

## Nanoparticles: Size-structure-reactivity interrelationships

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Nanometer-scale mineral particles are common products of chemical weathering reactions and microbial processes. Generation of metal sulfide nanoparticles by sulfate reducing bacteria (SRB) can have a profound impact on metal distribution and metal cycling in the environment. Our work began with a study of ZnS formed as the result of the metabolic activity of SRB in an anoxic groundwater zone associated with a flooded mine. The typical diameter of the ZnS product is ~ 1-3 nm. The ZnS particles are formed in a biofilm and aggregate to yield micron-scale colloids. High-resolution transmission electron microscope (HRTEM) observations reveal that the nanoparticles within aggregates contain complex microstructures, including twins and stacking faults. Small quantities of wurtzite were detected. The presence of wurtzite is interesting because it is not the stable phase below 1020°C in bulk material Scott and Barnes, 1976). These observations suggest the existence of interesting size-dependence of growth, microstructure development, and phase stability in nanocrystalline ZnS.

The observations of natural nanoparticle structure and behavior have been investigated using nanocrystalline ZnS synthesized in water, methanol, and mercaptoethanol-water solutions. Only in case the of the mercaptoethanol synthesis products, the nanoparticles form micron-scale aggregates that resemble those found in the biofilm.

Very small nanoparticles have structures that are quite distinct from the equivalent bulk material. This has been demonstrated by comparison between spectroscopic observations of nanoparticles and spectra predicted assuming atomic positions derived from the bulk structure. For example, average EXAFS-determined vibrational frequencies for mercaptoethanol-coated nanoparticles are significantly larger than those characteristic of bulk ZnS.

Hydrothermal experimental studies indicate that the mercaptoethanol-capped ZnS particles grow via a two stage process (Huang et al. 2003). The first stage can be explained by a pure oriented-attachment kinetic model. HRTEM observations clearly confirm the importance of this growth pathway. Specifically, larger crystals are composites of individual nanoparticles; twins and stacking faults frequently correspond with indentations on the crystal surface and mark boundaries between primary particles. Stacking faults and twins arise via junction of particles in a subset of possible orientations ( $\{111\}_{\text{sph}}$ ) that achieve congruence in the plane of the interface. In the second stage, diffusion-controlled growth becomes increasingly important as the crystal size increases.

## Increasing sulfate <sup>17</sup>O anomaly with depth in hyperarid regolith profiles

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Sulfur oxidation chemistry in the atmosphere may have gone through a drastic change after the rising of O<sub>2</sub> and the formation of ozone layer since ~ 2.5 billion years ago. The ending production of S-33 anomalous sulfides and sulfates marks the beginning production of <sup>17</sup>O anomalous sulfate. Positive sulfate <sup>17</sup>O anomalies have been found ubiquitous in hyperarid deserts in the world, e.g., the Central Namib Desert, the Atacama Desert, Chile, and the Antarctica Dry Valleys. The local source of sulfate normally does not possess <sup>17</sup>O anomaly whereas the atmospheric source does. Further more, in the atmospheric source exist two major components: the normal sea-salt sulfate (SSS) and the anomalous biogenic sulfate (i.e., sulfate derived from the oxidation of biogenic sulfur gases such as dimethylsulfide in the atmosphere). The observed magnitude and spatial differences, including sulfur isotope composition, among the different deserts can be explained by the variable contributions of these different sources.

There exists, however, an intriguing but consistent pattern of increasing sulfate <sup>17</sup>O anomaly with depth in many of the regolith profiles, as we first observed in the Dry Valleys. This pattern is not obvious in the Central Namib Desert or in the coastal area of the Dry Valleys. New data on several dozens of regolith profiles in the Atacama Desert has confirmed the phenomenon of increasing sulfate <sup>17</sup>O anomaly with depth. Some of the profiles have up to 3.6‰ increases in <sup>17</sup>O anomaly within 100 cm from the surface. There are three possible explanations: 1) If the regolith is accumulating materials, atmospheric condition favoured relatively more deposition of biogenic sulfate than SSS to the site in question in the past than it is now. 2) There has been a secular change in the atmospheric oxidation chemistry that produced higher <sup>17</sup>O anomaly for biogenic sulfate in the past. 3) A post-depositional leaching by rare precipitation events in the hyperarid climate preferentially moves the <sup>17</sup>O anomalous sulfate downward.

Multiple stable isotopic data, combining with anion content data, strongly suggest that the post-depositional leaching is the cause of isotopic separation along a vertical regolith profile. A preferential downward movement for biogenic sulfate can be explained by its smaller particle size and more soluble chemical composition than those for SSS. This rare case of isotopic separation is unique to hyperarid environment with extremely limited liquid water. The quantification of the separation factor could be a powerful tool in accessing moisture exchange between regolith and atmosphere in hyperarid environments.