



Experiment title: **A XAFS spectroscopy study of germanium speciation and the solubility of Ge(IV) oxides in near- and supercritical aqueous fluids: Implications for metal-solvent interactions at critical conditions, and the Ge/Si ratios in hydrothermal environments**

Experiment number:
HS-1945

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Report:

Experimental: Dissolution of synthetic argutite (GeO_2 , tetr., rutile-like) in pure water and local atomic structure around Ge(IV) in germanic acid aqueous solutions were characterized by *in situ* XAFS spectroscopy at temperatures to 500°C and pressures to 400 bar, using a special optical cell recently designed at the Laboratory of Crystallography (Grenoble). The new cell design utilizes a stainless steel bellow, allowing accurate control of pressure and long-term high T-P measurements. XANES and EXAFS spectra of aqueous solutions with and without oxide phase were recorded at the Ge K-edge (~ 11.1 keV) in both transmission and fluorescence modes at ID26 beamline of ESRF. Details on experimental procedure, spectra acquisition and treatment were similar to those described by Pokrovski et al. (2002) and Testemale et al. (submitted).

Results on Ge local atomic structure in solution: Accurate EXAFS fluorescence spectra were recorded on germanic acid aqueous solutions of 0.02-0.09m at ambient P and T and on a 0.04m solution at 400 bar from 20 to 450°C (Fig. 1a,b). Although all solutions were supersaturated with respect to the rutile-type oxide, no changes in concentration were observed (see below) for the whole temperature range. This is in agreement with the extremely low precipitation kinetics of GeO_2 (tetr) as reported in previous studies (Pokrovski & Schott, 1998). Spectra at all temperatures and concentrations exhibit the 1st-shell contribution from 4 ± 0.4 oxygens at $1.75\pm 0.01\text{\AA}$, consistent with a tetrahedral structure of the $\text{Ge}(\text{OH})_4$ complex, similar to $\text{Si}(\text{OH})_4$. Minor multiple scattering contributions within the regular GeO_4 tetrahedron were also detected. The constancy of the 1st shell Ge-O distance and Debye-Waller factor ($\sigma^2=0.0015\pm 0.0005$) over the wide temperature range is consistent with the strong covalent character of the Ge-OH bonds. The same behavior has recently been observed for the chemically similar $\text{As}(\text{OH})_3$ complex (Pokrovski et al., 2002).

Results on GeO_2 dissolution in high-temperature aqueous fluids: Because the optical path length is constant and well known in our cell configuration, and the density of dilute Ge aqueous solutions can be reliably approximated by that of pure water, the amplitude of the absorption edge of transmission spectra is a direct measure of Ge molality in solution. This allows the monitoring of Ge dissolution/precipitation kinetics and accurate determination of aqueous metal concentrations. Dissolution experiments in the GeO_2 - H_2O system with an initial solid/solution mass ratio of 1/20, carried out at 400 bar showed that a steady state for Ge concentrations was attained within ~ 2 hours at temperatures above 300°C (Fig. 2). These concentrations are in excellent agreement with those previously obtained below 350°C using batch reactors and solid/solution ratios ranging from 1/3 to 1/300 (Pokrovski & Schott, 1998). This strongly suggests that the solid-solution equilibrium is attained in our XAS experiments at $\geq 300^\circ\text{C}$. The solubility of Ge oxide increases with increasing temperature up to 400°C in agreement with the HKF model (Pokrovski & Schott, 1998), but decreases at 450 and 500°C , which is not predicted by the model (Fig.3). The solubility decrease is likely due to a significant drop of water density at these T-P, and is similar to that observed for quartz. This reflects a similar aqueous speciation of germanic and silicic acid, and thus similar interactions of both species with the solvent

over a wide range of T-P and densities. Work is currently in progress to better constrain $\text{Ge}(\text{OH})_4$ thermodynamic properties from these new high-temperature data using models that explicitly account for the fluid density (e.g., “density model”, Anderson et al. (1991), *Geochim. Cosmochim. Acta* **55**, 1769-1779).

