

## Cristobalite nanofibers in volcanic ash from the ongoing explosive eruption at Chaitén Volcano, Chilean Patagonia

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The presence of cristobalite, one of the most toxic polymorphs of silica, has raised concern about adverse health effects of long-term exposure to volcanic ash [1, 2]. Although crystalline silica has been widely identified to cause silicosis and in some cases lung cancer, there is a lack of information on its mineralogical form and morphological variety at the nanoscale. In this study, we report nanoscale observations of the respirable fraction of ash from the ongoing explosive eruption of the Chaitén Volcano, Chilean Patagonia, showing that cristobalite occurs as nanofibers and nanowires.

Transmission electron microscopy (TEM) observations reveal that crystalline silica is abundant in the respirable fraction of ash, occurring as fibrous aggregates. Detailed TEM examination reveals that the aggregates are composed of (beta) cristobalite nanofibers, as confirmed by energy-dispersive spectrometry (EDS) and selected-area electron diffraction (SAED). The average lengths of the fibers are between ~5  $\mu\text{m}$  and ~300 nm. The diameters of the nanofibers are uniform, on the order of tens of nanometers, with averages between ~20 and 50 nm. Nanofibers are usually associated with micrometer- to nanometer-scale fragments of amorphous silica glass.

The occurrence of beta cristobalite as nanofibers and nanowires raises new concerns about their toxicity because of the morphological resemblance to asbestos, known to induce progressive fibrotic disease of the lungs and potentially cancer. Therefore, more studies are needed for the better assessment of hazardous, mineralogical, and size-dependent effects associated with the short-term inhalation of nanofibrous silica during explosive eruptions and also long-term exposure in ash-covered areas.

[1] Baxter *et al.* (1999) *Science* **238**, 1142-1145. [2] Horwell & Baxter (2006) *Bull. Volcanol.* **69**, 1-24.

## Surface complexation modeling of Pb(II) adsorption on mixtures of hydrous ferric oxide, kaolinite, and quartz

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Metal speciation is a primary control on metal mobility and bioavailability in the environment, and adsorption reactions can play a significant role in determining metal speciation. Pb is a common environmental contaminant due to its past and current industrial use, therefore, a better quantitative understanding of its interactions with common environmental sorbents should produce better predictions of Pb transport and mobility. Thermodynamic surface complexation models are commonly used to describe metal adsorption on single sorbents, but few tests of these models exist for mixed sorbents. In this study, Pb adsorption was measured as a function of pH, ionic strength (0.001 to 0.1 M NaNO<sub>3</sub>) and sorbate/sorbent ratios (10<sup>-4</sup> to 10<sup>-6</sup> M Pb with 2 g/L solid) on hydrous ferric oxide, quartz and two varieties of kaolinite. Adsorption edges were measured by titrating 500 mL batch experiments from low to high pH, removing 10 mL aliquots at ~0.3 pH intervals. Aliquots were equilibrated for a further 24 hrs, centrifuged, and the pH of the supernatant remeasured. Pb sorbed was calculated by measuring supernatant concentrations by ICP OES with matrix-matched standards. A diffuse layer surface complexation model (DLM) was used with FITEQL to extract stability constants for the individual sorbent systems, testing a variety of reaction stoichiometries. Goodness-of-fit was assessed for best fit and median stability constants. For each sorbent, the stoichiometry yielding the statistically best fit for median stability constants was used in speciation calculations to predict Pb adsorption on binary and ternary mixtures of the three solids. Predictions are generally good, indicating that errors associated with DLM fits to individual sorbents are greater than uncertainties due to mineral-mineral interactions.