

## Influence of thiol-containing ligands for the aggregation and dissolution of metallic silver nanomaterials

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The environmental fate and mobility of metallic nanoparticles (NPs) in natural waters will be strongly influenced by reactions between the particle surfaces and metal-binding organic ligands that are prevalent in natural waters. Thiol-containing organics are known to dominate the speciation of soft-sphere metals such as ionic silver ( $\text{Ag}^+$ ) in the environment [1]. Furthermore, the type and reactivity of the synthetic coating that is used during the synthesis of the nanoparticles will be a key factor controlling interactions with thiol-containing organic ligands. The objective of this work was to examine how thiols can modify particle surfaces and their reactivity during aggregation and dissolution of the nanoparticles. We studied zero valent silver ( $\text{Ag}^0$ ) NPs with two types of coatings: citrate (CIT) and polyvinylpyrrolidone (PVP). Our studies involved cysteine (CYS) and N-acetylcysteine (NAC), two low molecular weight thiol ligands that we utilized as analogues for the natural organics that are expected to bind dissolved  $\text{Ag}^+$  in the aquatic environment.

Aggregation and dissolution experiments with CIT- and PVP-coated  $\text{Ag}^0$  NPs demonstrated that thiol-containing ligands increased aggregation rates of the particles, depending on solution ionic strength and type of thiol. The increase in aggregation was greater for the PVP-coated  $\text{Ag}^0$  NPs relative to the CIT-coated NPs. The addition of cysteine to  $\text{Ag}^0$  NP suspensions also increased the dissolved  $\text{Ag}$  concentration. These results indicated that cysteine was simultaneously sorbing to the  $\text{Ag}^0$  NPs and promoting their dissolution, resulting in surface modifications that increased aggregation rates. These results were supported by silver L-III-edge and sulfur K-edge X-ray absorption spectroscopy measurements that showed oxidation of the silver and the formation of  $\text{Ag}^+(\text{I})$ -CYS bonds for  $\text{Ag}^0$  NPs that were exposed to CYS.

Overall, our study highlights the importance of the coating and  $\text{Ag}^+$ -binding organic ligands for modifying the surface of silver nanomaterials in environmental settings. Sorption of natural organics alters the aggregation and solubility of the nanomaterials, and ultimately, will influence their persistence in the environment.

[1] Smith *et al.* (2002) *Comparative Biochemistry and Physiology Part C* **133**, 65-74

## The isotope evidence of ore-forming materials of the Erdaogou gold deposit in Beipiao Liaoning deriving from magmatic rocks mixed by the crust and mantle source

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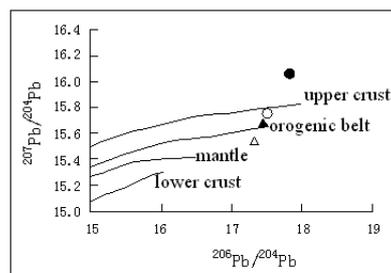
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The isotope characteristic value is one of most effective methods recognized to solve petrogenetic question. Because of its tracing function, more and more geologists home and abroad pay attention to it in recent years.

Initial ratio of strontium isotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) varied greatly in Mesozoic volcanic rock in western of Liaoning area (basalt is 0.70474-0.70875, andesite is 0.70496-0.70595, trachyte-andesite is 0.70496-0.70595, dacite is 0.7076, liparite is 0.7081-0.7199) (Wanglaichun,1985); but initial ratio of strontium isotope in Duimianguo rock-mass is between the range of 0.704-0.708, indicated that the granitic magma coming from the upper mantle, and was contaminated by Si-Al layer of crust. The strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) <0.710 and  $\delta^{18}\text{O}$  <10 ‰, it is in line with the characteristics features of crust and mantle source.

From the figure of lead isotope  $^{206}\text{Pb} / ^{204}\text{Pb}$  -  $^{207}\text{Pb} / ^{204}\text{Pb}$  in main alteration and mineralization rock (figure 1), we can see: a great number of the sample points of lead isotope fall within a wide range of the upper mantle and crust line, this reflects that lead in mineralization fluid comes from the magmatic rock of a mantle-crust mix, but majored in crust origin.



**Figure 1:** The Graphic of lead isotope  $^{206}\text{Pb} / ^{204}\text{Pb}$  -  $^{207}\text{Pb} / ^{204}\text{Pb}$  in main alteration and mineralization rock