

TLS 21A1 U90 – (White Light) Chemical Dynamics

- Photofragment Translational Spectroscopic
- Molecular Science, Chemistry, Gas phase, Photochemistry, Excited-state Reaction Dynamics

References

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New Insight into the Structure of Biogenic Amorphous Calcium Carbonate

X-ray absorption spectra recorded at ambient water vapor indicates that the structural transformation of hydrated amorphous calcium carbonate (ACC) to crystalline calcite is more involved and contains a heretofore overlooked step of nano-calcite formation.

Among six polymorphs of calcium carbonate (CaCO_3), amorphous calcium carbonate (ACC) is the least stable and transforms rapidly into a crystalline calcium carbonate polymorph such as calcite or aragonite. ACC constitutes a main ingredient in seashell creatures such as urchins, corals, mollusks etc., and is an important precursor phase of biogenic calcite. Researchers have been motivated by this so-called biomineralization in which living organisms, especially micro-organisms, can convert organic substances to inorganic derivatives, to design functional materials for multiple applications.

ACC in at least two distinct forms, *viz.*, types 1 and 2, relevant to the formation of biogenic calcite are postulated based on the study of the growth of sea-urchin larval spicules. ACC of type 1 has been unequivocally assigned to hydrated ACC, whereas the assignment of ACC of type 2 to anhydrous ACC is still under debate. During the spicule growth, the ACC is precipitated from mineral-rich sea water at the growth location and then dehydrates into the transient ACC of type 2 that transforms further into calcite, namely, $\text{ACC}\cdot\text{H}_2\text{O}$ (type 1) – ACC (type 2) – biogenic calcite. This path, although correctly describing the dehydration, provides no indication about the minute structural difference between ACC of these two types.

X-ray absorption spectra (XAS) recorded at the Ca L edge provide useful information about a change of the metal–ligand bonding environment, as experienced by the central Ca atoms during the course of a phase transformation of ACC from hydrated to crystalline form. This technique is hence powerful in addressing the structural transformation. Moreover,

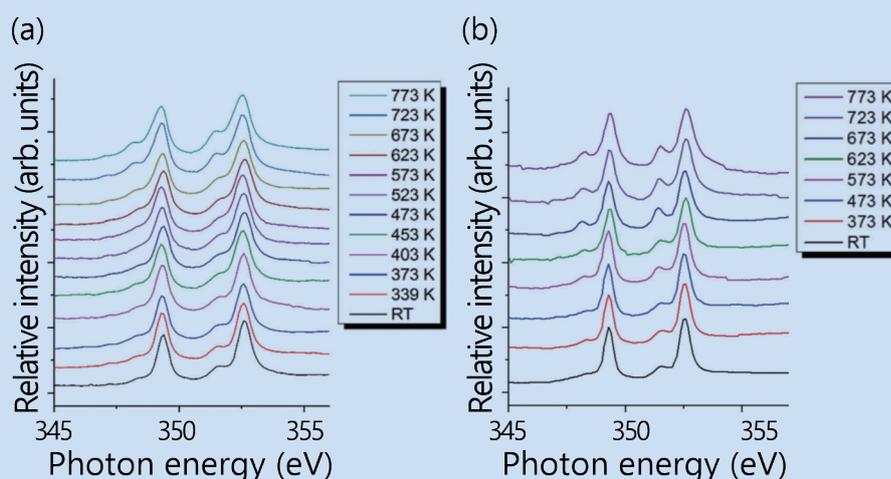


Fig. 1: Ca L edge X-ray absorption spectra of ACC acquired under ultrahigh vacuum (a), and under water vapor at pressure 0.4 mbar equivalent to 1.3% relative humidity (b). Two major features (L_3 and L_2) are separated by a spin-orbit interaction about 3.2 eV; each spin-orbit component is further split by crystal-field splitting (CFS) into two lines about 1.2 eV apart, yielding a smaller shoulder peak at the side of less photon energy. A careful analysis of the CFS parameters based on refined curve fitting provides revealing insight into the structural transformation of ACC. [Reproduced from Ref. 1]

the availability of an ambient pressure (up to 10 mbar) soft X-ray spectroscopy endstation at **TLS 24A1** added a new impetus to the research. Chun Chung Chan from National Taiwan University and his co-workers investigated the phase transformation from ACC to calcite in the presence of ambient water vapor using the Ca L-edge XAS technique *in situ*.¹

