



## Interaction Cu - bearing aqueous solutions with CaCO<sub>3</sub> polymorphs: a Nanoscopic and Microscopic Study

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Sorption of metals on mineral surfaces plays an important role in controlling both the dispersion and accumulation of these pollutants as well as their geo- and bioavailability in near-surface environments. Among sedimentary rocks-forming minerals, calcium carbonate arises as potentially useful to uptake a broad spectrum of dissolved metals because of its abundance in nature and the high reactivity of its surfaces. Here, we present an investigation of the effectiveness of both calcite and aragonite as Cu-sequesters. This metal is considered to be a moderately hazardous substance. This study combines nanoscopic and microscopic observations of the phenomena occurring during the interaction of Cu – bearing aqueous solutions with calcite and aragonite fragments. Thus, we have carried out in situ Atomic Force Microscopy (AFM), batch type and silica gel experiments. All the experiments have been conducted at room temperature under atmospheric CO<sub>2</sub> pressure. The results obtained indicate that a strong interaction exists between solids and aqueous solutions, even when Cu concentrations were very low (0.05 – 2 mM). Thus, the dissolution of calcite {10-14} surfaces is strongly enhanced in the presence of Cu in comparison to dissolution in pure water. This is evidenced by the measurements carried out on the images obtained in the AFM experiments, which evidenced that the dissolution rate is several times faster in the presence of Cu than in pure water. Moreover, a direct relationship can be established between the concentration of Cu in the aqueous solution and the dissolution rate enhancement. In addition, a significant modification of the etch pits shapes is observed in the presence of Cu. Such modification consists in the progressive acquisition of a rounded morphology, leading to the lost of the original straight edges observed in pure water. Once dissolution starts, and after a certain induction time, three dimensional nuclei of a new phase are formed on the calcite substrate when low Cu – concentrations (< 1.0 mM) are used. These precipitates preferentially form at the edges of the steps, although can also be observed on the terraces. Such precipitates appear as islands that rapidly develop in height to reach several nm and are equally oriented, showing a clear epitaxial relationship with the substrate. The adhesion of these nuclei to the substrate is very weak. The formation of overgrowing islands on calcite surface can be described as the result of a co-precipitation process due to a fast change of the physicochemical properties in the interphase (release of carbonate and subsequent increase of pH and supersaturation with respect to Cu – solid phases).

Batch and silica gel experiments give complementary information and allow us to obtain data on the interaction phenomena after long periods (up to ~ 300 hours). In these types of experiments crystals were recovered from the solution or the gel after specific reaction periods and studied by means of SEM and EDS – analysis. The results obtained in both types of experiments confirm a strong interaction between both calcite and aragonite surfaces and Cu-bearing aqueous solutions. Such interaction is characterised by an intense and continuous dissolution of the substrate, which leads to the development of rough surfaces, and the formation of aggregates of spherulites unequally distributed on the substrate. The behaviour of aragonite and calcite surface shows significant differences. Thus, for identical interactions periods, whereas aragonite reacts very intensively, with precipitates covering wide areas of the fragments, in the case of calcite the precipitates form isolated patches on specific areas. Preliminary EDX analysis of these precipitates point to copper carbonate as a possible reaction product. Additional XRD analysis will shed light on the nature of the precipitate.