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Conference Abstract

Organomineralization of dolomite in hypersaline microbial mats from Qatar sabkhas visualized by TEM & STXM

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Abstract

Deep insight into the low-temperature mineralization mechanism of dolomite in sediments has remained elusive. This issue is popularly termed “The Dolomite Problem” due to its multifactorial nature. Dolomite has been observed to mineralize in the exopolymeric substances produced by microbial mat communities (Bontognali et al. 2013), where productivity is high. One working hypothesis suggests that degrading organic matter in hypersaline environments releases the necessary component ions, increasing saturation with respect to dolomite (DiLoreto et al. 2019, Dupraz et al. 2009, Petrash et al. 2017). Other models suggest a dissolution-reprecipitation reaction of calcite to dolomite (Rivers 2023). High-resolution micro-spectroscopy techniques (such as transmission electron microscopy, TEM; and scanning transmission X-ray microscopy, STXM) can be used to determine chemical changes in crystals nucleating in a matrix, however to date very little studies have focused on observing dolomite mineralization at the nano-scale. The present study investigates microbial mats collected from hypersaline salt flats in the Persian gulf at micro- to nano-meter scales using high-spatial and -energy resolution TEM (Thermo Scientific Talos 200X at the Canadian Centre for Electron Microscopy) and STXM (PolLux Beamline at the Swiss Light Source at Paul Scherrer Institut), specifically to see changes in carbonate mineralization due to interactions with organic matter. C, Ca and O elemental

maps of carbonate crystals were obtained with EDXS (energy-dispersive X-ray spectroscopy) in TEM. These crystals were also indexed by SAED (selected area electron diffraction in TEM). Fine spectral signatures (near-edge X-ray absorption fine structures, or NEXAFS) at the C K-edge (280-290 eV) and Ca $L_{2,3}$-edge (344-356 eV) in STXM were used to determine the chemical identity of carbonate minerals and surrounding organic matter of the microbial mats.

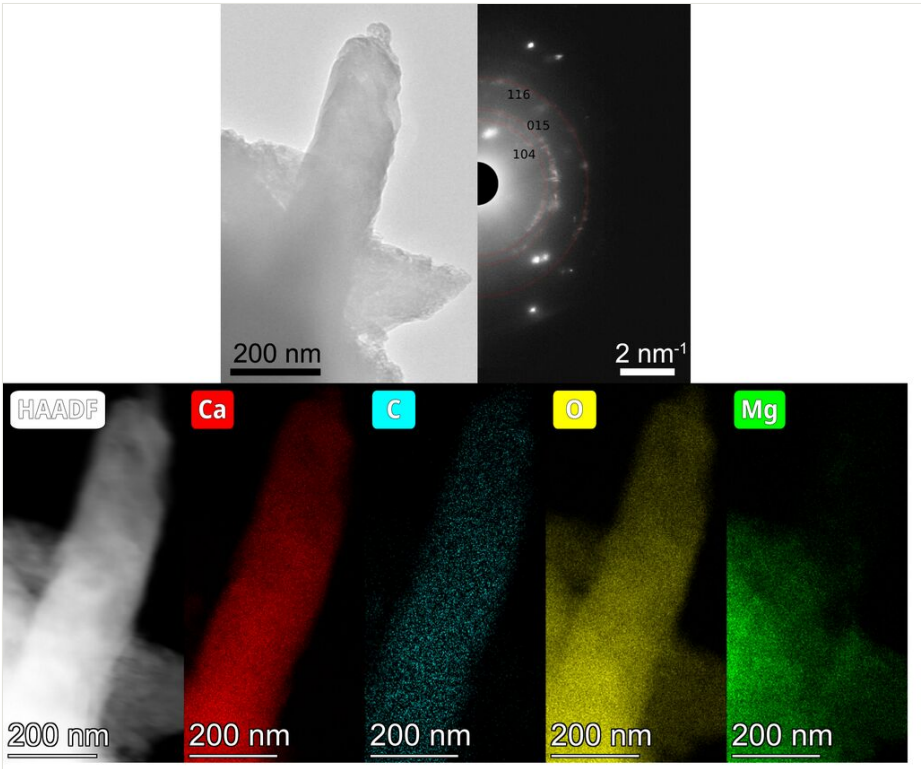

Figure 1. doi

Top: TEM micrograph and diffractogram of a polycrystalline dolomite particle in a microbial mat sample, showing characteristic dolomite crystal planar reflections. Bottom: The same particle scanned with EDXS showing atomic density of Ca, C, O and Mg.