As shown in **Fig. 1(a)**, when the hydrated ACC sample was heated under ultrahigh vacuum (UHV) toward 773 K to remove water of hydration, Ca L edge XAS spectra underwent small changes. In contrast, Ca L edge spectra for the hydrated ACC heat-treated to 773 K in the presence of 0.4 mbar exhibited richer spectral changes, as shown in **Fig. 1(b)**. Careful fitting of the XAS put the CFS parameter changes on a firmer footing, as summarized in **Fig.**

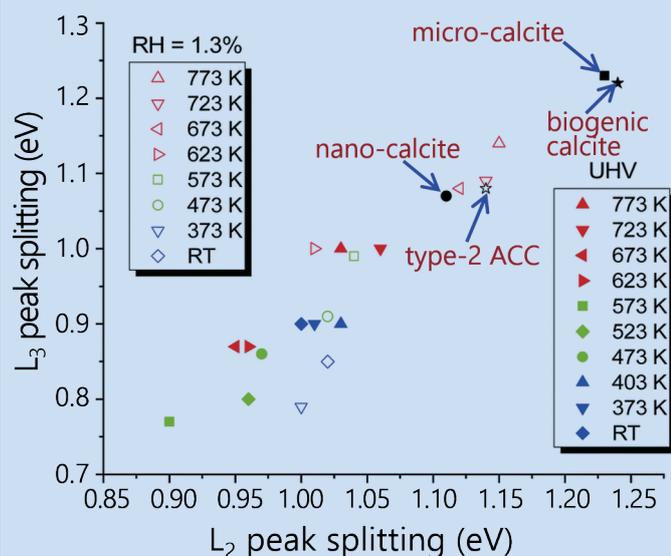


Fig. 2: CFS splittings of Ca L_2 and L_3 absorptions extracted from the spectra shown in **Fig. 1**. The filled symbols represent the data acquired under UHV (**Fig. 1(a)**); the open ones denote the data at RH 1.3% (**Fig. 1(b)**). The blue, green and red colors represent the temperature range in which the samples corresponded to hydrated ACC, anhydrous ACC and calcite in the TGA-DSC measurements. Also marked on the figure are the data corresponding to four other samples: type-2 ACC, biogenic calcite,² commercial nano-calcite, synthetic micro-calcite. [Reproduced from Ref. 1]

2. These data indicate that crystallization is promoted in the presence of water vapor; ACC of type 2 cannot be simply equated to anhydrous ACC and is in fact more structurally similar to commercial nano-calcite. A revised path of formation is depicted as follows: hydrated ACC \rightarrow disordered nano-calcite \rightarrow biogenic calcite. (Reported by Chia-Hsin Wang and Yao-Wen Yang)

This report features the work of Chun Chung Chan and his co-workers published in Chem. Commun. **55**, 6946 (2019).

TLS 24A1 BM – (WR-SGM) XPS, UPS

- UHV-XPS, AP-XPS, UPS, XAS-based on Electron Detection Modes
- Surface Science, Chemical State of the Material Surface, Catalytic Reaction

References

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Membranes Comprising Metal-Organic Frameworks for Gas Separation

Organic photovoltaics with improved carrier extraction efficiency can be an answer to cheap solar energy.

In recent years, metal-organic frameworks (MOF) composed of metal clusters and organic linkers have been considered to be emerging materials for membrane gas separations. One critical challenge to achieve high-performance MOF membranes for gas separation is the great flexibility of the MOF struc-

ture, which can lead to breathing effects and linker rotation. Both phenomena can be induced by gas molecules permeating through the MOF channels, and result in changes of the pore-limiting diameter (PLD) of the MOF. This PLD is the window size for molecular transport; it determines the cut-off of