

Research Paper

Zn-clay minerals in the Skorpion Zn nonsulfide deposit (Namibia): Identification and genetic clues revealed by HRTEM and AEM study



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ABSTRACT

Zn-clays worldwide occur in various supergene nonsulfide (Zn-Pb) ores, where they can be the prevailing economic minerals or represent minor concentrations in the mineral assemblage. The world-class Zn smectite-rich Skorpion mine (Namibia) is considered one of the most important supergene nonsulfide zinc deposits in the world. At Skorpion, the trioctahedral Zn-bearing smectite predominates over the other Zn-oxidized minerals. This work is focused on microtextural observation and chemical analyses on the clay nano-particles of the supergene nonsulfide ores from Skorpion, carried out for the first time using TEM/HRTEM and AEM investigations. This approach helped to better understand the formation mechanism of the Skorpion Zn-clays and related phases down to the nanoscale. The microtextures of the Skorpion Zn-clays suggest they formed from fluids, meteoric and/or hydrothermal in nature, in two textural contexts: smectites can grow on previously deposited phyllosilicates (mica) (CCP texture), and/or directly nucleate from Zn-rich solutions (PCA texture). The Skorpion sauconite is chemically characterized by a greater homogeneity if compared with natural sauconites from other occurrences; it is quite stoichiometric, with Ca as interlayer cation and limited quantities of Mg and Fe, with an average composition of $\text{Ca}_{0.14}\text{K}_{0.02}(\text{Zn}_{2.7}\text{Mg}_{0.09}\text{Al}_{0.14}\text{Fe}_{0.10})(\text{Si}_{3.4}\text{Al}_{0.6})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Contrary to Peru nonsulfide ores (Accha and Yanque), at the micro- and nanoscale the occurrence of Zn-beidellite at Skorpion is very subordinated. Chlorite and baileychlorite have been also detected. Detrital micas are commonly the template for epitaxial sauconite growth. Typical supergene processes at ambient temperatures should be considered for the genesis of the Skorpion sauconite-bearing deposit, with some local contribution of low-T hydrothermal fluids. The micro- and nano-features of the Skorpion mineral assemblage confirm the complex mineralogical nature of the smectite-rich nonsulfide (micro)systems, with remarkable implications for mineralogical evaluation and processing.

1. Introduction

Zn-clays occur in various supergene nonsulfide ores worldwide. In these ores, mainly deriving from the weathering of primary sulfide concentrations, the Zn-clays can be the prevailing economic minerals, or represent minor concentrations in the mineral assemblage (Arfè et al. 2017; Boland et al., 1992; Balassone et al. 2008; Boni et al., 2009a, b; Boni and Mondillo 2015; Borg et al. 2003; Buatier et al. 2016; Choulet et al. 2016; Coppola et al. 2008; Emselle et al. 2005; Frondel 1972; Hye In Ahn 2010; Kärner 2006; Mondillo et al. 2014, 2015). Zn-clay minerals, formed in slightly acidic to neutral conditions, are also commonly found in contaminated soils at mining and smelting sites (i.e. Manceau et al. 2000; Juillot et al. 2003).

Sauconite (Ross 1946; Newman and Brown 1987), which is one of the most common clay minerals in nonsulfide deposits, is a trioctahedral

saponite-like smectite with Zn in octahedral coordination. Experimental studies on its synthesis and stability (i.e. Higashi et al. 2002; Kloprogge et al. 1999; Pascua et al. 2010; Petit et al. 2008) demonstrated that this Zn-smectite can precipitate from solutions of silicic acid, variously mixed with Zn-compounds (Zn-chloride, Zn-oxide, or Zn-hydroxide) and Na- and Al-compounds, at a pH interval of 6–12 and temperatures ranging between 20 and 200 °C.

