The effect of size on nanoparticle dissolution rate

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The dissolution rate of nanoparticles affects both their persistence in the environment and the release rate of their metal content, and, hence, can control their toxicity. While previous studies concluded that nanoparticles dissolve faster than their bulk analogs, contradictory evidence suggests that nanoparticles dissolve more slowly. Furthermore, insufficient characterization of the nanoparticulate samples and the solution chemistry in past studies obscures the relationship between particle size, surface area, and dissolution rate. There is a critical need for additional studies, using well-characterized nanoparticles and reactive solutions, to develop a model of nanoparticle dissolution rate.

Dissolution rates are a function of both the distance from equilibrium (providing the driving force for dissolution) and a dissolution rate constant (reflecting the dissolution mechanism and the strength of bonds critical to maintain the structure). The current study takes the approach of studying dissolution rates at far-from-equilibrium conditions to quantify the effect of particle size on the dissolution rate constant, isolating any potential kinetic effect of particle size from the well-established effect of particle size on solubility.

Multiple samples of both nanotalc and amorphous silica nanospheres were synthesized, ranging in size from approximately 20 to 200 nm. Samples were characterized by XRD, SEM, TEM, dynamic light scattering, and gas adsorption. Flow-through experiments were performed at far-from equilibrium conditions with pH from 2-10. Batch experiments were performed at both far-from and approaching equilibrium.

Preliminary interpretation of these data suggests that any effect of size on dissolution kinetics is minor. Thus, as the dissolution rate constant appears to be size independent (within experimental error), the dissolution rate of nanoparticles as a function of size and departure from equilibrium can be modeled by using classical kinetic rate laws and taking account of the effect of size on solubility.

Marine redox conditions and sulfur cycling during the deposition of the 2.3 Ga Timeball Hill Formation

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Rhenium and Molybdenum concentrations in shales and sulfur isotopes in disulfides and organic matter provide new insights in the development of the ocean-atmosphere system during the deposition of the 2.3 Ga Timeball Hill Formation, South Africa. Relatively low enrichment factors (relative to average crustal abundances) of Mo between 0.1 and 2.4 and high Re enrichment factors between 1.1 and 25.0 can be distinguished. Marginal concentrations of Mo correlate with the highest enrichments of Re, and appear to be coupled to the most negative $\delta^{34}S$ values (down to -30 ‰ against V-CDT in disulfides) and highest concentrations of organic bound sulfur.

High Re concentrations over wide parts of the stratigraphy argue for a deposition under anoxic but, as indicated by low Mo concentrations, not for euxinic deepwater conditions. Pyrite from these stratigraphic levels show the lowest $\delta^{34}S$ values, thus high isotopic fractionation, which suggests the establishment of an oceanic sulfate pool. The absence of large Mo and Re enrichments in the middle parts of Lower and Upper Timeball Hill shales indicate potentially oxic oceanic conditions. These samples show high $\delta^{34}S$ values in disulfides which could indicate a low sulfate flux to the oceans.

These observations lead to the conclusion that the water column was constantly non-euxinic at 2.3 Ga. The intensity of continental weathering and the subsequent delivery of nutrients to the oceans was variable and a consequence of the fluctuations of the atmospheric oxygen content.