

ID: MSCA-19-Tielens01

Discipline: Chemistry

Title: Biomineralization - Comparison between Theory and Experiment

Abstract: One of the research topics of our group is the study of biomineralisation i.e. the formation of minerals produced by living organisms. In this frame, in vivo CaOx crystallization leads to the formation of kidney and urinary stones, constituting a serious health problem to mankind. Our group is especially interested in the study of the formation and characterization of these in vivo produced calcium oxalate minerals.

Calcium oxalate crystallization yields three main hydrates, i.e. thermodynamically favorable calcium oxalate monohydrate (COM), metastable calcium oxalate dihydrate (COD) and calcium oxalate trihydrate (COT). Monoclinic COM and tetragonal COD are the most commonly found in human stones, plants and fossils.

After an extensive investigation on CaOx kidney stones through FTIR, SEM and PND, our group recently started to investigate the calcium oxalate polymorphs using ab initio quantum chemical methods. Ab initio calculations based on periodic DFT (Density Functional Theory) enable to determine the crystal structure with high precision, and compare it with experimental X-ray based crystallographic and neutron diffraction methods, but also investigate the theoretically calculated vibrational frequencies of the bulk crystal. This information gives access to simulated IR spectra obtained on perfect (defect free crystals) with high accuracy. Note that the FTIR spectra of biological whewellite is not exactly the same than the one of synthetic whewellite. The shift in the bands can be due to the size of the crystal, the presence of structural defaults or other compounds. At this point it is of major importance to understand why the position of the absorption bands play a very important role in the chemical analysis of the kidney stone.

After the study of the bulk, the next step is the theoretical investigation of the different surfaces of the calcium oxalate polymorphs. Indeed, from the bulk crystal structures obtained through ab initio methods one can build for example the low index surfaces. Surface energy of the different surfaces can be calculated and the final crystal morphology predicted using the thermodynamic Wulff formalism for the construction of the crystals shape. Since the thermodynamic stability depends on the medium in which the surface is introduced, the calculation of the interaction of the calcium oxalate surface with water, urea, and other small molecules will give us the possibility to understand the change in crystal morphology of the final oxalate crystal in its natural medium. The final aim is the prediction of the shape of the kidney stone in its natural medium. On this topic it was shown recently that unusual morphological calcium oxalated dihydrate crystals were obtained in the presence of green tea extract containing catechin.

High resolution IR spectra will first help us to determine and/or confirm the crystal structure of the polymorphs. Second, the comparison of high resolution IR spectra of the pure calcium oxalate polymorphs as well as with real kidney stone samples with the theoretically obtained spectra might help us to understand and explain quantitatively the composition of an oxalate based kidney stone. And finally ATR measurements will help us to investigate adsorption properties at the molecular level, such as adsorption geometry and energies.

Concerning the investigation of the molecular adsorption properties, the molecular catechin will receive special attention because of their known effect on the kidney stone formation in particular their morphology and composition.

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