Nanoparticle aggregation state and aging: Implications for reactivity and toxicity testing

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Within the gray zone between the atomic and bulk scales, the properties of nanomaterials may be expected to change due to the formation of nanoparticle clusters to an extent that is intermediate between those when atoms cluster of form molecules and when colloidal particles aggregate. In this communication, we discuss the effects of aging and aggregation on fullerene fate and transport, as well as the implications for nanoparticle reactivity and toxicity. The interplay between physical forces that bring nanoparticles in contact, the chemistry of nanoparticles surfaces and environmental factors that may transform these surfaces, play an important role in determining nanoparticle transport, fate and reactivity through their effects on aggregate structure. We discuss the role of environmental and physiological conditions in determining nanoparticle aggregation rates and aggregate structure as well as the impact of aggregate structure on removal by sedimentation. Using photosensitization by fullerene nanoparticles as an example, we show how differences in aggregate structure and heterogeneity that results over time may affect nanoparticle reactivity. The production of reactive oxygen species, microbial inactivation, and the mobility of the aggregates of the nC60 in a silicate porous medium all increased as suspensions were fractionated to enrich with smaller aggregates by progressive membrane filtration. These size-dependent differences are attributed to an increasing degree of hydroxylation of nC_{60} aggregates with decreasing size. As the quantity and influence of these more reaction fractions may increase with time, experiments evaluating fullerene transport and toxicity endpoints must take into account the evolution and heterogeneity of fullerene suspensions.

Geophysical constraints on heat transfer to mid-ocean ridge hydrothermal systems

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Seismic reflection surveys show that most fast and many intermediate spreading rate ridges are underlain at mid-crustal depths by a thin steady-state magma chamber [1]. The melt content varies from pure melt to a crystalline mush with higher melt fractions beneath sections of the ridge that support black smoker vent fields [2]. The observed heat fluxes of black smoker fields can substantially exceed the steady state heat fluxes necessary to form the lower oceanic crust but are consistent with the rates at which magma is supplied episodically to terrestrial volcanoes [3]. For black smoker systems, one-dimensional models of heat transfer show that the conductive boundary layer separating hydrothermal fluids from the magma chamber must be only a few meters thick [4]. Without magma replenishment the heat fluxes are sufficient to solidify the magma chamber in tens of years [5]. In order to preserve a steady-state magma chamber and maintain a balance between average hydrothermal heat fluxes and the heat of crustal formation, the conductive boundary layer must thicken considerably, perhaps to as much as a few hundred meters, along portions of the ridge with no black smoker fields. Microearthquake data collected beneath the Endeavour segment of the Juan de Fuca Ridge suggests that the injection of pressurized magma into mid-crustal magma chambers leads to significant fracturing of the overlaying rock carapace [6]. This fracturing provides a mechanism to maintain a thin conductive boundary that would otherwise thicken due to the clogging of cracks by hydrothermal alteration products. Thus it appears that a simple model of heat transfer in which the conductive boundary layer decreases in thickness by up to two orders of magnitude during intervals of magma injection and black smoker activity is consistent with geophysical observations. A challenge to the geochemical community is to determine whether this model is also consistent with the chemistry of hydrothermal fluids and reaction zone rocks.

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