

# Using the replacement of calcium carbonate by hydroxyapatite in the presence of phosphate for cadmium capture from solution.

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Phosphate and cadmium water contamination caused by the overuse of fertilizers has become a concern in many areas throughout the last decades. Cadmium can be found in high concentrations in phosphate rocks which are used to synthesize fertilizers, resulting in high concentrations of cadmium in some fertilizers. These toxic elements concentrate in the soil and water and accumulate in the crops, entering the food chain and potentially leading to the contamination of some populations. Various minerals have been studied for cadmium capture from solution through mineralization and/or adsorption processes at mineral-fluid interfaces and both calcium carbonate and apatite have shown good uptake capacities toward this element. Furthermore, calcium carbonate minerals can be replaced pseudomorphically by apatite through a coupled dissolution-precipitation mechanism when immersed in a solution containing phosphate [1]. Hence, the combination of both previously mentioned reactions could be of use in water decontamination. Here, we report on the capture of cadmium from solution during the replacement of Carrara marble by hydroxyapatite [2]. Cubes of Carrara marble have been reacted in sealed hydrothermal reactors at 200°C in solutions containing various concentrations of phosphate and cadmium for times between 4 and 60 days. The samples were then sectioned and analysed by Scanning Electron Microscopy (SEM), BackScattered Electron (BSE) imaging, Electron Dispersive X-ray Spectroscopy (EDS) and Raman Spectroscopy. The nanoscale reaction at the sample surface has been observed with in-situ Atomic Force Microscopy (AFM) in fluid flow and static solutions on Carrara marble platelets and on the (10-14) surface of freshly cleaved calcite. The coupled dissolution-precipitation reaction observed and the capture of cadmium by the newly formed phase will be presented.

[1] Pedrosa, E.T., Putnis, C.V., and Putnis, A. (2016) The pseudomorphic replacement of marble by apatite: The role of fluid composition. *Chemical Geology*. 425 1–11.

[2] Wang, M., Wu, S., Guo, J., Zhang, X., Yang, Y., Chen, F., et al. (2019) Immobilization of cadmium by hydroxyapatite converted from microbial precipitated calcite. *Journal of Hazardous Materials*. 366 684–693.