

## **Nanoscale processes in the environment and biosystems at the nanoscale**

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### **Scope of the project**

Because nanoscale phenomena dominate many processes near the surface of the Earth, these phenomena are of special importance to the environment and human health. Nanoscale processes are intrinsically molecular; hence, there is an immediate synergy between the study of nanoscale particles in natural systems and the disciplines of mineralogy, chemistry, physics and materials science.

The geonanoscience research team at the University of Michigan is focusing on projects that cover a variety of environmental phenomena, such as ore formation, mineral exploitation and remediation, potentially hazardous atmospheric particles, and biomineralization. These systems have in common that we can study their natural and environmental occurrence and that we can create model systems for better analysis. Another feature that these systems have in common is that we can study the physico-chemical behavior of the nanoparticles and of the nanoparticle-environment interfaces at both the experimental and theoretical level at the atomic and electronic scale. Since nanoparticulates have unique properties as isolated entities, it is tempting to focus on the nanoparticle in isolation. However, especially for nanoparticles in the environment, it is important to analyze their properties in relation to their immediate atomic-scale environment, e.g., the nanoparticle-host interface. In many cases, the structure, stability, chemistry, charge, electronic and magnetic structure, and finally their reactivity are based on these interface properties. Thus, it is essential to develop an understanding of nanoparticle-host interface properties at the atomic level, using a combination of skills in nanoscale characterization.

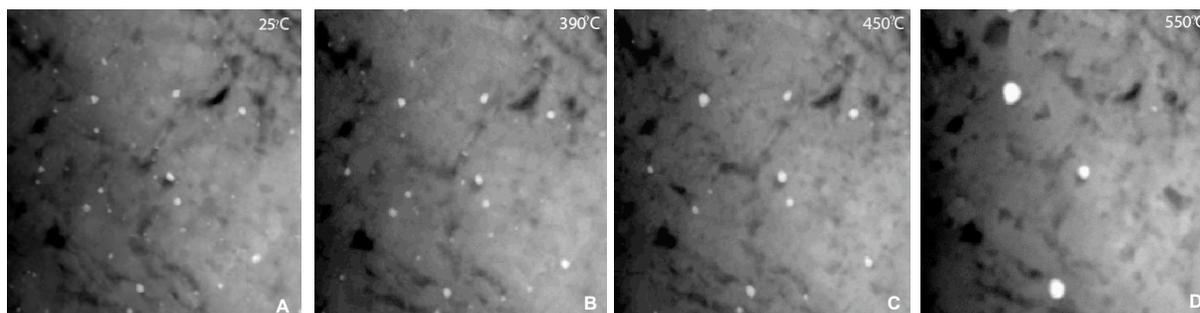
An intrinsic problem with studying nanoparticulates in natural samples is that one has to find them in order to be able to analyze them. That applies to a single nucleus as a precursor of biomineralization as well as to a gold cluster in a sulfide host mineral or to a metal adsorbate on a sulfide or oxide surface. The proposed research applies a wide variety of electron beam and spectroscopic techniques, the synthesis of nanoparticles under controlled conditions, and the study of surface and interface clusters. In addition, since a number of structural and electronic properties of nanoparticles and their interfaces are still difficult to be determined experimentally, quantum mechanical and molecular dynamics simulations are necessary to further a concise understanding of nanoscale phenomena in the environment. With this knowledge, significant progress can be made to understand ore formation as a function of host mineral chemistry, which will lead to more environmentally friendly extraction methods. Furthermore, this knowledge will help elucidate the processes of biomineralization, which have applications in medical sciences (bone and teeth growth), the formation of biominerals in nature and for the development of optimized biocomposites that have a number of applications in materials science and in medicine.

## Ongoing research

### Temperature-induced phenomena at the nanoscale

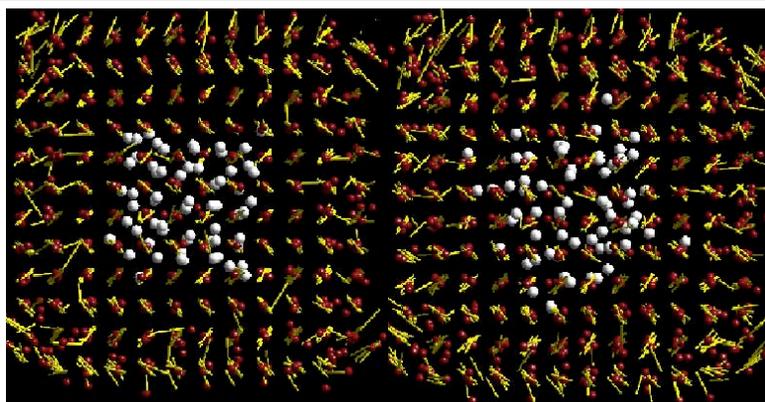
As temperature plays an important role in many geological and environmental processes, we have focused part of our efforts to study the effect of this intensive variable on model nanoparticulate systems. We have also given special attention to nanoparticle-host phenomena in these systems, as limited information is available on the role of interfacial energies on nanoparticle stability in natural systems.

