

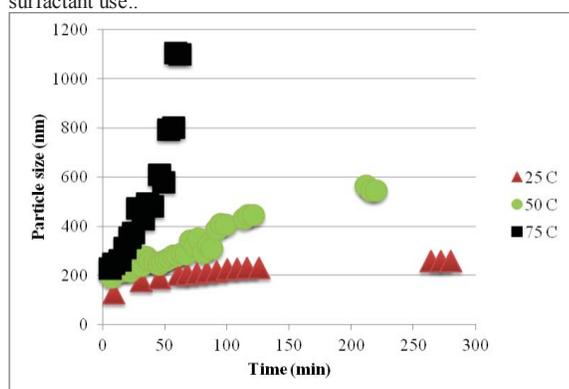
## Elemental sulfur nanoparticle coarsening kinetics and changes in Raman and voltammetric signals

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Elemental sulfur exists in a variety of forms in natural systems, from dissolved forms (noted as  $S^0$ , or in ring form as in  $S_8$  (rings)) to bulk elemental sulfur (most stable as  $\alpha$ - $S_8$ , but existing in at least 180 different allotropes and polymorphs). Elemental sulfur can form via a number of biotic and abiotic processes, many of which would begin with single  $S^0$  molecules that aggregate into larger and larger forms; this process is explained by the following pathway:  $S^0 \rightarrow S_8$  (rings)  $\rightarrow S_8$  (nano)  $\rightarrow S_8$  ( $\alpha$ - $S$ ) (bulk). Formation of elemental sulfur has been done in the lab via two primary techniques to create an emulsion of liquid sulfur in water called sulfur sols that approximate some mechanisms of possible elemental sulfur formation in natural systems. These techniques produce Wiemarn (hydrophobic) and Raffa (hydrophilic) sols [1]. These sols begin as single S molecules, but quickly become nanoparticulate and coarsen into micron sized particles via a combination of Ostwald ripening and aggregation processes. In an effort to investigate fundamental questions related to elemental sulfur particle size in natural systems, we conducted a series of experiments to study the rate of elemental sulfur particle coarsening using dynamic light scattering analysis under different physical and chemical conditions. Results showed that coarsening of  $S_8$ (nano) is partly pH dependent (with faster coarsening at pH 3 than at pH 7 or 10), and strongly temperature dependent (Figure 1). The addition of surfactants to emulate biotic mechanisms to transport elemental sulphur inside the cell shows a significant reduction in the rate of aggregation, in addition to known effects of these molecules on elemental sulphur solubility [2]. Initial cryo-SEM results additionally suggest coarsening is largely a product of ripening processes rather than particle aggregation. Raman spectroscopy and voltammetry (using Au-amalgam and mercury drop electrodes) signals change as a function of size and surfactant use..



**Figure 1: Elemental sulfur particle coarsening.** Nanoparticles form from  $S^0$  and  $S_8$ (rings) in seconds, followed by coarsening (ripening and aggregation) that is strongly T-dependent.

[1] Stuedel (2003) *Aqueous Sulfur Sols* **230**, 153-166.

[2] Stuedel and Holdt (1988) *Angew. Chem. Int. Ed. Engl.* **27**, 1358-1359.

## Large magnesite vein and fracture formation in peridotite rocks

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Large monomineralic cryptocrystalline magnesite ( $MgCO_3$ ) vein deposits hosted in ophiolitic peridotite provide insights into the chemical, structural, and temporal constraints on subsurface carbonation processes. The magnesite veins record the upward migration of deep mineralizing solutions to shallow crustal depths, which bear relevance to two fundamental problems important to industrial geologic sequestration of  $CO_2$  in peridotite rocks: (1) the kinetics of magnesite formation—the target carbonate for  $CO_2$  mineralization and (2) the generation of permeability required for modally abundant carbonate formation. Our field site, the Red Mountain Magnesite Mining District in the Diablo Mountain Range, California, provides information about these processes and a framework for comparison with the results of experimental and modeling studies of carbonation of Mg-silicates.

Mines at the Red Mountain Magnesite District, California, reveal more than 20 homogenous magnesite veins up to 40 m thick and >100s of m in length hosted in the variably serpentinized peridotite lithology of the Del Puerto ophiolite. The carbonate mineralization occurs primarily as cryptocrystalline magnesite veins with sharp mineralogical or structurally sheared/brecciated contacts with the host peridotite rock. Rapid, low-temperature mineralization is inferred from chemical, isotopic, and textural homogeneity of magnesite, and the lack of metasomatic reaction zones along the peridotite-magnesite interface. Opaline silica occurs as relatively small late-stage veins paragenetically distinct from the magnesite mineralization and the peridotite host rock. Silica expected from extensive peridotite dissolution and relic textures of peridotite in the carbonate are absent in the observed exposures, indicating that Mg was supplied from dissolution of Mg-bearing rocks below the mineralization zone and that silica did not inhibit magnesite precipitation. This suggests that the rates of Mg-silicate dissolution are decoupled from the rates of magnesite precipitation. At Red Mountain, magnesite precipitation was both effective and pervasive, implying that the experimental problems in magnesite formation (primarily slow nucleation kinetics) have been overcome in nature. These observations highlight both the complexity of natural analogues and the limitations in the chemical and temporal scope of dissolution-carbonation experiments in replicating natural systems. The magnesite veins evidence a structurally and paragenetically different carbonation mechanism than that proposed for carbon sequestration (direct Mg-silicate dissolution and creation of permeability via carbonate growth). Geochemical and geochronological work on the magnesite, silica, and peridotite rocks further constrain models of fracture-vein initiation and closure related to the carbonation at Red Mountain.