Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.37959

Size effects on the reactivity of nanoscale hematite in sulfidic spring water

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Particle size, crystallinity, and morphology are controlling factors in the chemical and physical characteristics of nanomaterials. Additionally, nanoparticles exhibit size-dependent changes in atomic and electronic structure, suggesting that the reactivity of nanoscale minerals may change based on size [1]. While laboratory studies of size-dependent reactivity often demonstrate greater reactivity for smaller nanoparticles, size-dependent reactivity experiments in the field produced an opposite trend: smaller particles were more quickly passivated by adsorption by organic matter [2]. Here we explore the size-dependent reactivity of nanoscale minerals in a highly-reactive sulfidic environment, where we expect the kinetics of the Fe-S reaction to control the reactivity rather than adsorption of organic matter. We synthesized three sizes of hematite particles (10, 100, and 200 nm), controlling the morphology and crystallinity, and exposed them to sulfidic spring water over time. We found systematic changes in surface roughness, crystallinity, and reaction products as a function of size using electron microscopy, where particle reactivity increased as the particle size decreased. In addition, we observed different reaction products based on the initial particle size. For example, aggregates of 100 nm hematite particles uniquely turned into particles that are morphologically and chemically consistent with layered double hydroxides and/or iron bearing serpentines. However, we observed no discernable reaction products or remaining hematite in samples initially loaded with 10 nm particles-- only spring water colloids or amorphous solution precipitates, suggesting complete dissolution occurred. By understanding the differences in reactivity of nanoscale hematite with sulfide, we expand our understanding of iron and sulfur cycles in this and other environmental systems where iron oxides are commonly observed as nanophase materials [3]. This is the first study to our knowledge demonstrating that size-dependent reactivity of nanoscale minerals in a complex field environment follows the expected laboratory-based trend of smaller nanoparticles reacting faster.

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