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Mineralogical characterization of the Hakkari nonsulfide Zn(Pb) deposit (Turkey): The benefits of QEMSCAN®

L. Santoro [a],*, M. Boni [a], G.K. Rollinson [b], N. Mondillo [a], P. Balassone [a], A.M. Clegg [c]

[a] *Dipartimento Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli Federico II, Via Mezzocannone 8, 80134 Napoli, Italy*
[b] *Camborne School of Mines (CSM), University of Exeter, Penryn Campus, Penryn TR10 9EF, United Kingdom*
[c] *Ebullio Resources & Mining A.S., Turkey*

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ABSTRACT

The development of relatively simple and low-cost processing technologies such as solvent-extraction, AmmLeach®, leach/solvent extraction/electrowinning and pyrometallurgy, combined with the increase in Zn prices, resulted in an increase in the study and exploration of nonsulfide Zn(Pb) deposits. The Hakkari deposit is an example of a supergene nonsulfide Zn(Pb) deposit located in Southeast Turkey, hosted in brecciated Jurassic limestone. The ore concentrations, mainly consisting of oxidized Zn minerals (smithsonite and hemimorphite) were examined in this study using QEMSCAN®. The formulation of a Species Identification File (SIP) was necessary to discriminate the mineral species. QEMSCAN® analysis allowed detailed mineralogical characterization of several Hakkari drill core samples, building on, and adding to previous studies of the deposit. In particular, the modal mineralogy for the ore and gangue minerals, and mineral association and spatial distribution data of the economic minerals provided information for the advanced exploration phase of the deposit, which could influence the feasibility study and ore processing options. The results show that smithsonite is the main ore mineral, occurring in two generations: one (FeO and PbO bearing) replaces sphalerite and host carbonates, and another (CaO-bearing) is concretionary in cavities. Hemimorphite occurs in cavities or replaces smithsonite in veinlets. Fe-(hydr)oxides can be enriched in Zn, Pb, As and SiO_2. Mn–Fe-(hydr)oxides ($Pb \gg Zn$ enriched) are rare. Remnant sulfides have also been detected. The QEMSCAN® study has confirmed the main mineral phases found in previous studies, but identified other phases not previously detected (e.g. minerals in trace amounts such as sauconite), being also able to distinguish and quantify impure phases (e.g. Zn-dolomite, Cd-calcite), and identify amorphous phases [pyrite/Fe-(hydr)oxides/jarosite mix] that XRD found challenging. Not detecting the detrimental minerals/elements may result in processing problems, penalties at the smelter, poor metal quality, and environmental damage. Thus the use of QEMSCAN® technology on this type of deposit is beneficial for both exploration and potential processing, provided that careful attention is paid to the complex mineralogy and limitation of the analysis technique.

1. Introduction

The development of relatively simple and low-cost processing technologies such as solvent-extraction, AmmLeach® (MetaLeach: http://www.metaleach.com), leach/solvent extraction/ electrowinning (Cole and Sole, 2002; ZincOx Annual Report, 2007; De Wet and Singleton, 2008) and pyrometallurgy (Clay and Schoonraad, 1976; Habashi, 2002), combined with the time-bound increase in Zn prices (the highest prices were recorded in 2006 and again between 2009 and the beginning of 2011), led to increased attention in the study and exploration of nonsulfide Zn(Pb) deposits. Skorpion in Namibia (Borg et al., 2003), Angouran in Iran (Boni et al., 2007), Vazante in Brazil (Monteiro et al., 2006; Slezak et al., 2014), Accha in Peru (Boni et al., 2009), Sierra Mojada in Mexico (Hye In Ahn, 2010), Hakkari in Turkey (Santoro et al., 2013), Jabali in Yemen (Mondillo et al., 2011, 2014) are only a few examples of this renewed commercial interest. As well as many other metal projects, nonsulfide zinc ores have also recently been put on hold, due to the current difficult global economic situation. However, research on the mineralogy and metallurgy is still active for most of them, ready to be applied to each individual deposit, should the economic conditions improve.