The results of the study show that dolomite nucleates in close association with the organic matter of the mats, where degradation is highest (defined in our adjacent study as the increase in C:N ratio). In TEM, polycrystalline dolomite is seen mineralizing in the matrix of the microbial mat organic material (Fig. 1). In STXM, the identity of the carbonate mineral changes from calcite on the outside to dolomite on the inside of the microbial mat particle (Fig. 2). In addition, our microsensor observations of elevated H_2S concentrations, surface oxygenation from oxygenic phototrophy, high reduction potential, high organic carbon, high Mg:Ca ratio and high organic matter degradation (by C:N ratio) in each of the studied

microbial mats confirms that the ideal dolomite mineralization conditions according to models of the dolomite problem are present in each case.

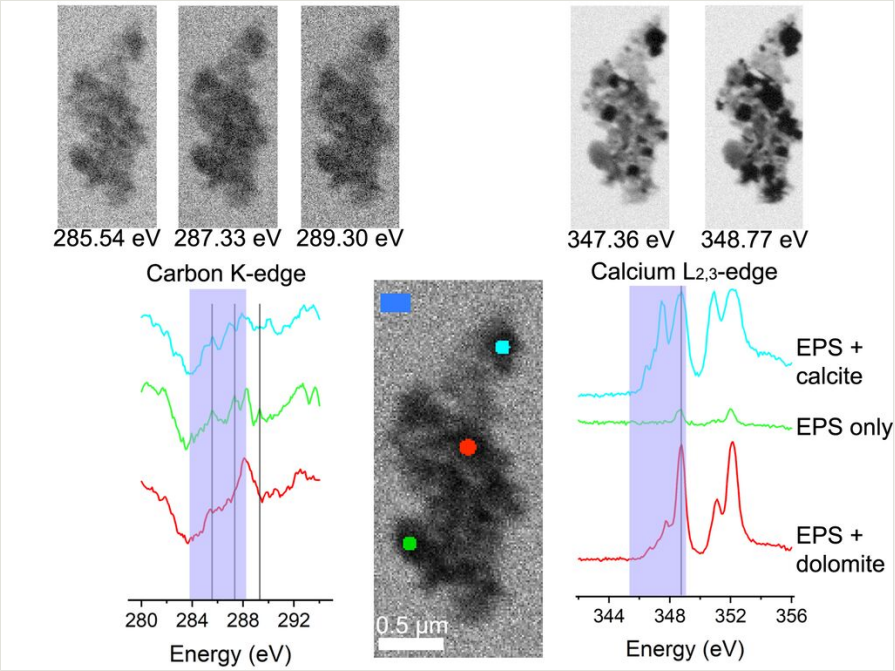

Figure 2. doi

STXM micrograph and spectra of three regions within a microbial mat particle. Each region has a unique signature within the NEXAFS (violet boxes in spectra) of the C and Ca X-ray absorption peaks. Region marked by green circle is primarily EPS. The spectra of the region at the blue circle expressed peaks typical for calcite identity, while red circle region has markedly dolomite identity in both C and Ca NEXAFS.

Keywords

Organomineralization, microbial mat, dolomite, carbonate, organic matter degradation, TEM, STXM

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Author contributions

Ivan Strakhov performed TEM & STXM analyses and collected field samples with Maria B. Dittrich.

Zach A. DiLoreto aided in sample preparation and instrumental analysis.

Maria B. Dittrich and Jassim A. Al-Khayat conceived and executed the study.

Conflicts of interest

The authors have declared that no competing interests exist.

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