Micro- and nano-characterization of Zn-clays in nonsulfide supergene ores of southern Peru

NICOLA MONDILLO1*, FERNANDO NIETO2 AND GIUSEPPINA BALASSONE1

ABSTRACT

Zn-clays are associated with several supergene nonsulfide ore deposits worldwide, where they are either the prevailing economic minerals, or minor components of the weathering-derived mineral assemblage. A TEM-HRTEM study on Zn-clays from nonsulfide ore deposits of Accha and Yanque (Peru) was carried out, to properly determine the chemistry and complex texture of these clays, not fully defined in other previous works on these (but also on other similar) deposits. The Zn-clays occurring at Accha and Yanque are constituted by a mixture of sauconite and Zn-bearing beidellite. The chemical composition of sauconite varies in a range of values, without any chemical gap, around the average composition:

$$\text{Ca}_{0.15}\text{K}_{0.05}(\text{Zn}_{2.1}\text{Mg}_{0.2}\text{Al}_{0.4}\text{Fe}_{0.15}\text{Mn}_{0.02})(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}.$$ 

Beidellites present an average composition close to stoichiometry with the addition of Zn:

$$\text{Ca}_{0.05}\text{K}_{0.15}(\text{Al}_{1.6}\text{Zn}_{0.25}\text{Mg}_{0.1}\text{Fe}_{0.15})(\text{Si}_{3.6}\text{Al}_{0.4})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}.$$ 

The chemical composition of both sauconite and beidellite is consistent through the samples, with sauconite affected by a wider variation in composition than beidellite. The textures of Zn-bearing smectites clearly indicate that a part of these clays grew on precursory mica-like phyllosilicates, whereas another part was derived from a direct precipitation from solutions. The occurrence of a paragenesis with trioctahedral and dioctahedral smectites demonstrates that, as observed in other environments, also in a Zn-bearing system both smectite types are stable. As proved for other analogous trioctahedral-dioctahedral smectite systems (e.g., saponite-beidellite), also in the sauconite-beidellite system a chemical compositional gap exists within the series. The texture indicating a direct precipitation from solutions does not exclude that a smectite amount could be genetically related to hydrothermal fluids, even if several other characteristics (e.g., the paragenetical association with Fe-hydroxides typical of gossans) confirm the supergene origin for the bulk of the deposit.

Keywords: Sauconite, Zn-beidellite, nonsulfide zinc ore deposits, TEM-HRTEM

INTRODUCTION

Zn-bearing clay minerals occur in several nonsulfide zinc ores (Hitzman et al. 2003; Large 2001). Zinc nonsulfide deposits are concentrations of economic Zn-oxidized minerals, mainly represented by smithsonite, hydrozincite, hemimorphite, sauconite, and willemite, markedly different from sphalerite ores, typically exploited for zinc (Hitzman et al. 2003; Large 2001). Nonsulfide ores are genetically related to supergene or hypogene processes: the supergene deposits primarily form from the oxidation of sulfide-bearing concentrations in a weathering regime, whereas the hypogene deposits form after mineral precipitation from hydrothermal or metamorphic fluids (Hitzman et al. 2003).

Zn-clays are worldwide associated with several supergene nonsulfide ores, where they are either the prevailing economic minerals or minor components of the weathering-derived mineral assemblage (Balassone et al. 2008; Boland et al. 2003; Boni et al. 2009; Borg et al. 2003; Coppola et al. 2008; Emselle et al. 2005; Frondel 1972; Ahn 2010; Kärner 2006). The best example is the world-class Skorpion mineralization (Namibia)—the largest supergene nonsulfide zinc deposit in the world (original reserves of 24.6 Mt ore at 10.6% Zn)—where sauconite, the trioctahedral Zn-bearing smectite (Newman and Brown 1987; Ross 1946), predominates over the other Zn-oxidized minerals (Borg et al. 2003; Kärner 2006).

Herein we present the first combined TEM-AEM and HRTEM crystal-chemical characterization of natural Zn-clay minerals, associated with two nonsulfide ore deposits in Peru (Yanque and Accha). In fact, TEM is pivotal for the characterization of crystalline materials at nano- and sub-nanometer scale, such as clays (Nieto and Livi 2013), allowing for a wide range of imaging and diffraction techniques. When coupled with AEM analytical tools,