Nonsulfide ores have been subdivided in *Hypogene* and *Supergene* deposits (Large, 2001; Hitzman et al., 2003; Boni, 2005). The *Supergene* Nonsulfide Zn(Pb) deposits, which are so

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* Corresponding author. Tel.: +39 3299362092.
E-mail address: licia.santoro@unina.it (L. Santoro).

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far the most economically sought, derive from the weathering of pre-existing Zn sulfide mineralization, which might also contain Pb (commonly Mississippi Valley Type [MVT], SEDEX, and Carbonate Replacement deposits). The metals (Fe, Zn, Pb), leached out from the sulfides, are transported in solution by meteoric waters through pore spaces and fractures of the host rock (Hitzman et al., 2003). Rocks with buffering capacity (commonly limestone, dolomite or sandstone) may trigger the precipitation of secondary minerals from the metal-rich solutions. Although the oxidization of primary Zn sulfides is a relatively common process, economic nonsulfide deposits are less common, owing to the unique conditions necessary to form and preserve these supergene concentrations. Moreover, the occurrence of favorable trap sites and a good hydrological circulation are fundamental in order to avoid the loss of zinc-rich fluids or a further leaching of metals from the newly deposited secondary minerals. The economic value of nonsulfide zinc ores is strictly dependent not only on the geological knowledge of each deposit, but mainly on the specific characteristics of the mineralogical association and on the interaction of zinc/lead-and gangue minerals during processing (chemical and physical) of the ore.

The typical mineral associations of a supergene Zn(Pb) deposit can be either very simple or extremely complex, depending on the mineralogy of the primary ores. Most deposits of this type consist of mixed blends of mineral phases: carbonates (mainly smithsonite [$ZnCO_3$], hydrozincite [$Zn_5(CO_3)_2(OH)_6$] and cerussite [$PbCO_3$]); silicates (hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$] and sauconite [$(Na_{0.3}Zn_3(Si,Al)_4O_{10}(OH)_2 \cdot 4(H_2O))$]), commonly associated with several Mn/Fe (hydr)oxides (goethite, hematite, coronadite) generally containing variable amounts of base metals. Zinc can also be hosted in phyllosilicates such as chlorite-like clays (Blot et al., 1995) and in kaolinite/illite (Mondillo et al., 2014). Minor Zn-sulfates and phosphates also occur.

The Hakkari deposit, subject of this paper, is an example of the above-mentioned supergene nonsulfide ores. The current study, which follows previously published papers (Grodner, 2010; Santoro et al., 2013), shows the results of the mineralogical characterization of several Hakkari drill core samples, via QEMSCAN® technology. With few exceptions (experiments by mining companies) QEMSCAN® analyses have seldom been used for Zn-nonsulfide ore characterization (Rollinson et al., 2011). The method is a fully automatized micro-analytical system, generally used for sulfide ore studies because of its ability to output detailed information useful for metallurgical applications. In the last decade QEMSCAN® has also been largely used for the characterization of many other ore deposit types, e.g. bauxites (Boni et al., 2013), Ni–Fe laterite deposits (Andersen et al., 2009; Anderson et al., 2014), gold deposits (Goodall et al., 2005; Goodall and Scales, 2007), rare earth elements (Smythe et al., 2013), and of course for characterization of oil and gas reservoirs (Dillinger et al., 2014). QEMSCAN® uses electron beam technology combined with high resolution BSE (Backscattered Electron) imaging, as well as Energy Dispersive Spectrometers (EDS) to analyze minerals. Analyzed phases are classified as specific minerals according to their BSE and chemical composition compared to that within a user developed, reference mineral library known as SIP file (Species Identification Protocol). During QEMSCAN® analysis, a detailed database of statistically representative mineralogical information is built up, which is later interrogated by the user. The major benefit of QEMSCAN® is that it provides both spatially resolved data (textures, inclusions, relationships between minerals) and modal mineralogy data, that is able to detect both major and trace minerals. For comparison, although optical microscopy can provide images, it cannot provide the detail and speed of quantitative analysis that QEMSCAN® can. Furthermore, XRD cannot provide spatially resolved data, nor can it provide analysis of trace minerals (below XRD detection), or non-crystalline phases. Overall, QEMSCAN® is a well-established method, because it offers a better solution for precise, repeatable and large datasets at high detail, and has been used in the mining sector for mineral processing applications since the early 1980s.

