

## Environmental bioremediation of carbon nanotubes via enzymatic catalysis

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Recent reports have shown cellular toxicity induced by carbon nanotubes [1]. Specifically, carbon nanotubes have demonstrated asbestos-like pathogenicity, resulting in pro-inflammatory response, generation of free radicals, and granuloma formation. Moreover, carbon nanotubes possess an inherent resiliency toward degradation. For instance, current methods of carbon nanotube oxidation involve thermal treating in air at temperatures in excess of 800 °C, or chemical oxidation from highly oxidizing compounds such as Piranha Solution (3:1 H<sub>2</sub>SO<sub>4</sub> : 30% H<sub>2</sub>O<sub>2</sub>). Pending their accidental release in the environment, carbon nanotubes (a potentially toxic threat), could circulate for years without their removal as a result of their stability.

Recently, we have demonstrated the ability to use a plant enzyme from horseradish, horseradish peroxidase (HRP), to enzymatically degrade carboxylated single-walled carbon nanotubes (SWNTs) under benign conditions (room temperature, 40 μM H<sub>2</sub>O<sub>2</sub>) over the span of 10 days [1],[2]. HRP forms an oxidizing complex known as Compound I by the addition of H<sub>2</sub>O<sub>2</sub>. Hydrophilic interactions between carboxylic acid groups on SWNTs and amino acid residues of HRP result in close proximal contact to the active heme site of HRP, facilitating oxidation of SWNTs to CO<sub>2</sub> gas.

While initial experiments demonstrated a necessity for carboxylation, current research is focusing on the degradation of pristine SWNTs and multi-walled carbon nanotubes (MWNTs). By appropriately coating pristine carbon nanotubes with polymers and surfactants, interactions between HRP and carbon nanotubes are enhanced, allowing for their degradation without prior covalent oxidation. Moreover, other peroxidase enzymes are currently being examined for their ability to degrade carbon nanomaterials. Such results allude to the promise of environmental toxicity mitigation of carbon nanotubes prior to their physiological inception.

[1] Poland *et al.* (2008) *Nature Nanotech.* **3**, 423–428.  
[2] Allen *et al.* (2008) *Nano Lett.* **8**, 3899–3903. [3] Allen *et al.* (2009) *J. Am. Chem. Soc.* **131**, 17194–17205.

## Silicate melts at high temperature and pressure: Structure and properties

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Accurate data on the bulk properties of molten silicates, such as density, heat capacity, and viscosity, are critical for the quantitative understanding of magmatic processes. The complex behavior of such materials points to fundamental questions of how the short- to intermediate-scale structure of the liquid changes with pressure and temperature. Although answers to many of these questions remain unresolved, considerable progress has been made in recent years through the application of spectroscopic and scattering methods to quenched glasses and, *in situ*, to high temperature and even high pressure liquids. One example is the increase in configurational disorder with temperature in molten aluminosilicates, which involves complex interactions between the distribution of the network cations (Si, Al), proportions of bridging and non-bridging oxygens, and coordination changes (e.g. of Al). All contribute substantially to the entropy and thus should be included in calculations of free energy and phase equilibria. A second example is the large effect of the size and charge (field strength) of both network-modifier and network-former cations on the rate of increase of Al and Si coordination in melts with pressure, one (not the only!) component of structural mechanisms of densification. Such effects are again complex and non-linear, suggesting that accurate models of compositional effects on melt density will also need to be complex. Between the short-range structure that is most readily observed by spectroscopy, and the macroscopic behavior that controls Earth processes, structures may emerge at the intermediate-range or ‘nano’ scale that can, on the one hand, provide clues to energetics, and, on the other, sometimes be critical to bulk properties. Phase separation and crystal nucleation are the obvious examples from high-temperature melt systems. Thus, a final example of the micro- to macro- connection is a newly-applied NMR spectroscopic method for detecting incipient liquid-liquid phase separation, and characterizing domain composition and structure.