two 35 s accumulations.

Supplementary Figures

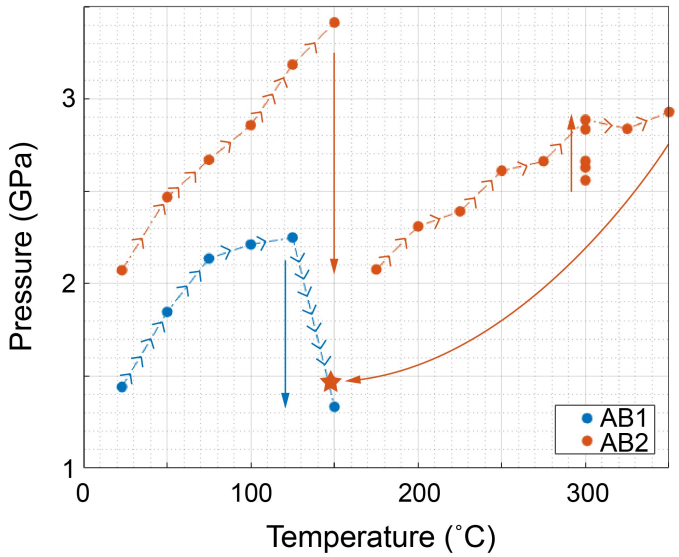

Figure S-1 Pressure-temperature paths of the diamond anvil cell runs AB1 and AB2. The star at 148 ° C for run AB2 indicates the end of run when the gasket cracked. Straight arrows indicate pressure addition (by tightening the cell) or pressure drop (due to gasket flow or leakage).

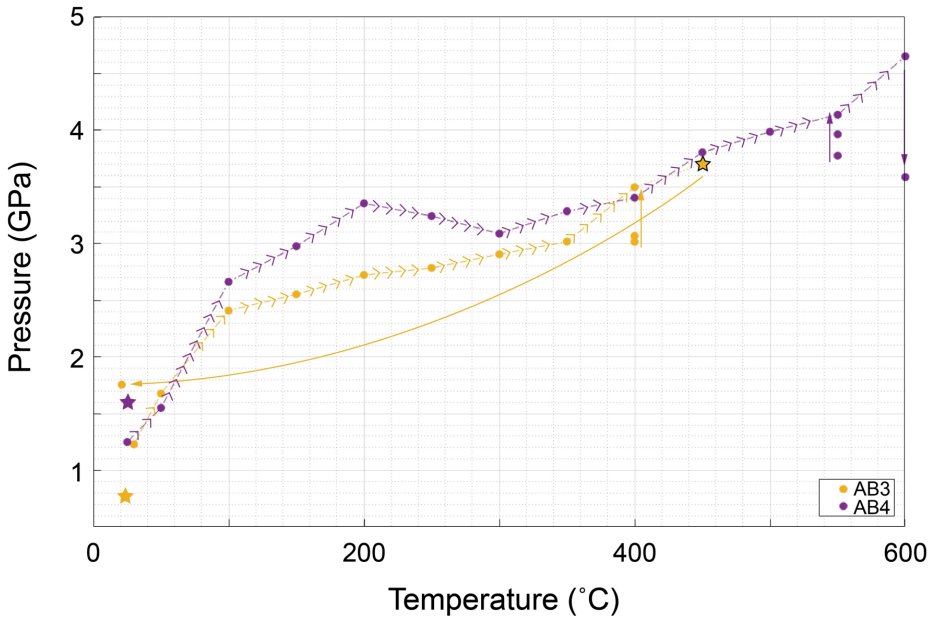

Figure S-2 Pressure-temperature paths of the diamond anvil cell runs AB3 and AB4. The black-outlined star for run AB3 at 450 °C marks a heater failure. The data point at 21 °C for run AB3 indicates the residual pressure immediately after the run. Stars indicates the pressures measured on the day after the runs.

