

Application for Molecular Imaging Corporation Endowment Scholarship

Personal Statement

I work with Prof. Peter Rez in the department of Physics. Our research applies Density Functional Theory (DFT) to bio-mineral systems like Calcite, Aragonite to study the mechanism of formation and stabilization of metastable phases such as amorphous calcium carbonate and high-magnesian calcites.

I am planning to defend my thesis in fall'2011. I strongly believe the scholarship will help me accelerating my research and complete the thesis on time as I can fully focus on my research. If time permits we are planning to investigate some interesting topics like, protein interaction on mineral surfaces, surface energy of Hydroxyapatite (bone mineral). The scholarship will definitely help in that direction.

After my graduation I would like to work in a field where I can use my expertise i.e. physics, mathematics, computation, programming etc. I am open to pursue a career both in academia or industry.

Below I summarize a brief description of the current research towards my PhD dissertation.

Models for Amorphous Calcium Carbonate based on Density Functional Calculations of Distortions Induced by Magnesium and Water in Calcite

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Introduction: The formation of minerals by organisms – Biomineralization – is a wide spread and fascinating phenomenon. Almost 70 different mineral types are known to be formed by organisms from all over the animal kingdom. These minerals adopt complex and genetically determined shapes, are often aligned to form arrays, and they fulfill many different functions. These include the mechanical functions of exo- and endo-skeletons, navigation in the earth's magnetic field, orientation in the gravity field, temporary storage, stiffening of soft tissues and much more. The most commonly used analytical instrumentation is scanning and transmission electron microscopy (especially in the hydrated mode), X-ray diffraction, infrared and Raman spectroscopy,^{1,2} a range of biochemical techniques, and most recently also molecular biological methods. Negating the century old belief, it was recently found that many of these species form amorphous calcium carbonate (ACC) precursor phases^{1,2} that subsequently transform into crystalline calcium carbonate. E.g. mapping of the Ca L edge by X-ray Photo Electron Emission spectro-Microscopy (X-PEEM) in the sea urchin larval-spicule^{3,4} and other studies of sea urchin spine² has shown that there might be more than one ACC phase. It is certainly possible that ACC might have up to 10 wt% Mg^{5,6} and small (less than 3 wt %) amounts of water. The structure of ACC, and the mechanisms by which it transforms to calcite are still unknown.

Purpose: To determine atomistic structure models that are consistent with diffraction and IR measurements of ACC phases and calculate free energies for transformation from ACC to the crystalline phase.

Methods: A calcite super-cell with 24 formula units was constructed by doubling the hexagonal cell along the **a** and **b** unit cell vector. Various configurations with 8 Mg atoms substituting for Ca, corresponding to 8 wt. %, were relaxed using the VASP plane wave pseudopotential code.

Distributions of inter-cation distance and carbonate group tilts were calculated. The relaxation was repeated with clusters of 3 to 5 water molecules (2.25-3.75 wt. %) and with random distributions of 4 water molecules inserted in the spaces between Ca atoms. The inter-cation distributions (i.e. Ca-Ca, Mg-Ca) and carbonate tilts were plotted. The total energies and the free energy were calculated using energies from either a range of configurations or from the expression for configurational entropy.

Results: When Mg is substituted for Ca, the carbonate groups were undistorted and there was a very narrow distribution of inter-cation distances, half width approximately 0.02 nm. The most noticeable effect was the tilt of the carbonate groups covering an 8° range. The insertion of water had even more dramatic effects. There were significant distortions in the cation sub-lattice in the vicinity of clusters and the carbonate groups were tilted over a range of 20° with 4 randomly placed water molecules and over a range of 40° near clusters with 5 water molecules. The total energy calculations indicated that random substitutions of Mg in Ca were favored over phase separation and that the entropic contribution was well described by the simple expression. It is possible that the large displacements of the oxygen atoms from the carbonate tilts would give an amorphous diffraction pattern since collectively they contribute more to X-ray scattering than the Ca ions.

Conclusions: The main effect of either plausible substitutions of Mg for Ca or insertion of less than 4 wt% water was tilting of the carbonate groups. There were significant local distortions of the Ca sub-lattice only when more than 3 water molecules were clustered together.

Recent Activities & future Plans: We presented our results in “International Conference on the Chemistry and Biology of Mineralized Tissues” (ICCBMT) in November’2010 at Carefree, Arizona. Currently we are involved in writing software for generating diffraction pattern of the input crystal structures which would enable us to compare our results with microscopy experiments. We plan to further extend the technique to Aragonite (a polymorph of CaCO₃). Also, as I mentioned earlier we want to investigate Hydroxyapatite because it is related to one of the open ended question so far – Why bone is made up of nano-crystals.

References:

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