

## Role of proteins in the formation of selenium nanoparticles

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Chemically or biologically produced nanoparticles (NP) might have different properties, structure, size or shape. Biological nanoparticle synthesis does not require extreme temperatures and pressures, which is an economic advantage.

The goal of the current project is to understand factors influencing the morphology and structure of metallic bacteriogenic nanoparticles. Redox-dependent NP synthesis in bacteria is believed to take place in two steps: (1) enzymatic reduction/oxidation of the metal, (2) nucleation/precipitation and growth of the NP. We believe that this second step is affected by the surrounding proteins and that they play a fortuitous role in biogenic NP synthesis.

The present study focuses on the effect of bacterial proteins on bio- and chemo-genic NP formation. We compared the binding of *E. coli* cell free extract proteins to (1) magnetite NP, (2) biogenic selenium NP, (3) chemogenic selenium NP and (4) evaluated the binding of *E. coli* proteins to selenium NP during their biological formation. We report the identification of proteins that selectively bind to iron or selenium using SDS-PAGE and nano-LC-IT-MS/MS. These proteins are strongly bound to NP as they remain associated to the NP after harsh treatments such as boiling in 10% SDS. The proteins that bind NP do not have activities related to metal transformation but rather are enzymes involved in carbohydrate biosynthesis or lipid metabolism. A comparison of the morphology and size distribution of selenium NP produced chemically in the presence and absence of *E. coli* cell free extract reveals that the proteins control the size distribution and aggregation of NP. In the absence of proteins the nanoparticles ranged from 20nm to 200nm in size whereas those produced in the protein matrix had a narrower size distribution around 100nm.

Using bacteria as micro-factories for industrial grade nano-materials is an environmentally friendly alternative to current practices and offers opportunities for green NP manufacturing.

## Lamellae of phyllosilicates in K-rich diopside from UHP marble of the Kokchetav massif, Kazakhstan: FIB-TEM and synchrotron IR studies

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Exsolution lamellae of pyroxene in garnet, coesite in titanite and omphacite from UHPM terranes are widely accepted as products of decompression. However, interpretation of oriented lamellae of phyllosilicates, framework silicates and oxides as a product of decompression of pyroxenes are very often under debate. We present here results of FIB-TEM, FEG-EMP and synchrotron assisted InfraRed spectroscopy studies of Phlog and Phlog+Qtz lamellae exsolution in diamond-bearing CPx from UHP marble. These techniques allowed collection of 3-dimensional information from the grain boundaries of both the single (Phlog), two-phase lamellae (Phlog+Qtz), and diamond included in K-CPx and understanding of reactions and PT-conditions responsible for their formation.

The CPx contains lamellae-I (topotactically oriented extremely thin lamellae of Phlog; their width is ~two atomic units), and microdiamond inclusions, situated in the CPx-core. The core composition:  $(Ca_{0.93}Fe_{0.03}K_{0.01}Na_{0.02})(Al_{0.07}Fe_{0.05}Mg_{0.88})Si_2O_6$ . Fluid inclusions rich in K and Si are recognized in the core of the CPx, having no visible connections to the lamellae-I. Lamellar-II inclusions consist of micron-size single laths of Phlog and lens-like Qtz, or slightly elongated Phlog+Qtz intergrowth; all are situated in the rim zone of the CPx. The rim  $[(Ca_{0.95}Fe_{0.03}Na_{0.02})(Al_{0.05}Fe_{0.05}Mg_{0.90})Si_2O_6]$  contains more Ca, Mg than the core, with no K there. Such chemical tests support our microstructural observations, and conclusion that the Phlog lamellae-I are exsolved from the K-rich CPx-precursor during decompression. We assume that Cpx-precursor was also enriched in H<sub>2</sub>O, because diamonds included in this CPx contain fluid inclusions. The synchrotron IR spectra of the diamonds record presence of OH stretching and H<sub>2</sub>O motion regions. Lamellar-II inclusions were formed partly due to modification of the lamellae-I in presence of the low TP fluid enriched in K, Fe and Si.