The “invisible” gold<sup>1</sup> in As-rich pyrite,  $\text{Fe}(\text{S},\text{As})_2$ , provides a unique opportunity to investigate the relatively unknown effects of temperature on nanoparticle size in geologic samples. When heated between 25-650°C, *in situ* high-resolution TEM observations show that Au nanoparticles remain unchanged up to ~370°C. Above this temperature, the particle-size distribution evolves by solid-state, diffusion-driven Ostwald ripening as larger particles (~8 nm) grow at the expense of smaller ones (< 4nm) until the initial array of ~100 nanoparticles was replaced by a few coarser (~35 nm) particles (Fig.1). We have captured these dynamical



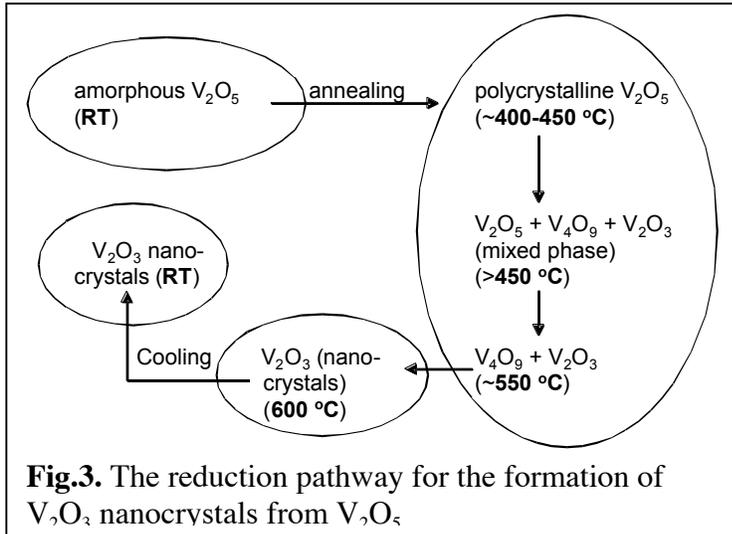
**Fig.1.** HAADF-STEM images taken for selected temperatures during heating experiment of AuNPs embedded in  $\text{Fe}(\text{S},\text{As})_2$ . No visible changes occur during heating from room temperature (A) until ~390°C (B), where smaller clusters disappear into the matrix and larger ones coarsen. Above 450°C (C), larger clusters have grown at expenses of the smaller ones. At 550°C (D), only three clusters of >20 nm diameter survive. Scale bar is 100 nm.

observations as movies, confirming that nanoparticle stability is not only dependent on particle size, but also on the surrounding mineral host. Whereas isolated Au nanoparticles melt as a function of size<sup>2</sup>, our results show that when embedded in a sulfide matrix, these particles dissolve into the matrix and form larger particles in a Ostwald-type ripening process.



**Fig.2.** Molecular dynamics (MD) simulations of a Au nanoparticle embedded in pyrite. (A) at 300 K; (B) at 900 K

Furthermore, preliminary molecular dynamics (MD) simulations of the gold/pyrite system have confirmed the diffusional nature of this process in the solid state (Fig.2), although we are still investigating its physico-chemical mechanisms. These results give us significant insight on the behavior of embedded metal nanoparticles during natural processes, as well as during metallurgical recovery in mineral processing plants.



**Fig.3.** The reduction pathway for the formation of  $V_2O_3$  nanocrystals from  $V_2O_5$

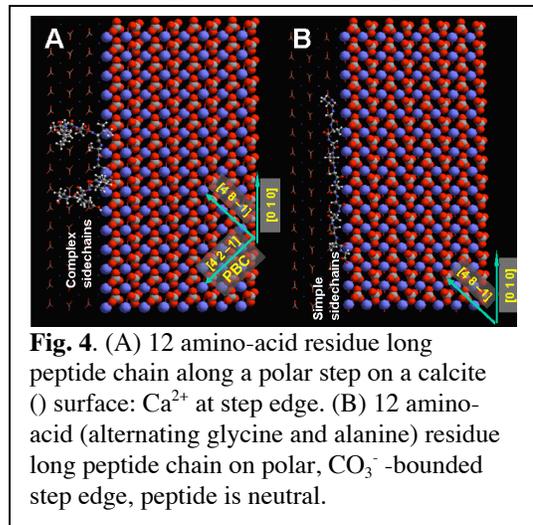
### Phase transitions of vanadium oxide nanoparticles

Another project on vanadium oxide systems<sup>3</sup> at elevated temperature deals with more technological applications. The results of our heating experiments and observations using TEM offer a novel route for the fabrication of  $V_2O_3$  without any need for processing at very high temperatures or involving hazardous gases. The crystals formed are homogeneous and stable even with further increasing the temperature above their formation temperature or after

cooling to room temperature. These investigations in a chemical-free environment (in vacuum) could provide the basis for understanding the complex reduction processes in the presence of various chemical species, as they occur in chemical catalysis, and thereby controlling the process to produce other oxide nanocrystals for technological applications.

### Biom mineralization phenomena at the nanoscale

We are beginning to evaluate the plethora of possibilities to let polypeptide chains interact with specific steps on calcite surfaces to understand certain principles, for example steric hindrances caused by “bulky” sidechains (Fig. 4A) or the stabilization of calcite steps with periodic biomimetic polypeptides. Future work will use adsorption energy calculations in a genetics-like way to find optimized peptide sequences for specific biom mineral faces and step directions.



**Fig. 4.** (A) 12 amino-acid residue long peptide chain along a polar step on a calcite ( $\text{Ca}^{2+}$ ) surface:  $\text{Ca}^{2+}$  at step edge. (B) 12 amino-acid (alternating glycine and alanine) residue long peptide chain on polar,  $\text{CO}_3^-$ -bounded step edge, peptide is neutral.

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