First in situ measurement of sulfur speciation and partitioning in fluid-melt systems

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Our current knowledge of sulfur speciation and partitioning in aqueous fluid-silicate melt systems is based on studies of natural or synthetic samples of fluids and glasses brought to ambient conditions, and lacks direct data at elevated temperatures and pressures. Here we report on first in-situ measurement of sulfur speciation and partitioning in fluid-melt systems using micro-Raman spectroscopy in a diamond-anvil cell [1, 2]. Experiments were performed on S-bearing aqueous solutions in contact with alkaline or peralkaline silicic glasses. Results show that sulfur speciation in the fluid is dominated by sulfate (SO_4^{2-}) and sulfide (HS^- and/or H_2S) with a contribution from the radical S_3^- and S_2^- ions that grows with temperature, in agreement with thermodynamic predictions [3, 4]. In the coexisting silicate melt formed at 700°C (Fig. 1), sulfate and sulfide were clearly detected, whereas only very small, if any, amounts of S_3^- and S_2^- were found. The fluid/melt distribution coefficients estimated from Raman peak intensities indicate that S_2^- and S_3^- partition strongly into the aqueous fluid phase. These first measurements open new perspectives for applying in-situ spectroscopic methods to deep fluids and melts, thus avoiding potential artifacts of less direct techniques.

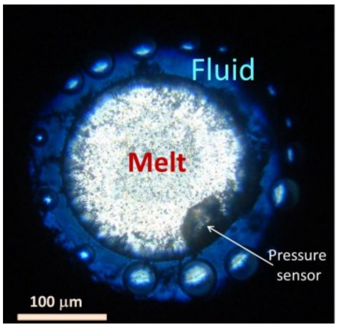

Figure 1: Coexisting fluid and melt imaged at 700°C and 10 kbar in the diamond-anvil cell. The deep blue color of the fluid is due to the S_3^- ion.

[1] Schmidt (2009), *GCA* 73, 425-437. [2] Schmidt & Chou (2012), *EMU Notes in Mineralogy*, 12, 247-276. [3] Pokrovski & Dubessy (2015), *EPSL* 411, 298-309. [4] Pokrovski et al. (2015) *PNAS* 112, 13484-13489.