

## Size and element specific solubility of aerosols from NE U.S. Sources

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Aerosol samples were collected in Steubenville, OH where a mercury deposition hot spot [1] and an association between air pollution and mortality has been postulated [2]. The samples were collected over 26 consecutive days in summer 2004 using a ten stage MOUDI. The particulate from each size fraction was leached to provide a water soluble fraction (1 day leach) as well as a dilute acid extractable fraction (30 day leach) [3]. Metal concentrations in the extracts were then quantified using SF ICP-MS.

Event precipitation samples from this area indicate significant wet deposition contributions from coal combustion, iron/steel production, oil/incineration and crustal sources [1]. This study was designed to assess aerosols at this location from inhalation perspectives. When examined from a coupled size fractionation and solubility perspective, the elements from the aerosols clustered into six groupings. Water soluble elements mostly in the finer fractions included As, Cd, Rb, Ge, S, Se, and V; those requiring acidification to increase solubility included Cr, Cu, Mo, Sb, Sn and Pb. S and Se were key indicators for monitoring condensation processes in the fine fractions. Water soluble elements mostly in the coarser fractions included Ba, Ca, Mg, P, and Sr, whereas La, Ce and Ti required acidification to increase solubility. Some elements displayed a bimodal distribution with relatively equal contributions from the coarse and fine fractions. Of these elements Co, K, Mn, Na, and Zn were water soluble, whereas Al and Fe were acid extractable. Aerosols from both anthropogenic and natural sources are of concern from an inhalation perspective; and some of the elements predominantly in the water soluble fraction from this study include metals that are known to be cytokine-active [4] and have produced toxic responses in epidemiologic studies [5].

[1] Keeler *et al.* (2006) *Environ. Sci. Tech.* **40**, 5874–5881.

[2] Dockery *et al.* (1993) *N. Engl. J. Med.* **329**, 1753–1759.

[3] Graney *et al.* (2004) *Atmos. Environ.* **38**, 237–247.

[4] Suarez & Ondov (2002) *Energy Fuels* **16**, 562–568.

[5] Cho *et al.* (2009) *Environ. Health Perspectives* **117**, 1682–1689.

## Water structure and vibrational properties in fibrous clays

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The behavior of water confined in porous materials influences macroscopic phenomena such as solute and water mobility, ion exchange, and adsorption. While the properties of bulk water are generally understood, that of nanoconfined water remains an active area of research. We used molecular simulation and inelastic neutron scattering (INS) to investigate the effect of local structure on the vibrational behavior of nanoconfined water. We focus specifically on the nanosized pores found in the 2:1 phyllosilicate clay minerals palygorskite and sepiolite. These are charge neutral, Mg-rich trioctahedral clays with idealized formulas  $Mg_5Si_8O_{20}(OH)_2 \cdot 8H_2O$  and  $Mg_8Si_{12}O_{30}(OH)_2 \cdot 12H_2O$  for palygorskite and sepiolite, respectively. The regular pattern of inverted phyllosilicate layers results in narrow channels with effective van der Waals dimensions of  $3.61 \text{ \AA} \times 8.59 \text{ \AA}$  (palygorskite) and  $4.67 \text{ \AA} \times 12.29 \text{ \AA}$  (sepiolite). These clay minerals represent a unique opportunity to study water adsorbed at ‘inner edge’ sites of uncoordinated  $Mg^{2+}$ .

INS spectra taken at 90 K reveal a large shift in the water librational edge between palygorskite ( $358 \text{ cm}^{-1}$ ) and sepiolite ( $536 \text{ cm}^{-1}$ ), indicating less restricted water motion in the smaller-pore palygorskite. The librational edge of the reference sample (ice  $I_h$ ) is similar to sepiolite, which confirms the unique water behavior in palygorskite.

We used both classical molecular dynamics (CMD) simulations and more rigorous density functional theory (DFT) calculations to investigate the hydrogen bonding environment and vibrational behavior of structural water, defined as those water molecules coordinated to  $Mg^{2+}$  along the pore walls. These waters remain coordinated throughout the 1-ns timescale of the CMD simulations, and the resulting vibrational spectra indicate a similar shift in the water librational edges seen in the INS spectra. The DFT-optimized structures indicate differences in hydrogen bonding between palygorskite and sepiolite, which could explain the librational shift. Corner-sharing silicate tetrahedra in palygorskite are tilted with respect to the crystallographic *a*-axis due to the induced strain of layer inversion. As a result, only two short ( $1.9 \text{ \AA}$ ) hydrogen bonds form between each water and the framework. In contrast, the relatively unstrained sepiolite structure, each water forms three hydrogen bonds with the framework, and at greater distances ( $2.0 \text{ \AA} - 2.5 \text{ \AA}$ ).