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

RAFAEL P. LOZANO,1,* CARLOS ROSSI,2 ÁNGEL LA IGLESIA,3 AND EMILIO MATESANZ4

1Museo Geominero, Instituto Geológico y Minero de España, Ríos Rosas 23, Madrid 28003, Spain
2Departamento de Petrología y Geoquímica, Universidad Complutense, Madrid 28040, Spain
3Instituto de Geología Económica (CSIC-UCM), Universidad Complutense, Madrid 28040, Spain
4CAI de Difracción de Rayos X, Universidad Complutense, Madrid 28040, Spain

ABSTRACT

We have recently discovered significant amounts of zaccagnaite, a natural Zn-Al-CO3 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) Å and c = 22.6164(1) Å [α = β = 90°, γ = 120°; V = 184.139(1) Å³; Z = 3], consistent with a new trigonal polytype of zaccagnaite: zaccagnaite-3R. 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-3R has an unusual chemistry for natural hydrotalcites, as it is significantly more rich in Al (Zn2+/Al3+ = 1.6) than the hexagonal (2H) polytype (Zn2+/Al3+ = 2.0). The simplified chemical formula deduced from electron microprobe analysis is (Zn9.4Al0.4)(OH)0.4(CO3)0.25H2O, 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 CO3 groups was confirmed by thermogravimetric analysis coupled to mass spectroscopy, and by the infrared analysis of the infrared spectrum.

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

INTRODUCTION

Hydrotalcites, also called anionic clays, represent a relatively rare and not very well-known group of clay minerals. However, their study is becoming increasingly important for practical purposes: their synthetic counterparts, known as layered double hydroxides, have important industrial applications, especially in catalysis (Othman et al. 2009), water treatment (Douglas et al. 2010), and human health (del Hoyo 2007).

Hydrotalcites are formed by positively charged, octahedral brucite-like layers alternating with layers of charge-balancing anions such as carbonate, sulfate, and others. The general formula of the octahedral layers is [M2+nM′2−2n(OH)2]2−n, where M2+ can be Ca2+, Mg2+, Zn2+, etc. and M′2+ can be Al3+, Fe3+, Ni2+, etc. Typically, x ranges between 0.17 and 0.33 (Frost et al. 2005). However, in some species this range is larger, especially in Al-hydrotalcites where x may vary between 0.14 and 0.80 (Tumiati et al. 2008). The hydrotalcite minerals usually show two polytypic modifications, trigonal (3R-6R) and hexagonal (1H-2H-3H) (Bookin and Drits 1993), with monoclinic (1M) polytypes being rare (Martini 1980a; Krikovich and Orlandi 2001).

Zaccagnaite is a Zn-Al-CO3 natural hydrotalcite discovered in Carrara, Italy (Merlino and Orlandi 2001). The Carrara zaccagnaite corresponds to the 2H polytype (space group: P63/mmc) and has a M2+:M′2+ (i.e., Zn2+:Al3+) ratio of 2:1 (x = 0.33) (Merlino and Orlandi 2001). The original description of zaccagnaite-2H was based on scarce, micrometric-sized crystals, and its X-ray diffraction pattern was obtained with a Gandolfi camera (Merlino and Orlandi 2001). Thus, important data such as the X-ray powder-diffraction pattern, thermogravimetry, or the infrared spectrum of zaccagnaite are still unknown. The presence of zaccagnaite has been also reported in St. Constantine, Greece (Witzke and Raade 2000), but no further structural or chemical data were provided.

We have recently discovered significant amounts of zaccagnaite in the El Soplao cave (north Spain). The El Soplao zaccagnaite is a speleothem, i.e., formed in a 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. The zaccagnaite-hosting stromatolites were induced by Mn-oxidizing microbes in a karstic cave stream passage, and represent the first reported occurrence of stromatolites formed in the deep interior of a cave (Rossi et al. 2010). In some stromato-