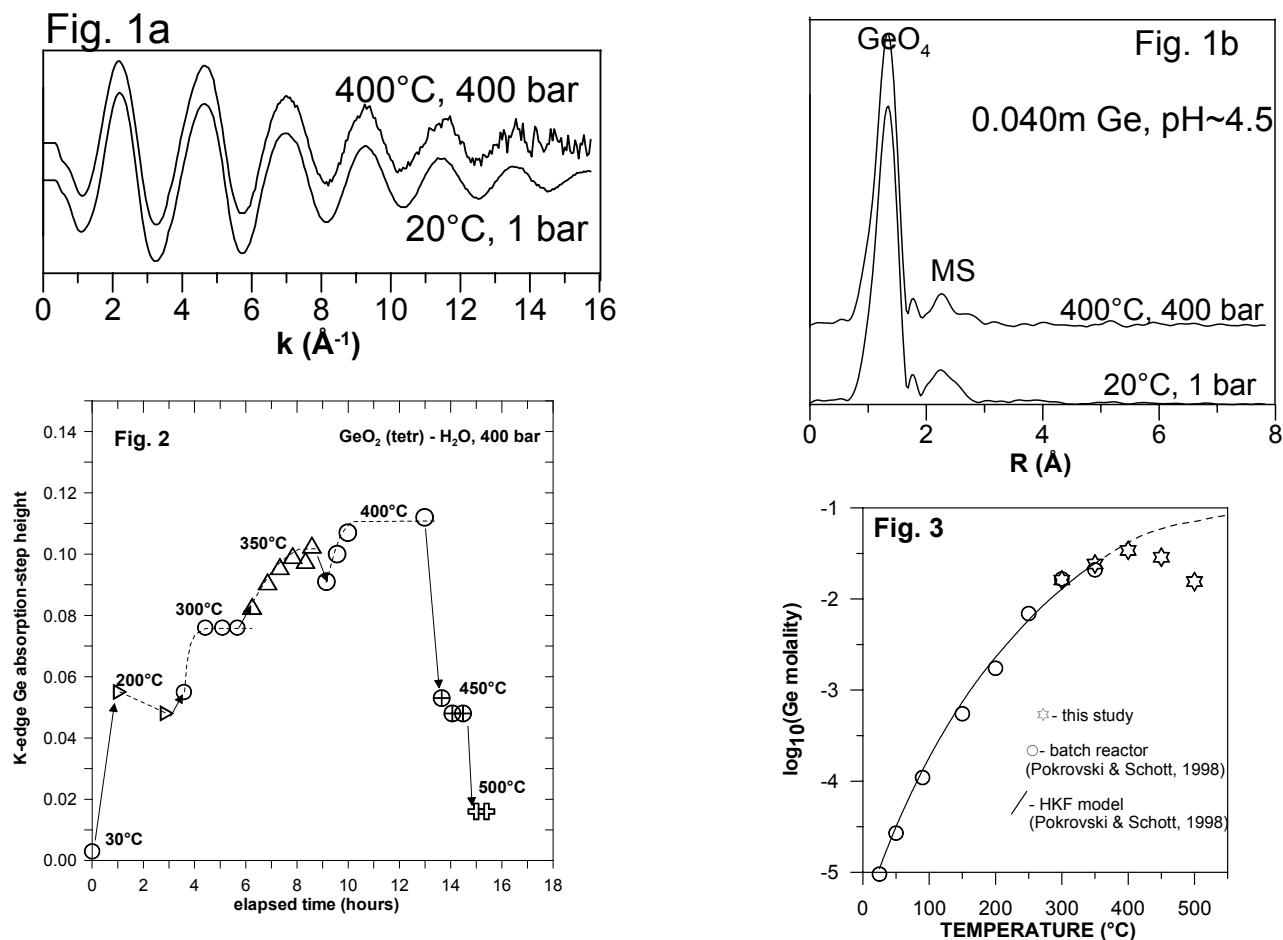


Fig. 1 Normalized k^2 -weighted EXAFS spectra of a 0.04m Ge aqueous solution at indicated T and P (a), and their corresponding Fourier Transforms (b).

Fig. 2 Evolution of the absorption edge height of aqueous Ge as a function of time in the presence of GeO_2 solid. The arrows indicate temperature changes during the experiment.

Fig. 3 $\text{GeO}_2(\text{tetr})$ solubility in water as a function of temperature at 400 bar.

Conclusion and perspectives: This experiment demonstrated the capabilities of the XAFS technique for not only characterization of structural atomic environment around the absorbing atom, but also *in situ* measuring mineral solubilities in high-temperature/pressure near- and supercritical solutions. This study provides new data about $\text{Ge}(\text{OH})_4$ high-temperature stability and structure, that can help in developing more accurate thermodynamic models for Ge in crustal fluids. These data are needed for the interpretation of the Ge/Si ratios and Ge isotope fractionation during water-rock interactions and crustal evolution. The next step would be to expand at higher values the temperature and pressure range investigated (500-900°C, 2-5 kbars), using an improved cell design and high X-ray flux provided by ID26 or FAME beamlines. This would better constrain the adjustment to theoretical models and make accurate and reliable *in situ* measurements of solubilities of oxides and sulfides, and vapor-liquid partitioning of metals at the middle- and lower-crust conditions.

References:

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