Among the other Zn-“clay” phases found in nonsulfide ore deposits, we should mention fraipontite (a serpentine-like Zn-clay mineral, Fransolet and Bourguignon 1975) and baileychlorite (a Zn-chlorite, Rule and Radke 1988). Recently Kaufhold et al. (2015) characterized Zn-smectites from the Silver Coin Mine (USA), while Choulet et al. (2016) and Buatier et al. (2016) have described Zn-clays consisting of interstratified fraipontite/smectite (fraipontite-prevailing), closely associated to willemite in several nonsulfide Zn deposits in the Moroccan

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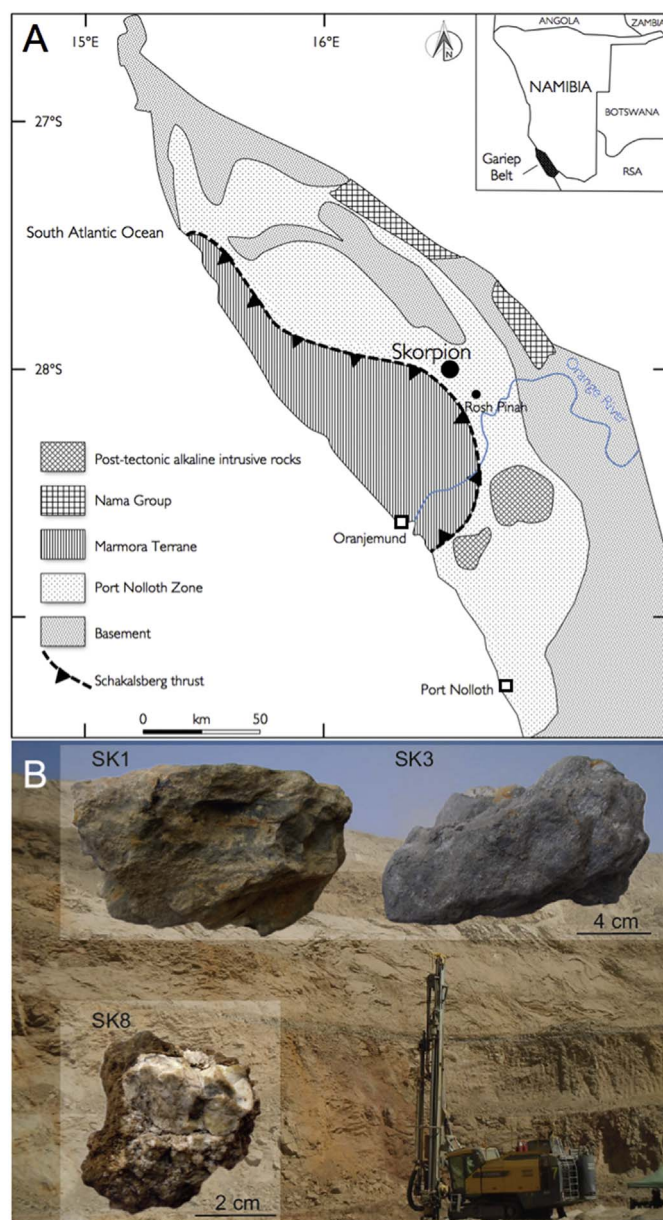


Fig. 1. (A) Schematic geological map of southern Namibia (modified after Borg et al. 2003 and references therein), with location of the Skorpion deposit in the Gariep belt area. (B) The Skorpion open pit at the date of the sampling (2014), with the samples investigated in this study (see text).

High Atlas, which formed by direct precipitation of meteoric and/or hydrothermal fluids. With the increasing quest of mineral resources (and the rising Zn price), mining industries must afford the complex issues related to the extraction and processing of low grade and/or finely disseminated ores. Clay minerals, including Zn-clays that have been detected in several deposits, are not only a resource (the Skorpion case) but can affect the industrial treatment to a various extent (Choulet et al. 2016 and references therein). Hence, their detailed mineralogical study, as well as the investigation of their crystallization and post-crystallization processes can provide crucial geological information, particularly useful from the perspective of industrial and economic evaluations.

