Simulation of non-classical crystallization of carbonate minerals

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The crystallization mechanisms of carbonate minerals have long attracted significant interest and none more so than calcium carbonate. Ion pairs have long been known to exist in carbonate solutions [1], while the existence of a range of $CaCO_3{}^0{}_{(aq)}$ species of varying hydration was proposed [2]. Recently, the demonstration that these pre-nucleation species are actually stable has sparked considerable interest in the non-classical nucleation of carbonates [3,4]. How this relates to the observation of amorphous states, such as Polymer Induced Liquid Precursors (PILP) [5] and Liquid Amorphous Calcium Carbonate (LACC) remains an open to debate [6].

In the present work we have utilized molecular dynamics simulation, based on both reactive [7] and conventional atomistic force fields, to identify the nature of the stable pre-nucleation clusters as being rapidly varying hydrated supramolecular polymers labelled as Dynamically Ordered Liquid-Like Oxyanion Polymers (DOLLOP) [8]. These DOLLOPs consist primarily of 1, 2 and 3-coordinate calcium and carbonate ions, leading to linear or branched polymer chains. However, ions remain in equilibrium with the solution through rapid exchange. The evolution and lifetime of the DOLLOP species depends on the size of the cluster; once a critical size is reached the properties are found to alter while remaining distinct from ACC. A preliminary examination of the influence of the presence of species other than calcium, carbonate and bicarbonate on the behaviour of DOLLOP has also been carried out.

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U(VI)-organic phosphate complex formation studied by ESI-FTMS

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Introduction

Complexation studies using model molecules with P=O and P-OH functionalities are highly required to assess to which extent organic phosphorus, present in the humic fraction of natural organic matter as derivatives of phospholipids, phosphonic acids, phosphoric esters, is involved in the binding of uranyl ions by humic acids. Electrospray ionization-Fourier transform mass spectrometry (ESI-FTMS) was used to investigate the formation of uranyl complexes in native solutions containing phenylphosphonic acid (H_2L) or phenylphosphoric acid and U(VI) at trace concentration level (µmolar range). Positive identification of the species was achieved, thanks to the high resolving power, high mass accuracy and reliability in ion abundance of the linear ion trap/orbitrap hybrid mass spectrometer.

Results and conclusion

Two types of complexes of stoechiometry of 1:1 (UO_2HL^+) and 1:2 ($UO_2(HL)_2$) were identified in native solutions at pH 3 containing U and phenylphosphonic acid, and the stability constants were evaluated. The technique was also successfully applied to elucidate the interactions between U(VI) and phenylphosphoric acid in native solutions with pH values favouring the hydrolysis of the organic ligand. Evidence was given for the presence of U(VI)-phenylphosphate complexes and for the formation of uranyl complexes with the degradation by-products of the ligand, with the relative contributions of species varying with time.

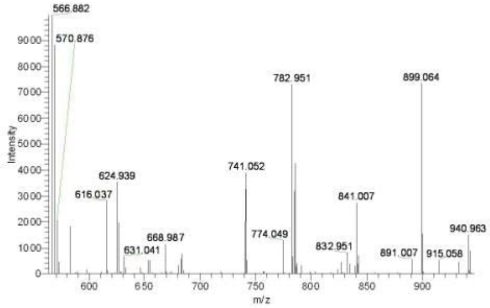

Figure 1: Negative ion mode ESI-FTMS spectrum showing presence of uranyl-phenylphosphonate complexes (detected as clusters formed with ClO_4^- electrolyte ions during ionization).

Studies of native solutions by means of ESI-FTMS has provided structural and quantitative information on the complexes formed between U(VI) and model molecules with P=O and P-OH functionalities. A complete speciation model was obtained for the uranyl - phenylphosphonic acid system, which is useful to model the binding of U by humic acids. The study was performed for trace level concentration of U, which is important for the applicability of the model to the speciation of uranyl in soil systems.