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Structural properties of biologically controlled hydrozincite: An HRTEM and NMR spectroscopic study

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Abstract

The microscopic properties of biomineral hydrozincite [$Zn_5(CO_3)_2(OH)_6$] from Naracauli Creek (SW Sardinia) were investigated by using X-ray diffraction (XRD), nuclear magnetic resonance spectroscopy (NMR), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). Because the biomineral hydrozincite turned out to significantly deviate from the ideal structure of hydrozincite, synthetic and geologic hydrozincite samples were also investigated for comparison.

SEM imaging shows that biomineral hydrozincite is made of small platelet-shaped crystallites having a 20–50 nm long side at the shortest and other sides measuring hundreds of nanometers long. These are interlaced to form sheaths several micrometers long. HRTEM analysis of the biomineral samples shows an imperfectly oriented aggregation of the nanocrystals that is discussed in terms of mesocrystals. Transmission electron microscopy (TEM) and XRD analysis indicate a progressive decrease in the size of the particles in the biomineral compared to the synthetic and geologic hydrozincite samples, with coherent diffraction domains in the biomineral hydrozincite that are smaller by 30–50% than in the other samples investigated in this study. ^{13}C magic angle spinning (MAS) and cross polarization magic angle spinning (CPMAS) NMR spectra show more than one peak for all the investigated samples, despite the fact that carbon atoms have a unique crystallographic position in the hydrozincite structure. The additional peaks can reflect the presence of lattice defects typical of nanocrystals as indicated by the HRTEM images, where high concentration of lattice defects, such as grain boundaries and stacking modes, can be observed both in the biomineral and in the synthetic samples. Further additional peaks in the NMR spectra of biomineral samples are attributed to organic molecules, relicts of the biomineralization process, in agreement with the filaments observed in SEM images of biomineral samples.

Keywords: Biomineralization, hydrous carbonates, hydrozincite, nanocrystals, lattice defects