This paper focuses on two main results that could be obtained with this technology: the *"quantitative modal mineralogy"* of the mineral species occurring in the deposit, and the *"average mineral association"* of the economic minerals that were detected. Both types of information are crucial in the advanced exploration phase of deposits, when the accuracy of the ore characterization can influence the results of the feasibility study. The "*average mineral association*" of the most abundant economic minerals, which is a parameter indicating the adjacency of these phases with other minerals (i.e. the amount% they are in contact), may be extremely useful in order to establish an effective mineral processing route. This is especially true for Zn–Pb nonsulfide ores, because there might be metals or compounds adjacent to the nonsulfide minerals, which are detrimental to the electrowinning/electrorefining process (Hitzman et al., 2003; Boni, 2005).

2. The Hakkari deposit

2.1. Location and geological setting

The Hakkari Zinc Project is located in the southeastern region of Turkey, approximately 10 km west of the town of Hakkari, within a broad 20 km wide and 100 km long east–west belt extending from 60 km east of Hakkari and Şirnak Provincial boundary (Fig. 1). The Hakkari deposit, currently owned by Ebullio Resources & Mining A.S. Turkey ("Ebullio"), contains mostly supergene nonsulfide Zn ≫ Pb ores. The mineralization occurs as a series of small deposits (approximately 2.5 Mt each), in a narrow band of Mesozoic, structurally deformed sedimentary rocks. The ore is mainly hosted in locally dolomitized and brecciated limestone, interbedded with minor clastic layers (Grodner, 2010). The nonsulfide ore (with estimated compliant resources so far of at least 10 Mt @ 15% Zn) mainly consists of economic amounts of smithsonite and hemimorphite (Santoro et al., 2013). But the potential is believed to be several hundreds of millions of tonnes across the >100 km available strike length of the deposits. Some 50,000 tonnes at 26.7% Zn, 6% Pb and 300 g/t Ag have been mined and shipped as DSO (direct shippable ores) to smelters in Thailand. Preliminary metallurgical test-work on several stockpiles samples first indicated that the Hakkari nonsulfide Zn concentrations were amenable to direct acid leaching. Further test-works proved that it was possible to upgrade the 7.5% Zn feed to 22% Zn by gravitational concentration (MSA report, 2013). However, the current owner, Ebullio, plans to use ammonia leaching to process the Hakkari nonsulfide ores. Test-work indicates that AmmLeach® has at Pilot Plant scale extracted zinc economically from the Hakkari carbonate ores, where physical separation is largely ineffective (Clegg et al., 2014). A proprietary solvent extraction step is also used to avoid ammonia carry-over into the electrolytic metals recovery. There is potential for significant cost savings, as AmmLeach® does not use acid, which is a great advantage for carbonate-hosted deposits. It also uses conventional equipment at atmospheric pressures and temperatures with the electro winning identical to conventional acid circuits (MetaLeach, http://www.metaleach.com/).

2.2. Previous mineralogical studies

Optical Microscopy (OM), cathodoluminescence (CL), energy dispersive spectroscopy by Scanning Electron Microscopy (SEM-EDS), wavelength dispersive spectroscopy (WDS) and chemical analyses (ICP-MS) had been previously carried out (Santoro et al.,