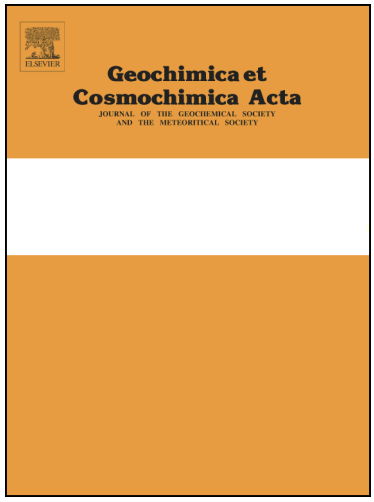

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Daniela Medas, Giovanni De Giudici, Francesca Podda, Carlo Meneghini, Pierfranco Lattanzi

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Apparent energy of hydrated biomineral surface and apparent solubility constant: an investigation of hydrozincite.

Daniela Medas[a], Giovanni De Giudici[a]*, Francesca Podda[a], Carlo Meneghini[b], Pierfranco Lattanzi[a].

[a]Department of Chemical and Geological Sciences, University of Cagliari, 09127 Cagliari, Italy

[b]Physics Department, University of Roma Tre, 00146 Rome, Italy

*Corresponding author. Tel.: +39 070 675 7720; fax: +39 070 675 2308.
Email address: gbgiudic@unica.it

Abstract

The apparent solubility (K_s^{app}) of hydrozincite [$Zn_5(CO_3)_2(OH)_6$] was measured in samples of different nature, including natural abiotic ("geologic"), synthetic (abiotic), and natural biominerals. A systematic variation is recorded from $\log K_s^{app}$ = 6.2 ± 0.1 in geologic sample, $\log K_s^{app}$ between 7.0 ± 0.2 and 7.5 ± 0.2 in synthetic analogues, and $\log K_s^{app}$ between 8.8 ± 0.2 and 9.1 ± 0.2 in biomineral samples. Samples were thoroughly characterized by using SEM, TEM, synchrotron radiation X-rays powder diffraction (SR-XRPD), and Zn K-edge X-rays absorption spectroscopy (EXAFS). Refining SR-XRPD data, it was found a significant increase (up to 10%) in the cell volume of synthetic and biologic hydrozincites with respect to geologic samples. EXAFS analysis indicates small, but significant differences in the interatomic distances between samples of different nature. Previous studies had shown that crystal size is in the nanometer range for all samples, but decreases going from geologic to synthetic to biomineral samples. Combining these data with structural data obtained in this study, the effects on solubility of particle size and of cell volume increase were calculated by classical thermodynamic equations. The surface energy of hydrated hydrozincite increases by at least one order of magnitude from geologic to biologic sample. The effect of cell volume variation on apparent solubility is deemed negligible, being of the same order of magnitude of the error in solubility measurements.

Thus, the different solubility of investigated samples is most likely ascribed to crystal size and surface energy. The measured apparent solubility constants were used to build predominance diagrams; specifically for biominerals, only the use of apparent K_s^{app} derived in this study predicts fairly well the seasonal variation of hydrozincite biomineralization at Naracauli, Sardinia.