American Mineralogist, Volume 97, pages 513–523, 2012

Zaccagnaite-3*R*, a new Zn-Al hydrotalcite polytype from El Soplao cave (Cantabria, Spain)

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Abstract

We have recently discovered significant amounts of zaccagnaite, a natural Zn-Al-CO_3 hydrotalcite in the El Soplao cave (north Spain). The El Soplao zaccagnaite is speleothemic, i.e., formed in the cave, and therefore it represents a new cave mineral. The origin of El Soplao zaccagnaite is related to the diagenesis of Zn- and Al-rich ferromanganese speleo-stromatolites, where it occurs as a pore-filling cement that likely precipitated at low temperature (≤ ~11 °C). In some stromatolite layers, the abundance of zaccagnaite crystals is large enough to enable their physical separation. This has allowed us to obtain its X-ray powder-diffraction pattern, infrared spectrum, and differential thermal/thermogravimetric profiles.

The cell parameters of the El Soplao zaccagnaite, refined from X-ray powder diffraction data are: a = 3.06616(1) and c = 22.6164(1) Å [$\alpha = \beta = 90°$, $\gamma = 120°$; V = 184.139(1) Å^3; Z = 3], consistent with a new trigonal polytype of zaccagnaite: zaccagnaite-3*R*. Besides, the El Soplao zaccagnaite shows some features previously unknown in natural hydrotalcites, such as octahedral-like morphologies and fluorescence zoning. Electron microprobe analyses revealed that the El Soplao zaccagnaite-3*R* has an unusual chemistry for natural hydrotalcites, as it is significantly more rich in Al (Zn^{2+}/Al^{3+} = 1.6) than the hexagonal (2*H*) polytype (Zn^{2+}/Al^{3+} = 2.0). The simplified chemical formula deduced from electron microprobe analysis is $(Zn_{0.6}Al_{0.4})(OH)_2(CO_3)_{0.2}\cdot 0.5H_2O$, where C and water were calculated by stoichiometry. The carbon content calculated by stoichiometry (2.2 wt%) is in good agreement with that measured with the electron microprobe on gold-coated samples (2.5 wt%). The presence of interlayer water and CO_3 groups was confirmed by thermogravimetric analysis coupled to mass spectroscopy, and by the analysis of the infrared spectrum.

Keywords: Zaccagnaite, hydrotalcite, speleothem, El Soplao, Cantabria