One of the best examples of a Zn smectite-rich supergene orebody is the world-class Skorpion mine (Namibia, Vedanta Ltd.) (consisting of 21.4 Mt. of ore reserves, grading 10.6% Zn at the beginning of the exploitation). The Skorpion base metals deposit is considered to have been an equivalent of the Rosh Pinah massive sulfides concentration

that was subjected to weathering processes, started after the end of the pan-African tectonic phase (Kärner 2006). The pan-African phase was followed by uplift and denudation, and concluded with the onset of a strong arid period that had its first maximum in Oligocene (Borg et al. 2003; Kärner 2006; Arfè et al. 2017). At Skorpion, the trioctahedral Zn-bearing smectite (sauconite) predominates over the other Zn-oxidized minerals (Borg et al. 2003; Kärner 2006).

The chemical and structural features of sauconite from Skorpion have never been examined in detail before; hence, the present research is focused on microtextural observation and chemical analyses on the clay fraction of the supergene nonsulfide ores, carried out for the first time using TEM-STEM and HRTM investigations. This approach by means of transmission electron microscopy, coupled with high-resolution observations, integrated with other mineralogical and geochemical analyses, allows the investigation of clay textures down to the nanoscale, and consequently a better understanding of their genesis.

2. Geology of the Skorpion zinc deposit area

The Skorpion zinc deposit (Fig. 1A) is hosted by metamorphosed volcano-sedimentary rocks of the Port Nolloth Zone (PNZ), within the late Proterozoic Gariep Belt (Borg et al. 2003). This belt is subdivided into an eastern para-autochthonous zone, the PNZ, and a western allochthonous zone, the Marmora Terrane. The Gariep Belt is regarded as the southern extension of the Damara orogenic front of central and northern Namibia (Davies and Coward 1982; Reid et al. 1991; Stanistreet et al. 1991; Gresse 1994; Frimmel 2000; Jasper et al. 2000; Frimmel et al. 2002). The rocks of the PNZ contain stratiform Zn-Pb-Cu-Ag-($\pm$ Ba)-sulfide mineralization in sedimentary and felsic meta-volcanic rocks. The best examples are the Rosh Pinah Pb-Zn (Page and Watson 1976; van Vuuren, 1986; Alchin and Moore 2005) and the Skorpion Zn-(Cu) deposits (Borg et al. 2003; Kärner 2006), which were attributed to either the Volcanic-hosted Massive Sulfides (VHMS) or Sedimentary-hosted Massive Sulfides (SHMS) types. The mineral concentrations were formed in an extensional environment during a phase of increased volcanogenic-hydrothermal activity between 740 and 754 Ma (Borg and Armstrong 2002). The deformation of the ore-bearing units (due to the pan-African tectonic phase) took place during continental collision that produced the closure of the Adamastor oceanic basin 545 million years ago (Alchin and Moore 2005). The sedimentary and bimodal volcanic rocks hosting the mineralization have been strongly folded, faulted and overprinted by a lower amphibolite facies metamorphism (Frimmel et al. 1995). Exhaustive summaries about the geomorphological evolution of southern Africa and Namibia, including the Gariep Belt, which took place after the pan-African tectonic phase (King 1951), have been presented by Partridge and Maud (1987) and Partridge (1998). The maximum peneplanation, coupled with intense lateritic weathering, causing also part of the Skorpion supergene mineralization, was reached between Late Cretaceous and Oligocene. During Late Cretaceous-Eocene, a denudation event eroded a 3 km-thick section of southern Africa and Namibia, reaching several hundred km inland and producing the so-called “African Erosion Surface” (Gallagher and Brown 1999). This surface was then rejuvenated and intersected by younger erosion planes, related to discrete uplifts that took place in early Miocene and Pliocene (Partridge and Maud 1987).

The Skorpion deposit cuts across the deeply weathered Rosh Pinah Formation metavolcanics and the Hilda Subgroup carbonate rocks. The Zn-oxidized minerals are mainly hosted by arkoses and subordinately by quartz-sericite schists of volcanic origin. Other rock types associated with the orebody include limestones and mafic volcanics (Borg et al. 2003; Kärner 2006). The Skorpion nonsulfide orebody is covered by a transported barren regolith, consisting of a surficial layer of wind-blown sand above a massive calcrete layer, covering a sequence of alluvial interlayered gravels and conglomerates. Great part of the oxidized orebody is considered to have been formed in a paleo-channel,

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