What makes biogenic sulfur special? Insights into surface chemistry and mineralogy of sulfur globules

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Elemental sulfur, S(0), is a widespread intermediate in global sulfur cycling. While microbes produce and dissolve S(0) biominerals, little is known about the mechanisms of cell-S(0) interactions. This is particularly true for extracellular S(0), where these interactions can influence abiotic geochemical reactions, microbial reactions and ecology. To better understand the these interactions, we investigated the biogenic S(0) produced and consumed by *Chlorobaculum tepidum*, a model phototrophic S-oxidizer.

XRD and micro-Raman spectroscopy show that the globules produced by *C. tepidum* contain nanocrystalline α-cyclo-octasulfur (α-S_8). AFM measurements of modulus confirm that globules are indeed solid, contrary to claims of liquid or liquid-like sulfur. Instead, the solid S(0) globules appear to be both soft and pliable. Once sulfide is exhausted, *C. tepidum* uses S(0) as an electron source. After sulfur globules are consumed by *C. tepidum*, a thin, membrane-like material is left behind. This material is most likely the remnant of a recalcitrant organic surface layer of the globule. Indeed, a number of analyses have shown the surface of S(0) globules is enriched in organics. AFM adhesion measurements and contact angle experiments also show that biogenic S(0) globules are much more hydrophilic than abiotic elemental S(0), a property likely conferred by the organic-enriched surface of the globule, which is the subject of Nano-IR analyses and ongoing Raman experiments.

While the mineralogy of biogenic S(0) globules is α-S_8, the stable form of elemental S(0), *C. tepidum* cannot grow on abiotic S(0), such as Weimarn sols and other sols composed of α-S_8. The key distinction between biogenic S(0) globules and these abiotic S(0) sols the surface. Thus, our results suggest that the surface of biogenic S(0) globules is key to cell-S(0) interactions and reactivity of biogenic S(0) in the environment.