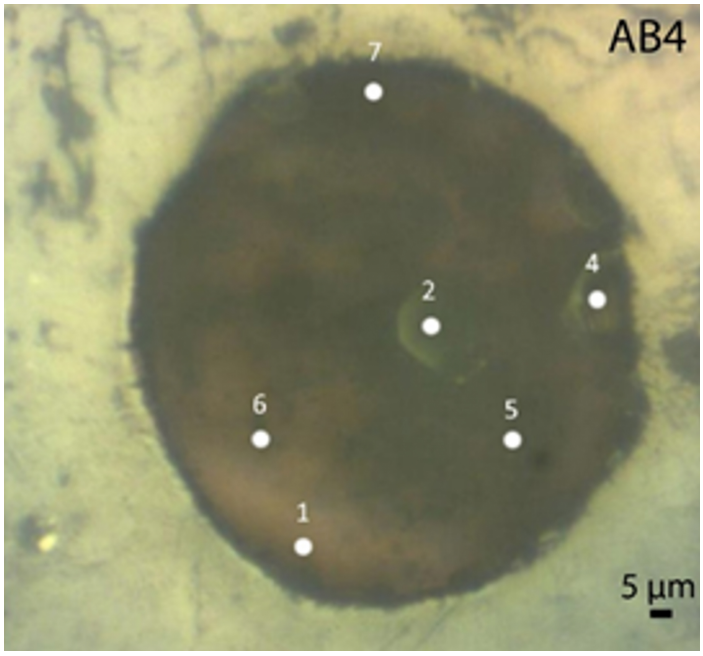

Figure S-3 Sample chamber of experiment AB4 after cooling back to room temperature from 600 °C and 4.65 GPa. Note the dark, carbonaceous material floating inside the solution. White spots refer to the location of Raman measurements given in Figure S-4.

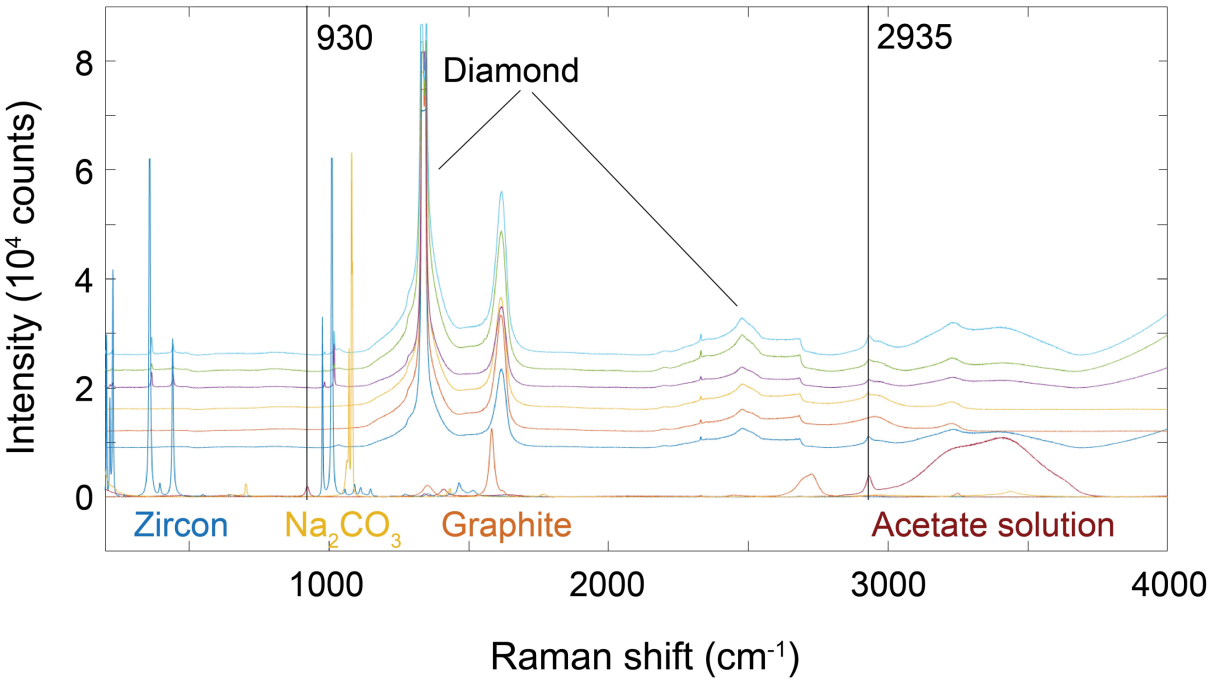

Figure S-4 Raman spectra of quench products from run AB4. The presence of a carbonaceous material resembling disordered graphite is obvious in all spectra. While there is a band in the C-H stretching region close to 2935 cm^{-1}, similar to acetate, the C-C stretching band of acetate at 930 cm^{-1} is clearly missing. The sequence of the spectra from bottom to top is from point 1 to point 7 according to Figure S-3.

Supplementary Information References

Bassett, W.A., Shen, A.H., Bucknum, M., Chou, I.M. (1993) A new diamond anvil cell for hydrothermal studies to 2.5 GPa and from −190 to 1200 °C. *Review of Scientific Instruments* 64, 2340–2345. https://doi.org/10.1063/1.1143931

Boyd, F.R., England, J.L. (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kbars and temperatures up to 1750°C. *Journal of Geophysical Research* 65, 741–748. https://doi.org/10.1029/JZ065i002p00741

Schmidt, C., Steele-MacInnis, M., Watenphul, A., Wilke, M. (2013) Calibration of zircon as a Raman spectroscopic pressure sensor to high temperatures and application to water-silicate melt systems. *American Mineralogist* 98, 643–650. https://doi.org/10.2138/am.2013.4143