# The role of pH and simple organic molecules in amorphous calcium carbonate (ACC) structure

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$CaCO_3$ crystallization controls a large part of the global carbon cycle through fluid-rock interactions, the formation of biominerals and also industrial processes. The initial steps of $CaCO_3$ crystallization are known to occur via the formation of amorphous calcium carbonate (ACC). The stability of ACC and its crystallization kinetics have been shown to be affected by temperature, pH and (in)organic additives [1]. However, little is known about the effect of these parameters on the structure of ACC at the atomic scale. Obtaining this information would help explain the different stabilities, morphologies, surface properties and formation mechanisms of $CaCO_3$ biominerals.

We carried out atomic pair distribution function (PDF) analysis using synchrotron radiation to determine the ACC structure formed under various conditions of pH and organic compounds. The results were combined with data from X-ray photoelectron spectroscopy, powder X-ray diffraction, infrared spectroscopy (FTIR) and electron microscopy.
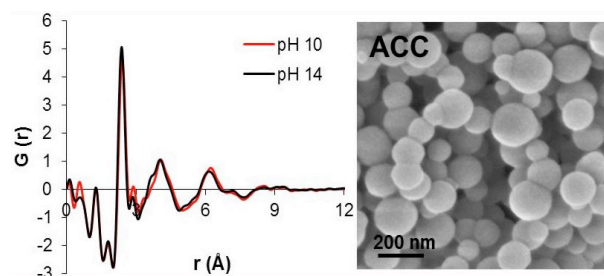
PDF results showed that the short range ordering for ACC (<15 Å) was notably affected by increasing the initial pH of the Na_2CO_3 solution from 10 to 14 (figure left). This difference could indicate an association of the hydroxyl ions with ACC at higher pH, possibly affecting the water content. Conversely, ACC structure remains virtually unaffected when it forms in the presence of several organic compounds (e.g., amino acids, polysaccharides). FTIR revealed small changes in the mode of vibration of carbonate bands and also in water content for certain organic compounds (e.g. citric acid) indicating considerable surface interaction between the organic material and ACC.

[1] Radha *et al*. (2012) *GCA* **90**, 83-95.

Spatial distribution of heavy metals in the urban soils of Chisinau city (Republic of Moldova)

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The study area comprised the entire area of Chisinau city and has an approximate dimension of 15/15 km^2. Soil samples were collected inside the network of 1km/1km^2, from the depth 0-20 cm. On the grid surface, 120 soil samples have been analyzed. The heavy metal content was analyzed using X-ray Fluorescence Spectrometry (EDXRF Epsilon 5). The analyses for physicochemical parameters were carried out with the following methods: particle size distribution (Kachinsky, 1958), organic matter content (Tiurin, 1965), $CaCO_3$ (Arinuskina, 1970) and the pH was determined using a Corning M-555 pH/Ion Meter. Assessment of anthropogenic contribution in urban soils has been determinate by means of enrichment factor (EF), geoaccumulation index (Igeo) and pollution index (PI) [1].

Correlation matrix for analyzed heavy metals and physicochemical parameters was performed to observe relationship between the analyzed parameters. Results presented the chemical association of heavy metals in the study area. The physicochemical proprieties of urban soils showed a significant positive correlation with each other and with Co, Ni and Cr whose origin is predominantly geogenic. The conclusions highlighted the organic matter has an influence an accumulation of heavy metals. As well is evident that the elements showed a good correlation with each other indicating a common source. The geochemical background range at urban scale has been defined by applying the iterative 2σ technique method. The background geometric mean values for heavy metals (mg/kg) are: Cr (64.2); Co (12.9); Ni (32.7); Cu (28.4); Zn (82.7); Pb (22.8) and As (9.4). The means concentration of analysed chemical elements in Republic of Moldova rocks are Cr (86 mg/kg); Co (11 mg/kg); Ni (38 mg/kg); Cu (22 mg/kg); Zn (83 mg/kg); Pb (17 mg/kg) and As (1.7 mg/kg) [2].

The calculated EF and Igeo results revealed the following order As > Pb > Zn > Cu > Ni > Cr > Co. The PI recorded content from heavily contaminated to uncominated in follwing order Zn > As > Cu > Pb > Co > Ni > Cr.

[1] C. Reimann and P. de Caritat (2005) J. Sci. Tot. Env. 337, 91-107 [2] V.P. Kiriliuk (2011) Collect. Scient. Art. 32-35