ESRF	Experiment title: Structure determination of a high-pressure hydrated aluminosilicate	**Experiment number:** CH129
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Report:

The crystal structure of this phase, which has composition $AlSiO_3OH$, has been solved (including the position of the hydrogen) and refined from a high-resolution powder pattern. This phase is stable above 11 GPa and 700°C. Its upper stability limit is unknown, but it has been synthesized at 17.7 GPa (1200°C), therefore it could be very important in transporting water into the deep earth.

The sample was placed in a capillary with an inside diameter of 0.5 mm, and spun about the cylindrical axis during data collection. In this experiment, there was an initial scan of 2°/min for the center detector between -2 and 140°, followed by subsequent scans of 2°/min from -2 to 38°, l°/min from 38 to 68 °, 0.5°/min from 68 to 88°, and 0.25°/min from 88 to 118 °. After rebinning to a constant step size of 0.004°, a total of 39,472 data steps were obtained. Of these, the 28,750 between 5 and 120 degrees were used in further calculations. The wavelength for this experiment was determined from a Si standard to be 0.84933(l) Å, thus the resolution of the pattern is 0.49 A. There are very significant peaks, even at the highest diffraction angle.

Individual peaks to 1.3 Å were extracted from the pattern to check the previous phase identifications and to determine initial profile parameters. The diffractometer uses a detector opening of nearly 10 mm, and a sample illumination length of 4.5 mm, therefore, there is considerable asymmetry for low-angle peaks due to axial-divergence. This asymmetry was modeled and the positions corrected using the method of

Finger *et al.* (1994). The resulting peaks had three distinct widths, confirming that the sample consists of three phases - stishovite, diaspore, and phase egg. All 52 spacings in this subset for the latter material could be indexed by program TREOR with a monoclinic cell. Figures of merit are M(20) = 117, and F20 = 182, leaving no doubt as to the correctness of the indexing. Systematic absences are consistent with space group $P2_1/n$. To determine the structure, the intensity extraction was accomplished with the method of LeBail *et al.* (1988), with pseudo-Voigt peak profiles. After convergence by refinement of a full set of instrumental parameters, the slope of the normal probability plot was 2.5, indicating a significant underestimation for the standard deviations of the intensities. After the previous sigmas were increased by this factor, the slope of the normal probability plot was changed to 1.02. At this stage, $x^2 = 1.4$. The extracted structure factors used as input to program SIRPOW, which yielded a solution using default parameters. As expected, both Al and Si are octahedrally coordinated, and a preliminary assignment was based on average bond distance. At this stage, all instrumental parameters were held fixed, and the initial atomic coordinates were refined with the Rietveld method. After convergence, the method of bond-valence sums (Brown, 1992) was used to check the assignment of Al and Si, to determine the identity of the hydroxyl, and to determine which oxygen is involved in the expected hydrogen bond. The sums for the four oxygens are 1.93,2.00, 1.66 and 1.27 for 01 to 04, respectively, leading to the conclusion that 04 is the hydroxyl, and 03 participates in a hydrogen bond. When a difference electron density was computed, a peak of 0.8 e/cm^3 was found in the position expected for the hydrogen atom. This atom was added to the structural description and its position and temperature factor refined. The refinement converged to a reduced x^2 of 1.66. Residuals for the pattern are Rwp = 0.112, and Rp= 0.087. Bragg R's for phase $AlSiO_3OH$ are $R(F^2) = 0.045$, R(F) = 0.027.

References:

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