Heavy metal (Cd²⁺, Co²⁺, Ni²⁺ and Zn²⁺) uptake from seawater by calcite

J. CARNEIRO*, H. STOLL AND M. PRIETO

Departamento de Geología, Universidad de Oviedo, C/ Jesús Arias de Velasco s/n, 33005 Oviedo, Spain (*correspondence: joana@geol.uniovi.es) (hstoll@geol.uniovi.es, mprieto@geol.uniovi.es)

In some coastal areas, the anthropogenic inputs of trace metals to the surface ocean exceed the natural inputs from continental sources. One example is found in the southwestern coast of Spain, where the waters from Rio Tinto, that drain the Iberian Pyrite Belt, transport enhanced concentrations of dissolved metals into the ocean [1].

Several studies have demonstrated that the mobility of divalent metals such as Cd, Co, Ni and Zn, in freshwater environments, is reduced when the metals are sorbed to calcite forming $(Me^{2+},Ca)CO_3$ solid solutions. This sorption was shown to be especially effective in the case of Cd (e.g. [2]). In the oceans, however, calcite is usually not considered to be a significant scavenging phase for these trace elements [3] and there are few experimental studies on the uptake of metals from seawater.

The aim of this work is to determine if these metals could be inorganically removed from seawater by sorption to calcite, thus contributing to a natural attenuation of high metal concentrations in marine environments. To study the effect this uptake might have on the metal concentrations in seawater, sorption experiments were carried out by reacting calcite particles (1-25 μ m) with metal-enriched artificial seawater solutions, in continuously stirred vessels at ambient conditions. Experiments for each metal were done in separate, with initial concentrations of ~1 ppm in all cases. Samples of the seawater were collected throughout the duration of the experiments, and the concentrations of the considered dissolved metals were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

A decrease in concentration in seawater was observed for each metal. Our preliminary experiments suggest that the sequence of metals, from the most to the least sorbed to calcite, might differ from the sequence determined by [2] regarding the preferential partitioning of the metals in freshwater solutions.

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Investigation of nanoparticles and carbon nanotubes toxicity and transfer in bacteria and plants

M. CARRIÈRE¹*, A. SIMON-DEKERS¹, C. LARUE¹, M. MAYNE-L'HERMITE², N. HERLIN-BOIME² AND C. REYNAUD²

 ¹CEA Saclay, SIS2M, 91191 Gif sur Yvette, France (*correspondence: marie.carriere@cea.fr)
²CEA Saclay, SPAM, 91191 Gif sur Yvette, France

If released in the environment, nanoparticles and carbon nanotubes might have devastating effects on ecosystems. This work explores the relative toxicity of TiO₂, Al₂O₃ nanoparticles and multi-walled carbon nanotubes water suspensions towards two bacterial strains (*Cupriavidus metallidurans* CH34 and *Escherichia coli* MG1655) and three plants species (*Arabidopsis thaliana*; wheat, *Triticum aestivum* and the Indian mustard, *Brassica juncea*). A panel of nanoparticles have been used, the aim of this work being to evaluate the influence of physico-chemical characteristics, *i.e.* size, shape, crystal phase, purity, surface charge, on bacterial and plant response.

Firstly, nanoparticles were precisely characterized. Nanoparticle dispersion and stability was optimized by using biologically-compatible surfactants. Antibacterial properties and seed germination inhibition were assessed on the test organisms. Uptake of nanoparticles was observed by transmission electron microscopy.

In our conditions, nanoparticles display antimicrobial activity on *E. coli* MG1655, but not on *C. metallidurans* CH34. This activity does not depend on nanotubes length and purity, but depends on TiO_2 diameter and crystal phase. It is not linked to nanoparticle uptake, since some TiO_2 nanoparticles are internalized by *C. metallidurans* CH34, where they do not exhibit any antibacterial properties. Seed germination inhibition also varies with nanoparticles physico-chemical characteristics.

Taken together, these results suggest the need for improved understanding of nanoparticles behavior and lifecycle, both in the environment and towards living species, in order to guarantee their safe handling and disposal.