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Calculating the deportment of a fine-grained and compositionally complex Sn skarn with a modified approach for automated mineralogy

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ABSTRACT

A method was developed to determine the modal mineralogy and Sn deportment of a fine-grained skarn ore. Mineral Liberation Analysis (MLA) and electron probe microanalysis were applied to crushed and uncrushed samples for mineralogical characterization. A comprehensive list of mineral references consisting of energy-dispersive X-ray spectra and information about elemental concentration and density was created. This *conventional approach* did not achieve reliable results in the characterization of some of the analyzed ore types. Small grain sizes and the variety of Sn-bearing minerals required adding mineral references with manually mixed EDX-spectra, calculated elemental concentrations and densities. Comparison of MLA data using this *modified approach* with bulk geochemistry and X-ray powder diffraction illustrates very good agreement for all ore-types characterized. The new approach may well be considered for other mineralogically complex ores containing a multitude of ore minerals and complex deportment of metals.

1. Introduction

Tin (symbol Sn from Latin: *stannum*) is a post-transition metal in the carbon group of the periodic table with the atomic number 50. The primary source of commercial Sn is the mineral cassiterite (SnO_2). Motivated by the predicted rise of global consumption and a lack of global exploration success, Sn deposits that have previously been regarded as uneconomic are currently attracting considerable interest (Deutsche Rohstoffagentur, 2014). Sn-bearing skarns provide typical examples of major geological Sn resources (Ray and Webster, 1997) that have thus far remained unexploited due to their difficult beneficiation characteristics.

Skarn is a calc-silicate-dominated rock type that typically forms at the expense of carbonate rocks during regional or contact metamorphism including intense metasomatic alteration by magmatic hydrothermal fluids (Meinert et al., 2005). Some skarn deposits contain economically significant concentrations of metals, including Pb, Zn, Fe, W and Sn. One unusual attribute of Sn skarns is the abundance of Sn in the crystal lattice of typically Sn-poor rock-forming minerals, such as garnet and titanite. Cassiterite abounds in most (e.g. Chen et al., 1992; Mitrofanov and Stolyarov, 1982; Ray et al., 2000), but not all Sn skarn deposits (e.g. Alderton and Jackson, 1978), and may form during late retrograde skarn alteration or a post-genetic greisen-style alteration (Meinert et al., 2005). Major reviews for the genesis of Sn skarn deposits include Einaudi et al. (1981), Kwak (1987), Newberry (1998), and Meinert et al. (2005).

The Hämmerlein deposit in the Western Erzgebirge, Germany, is an example of a stratabound, compositionally complex and polymetallic ore deposit that comprises two parts: a shale-hosted unit and a Sn-In-Zn skarn (Schuppan and Hiller, 2012). This paper deals with the skarn portion of the Hämmerlein deposit only. Currently known resources amount to 21400 t contained Sn at a cut-off grade of 0.2 wt.% (Treliver Minerals, 2015). Together with two similar orebodies that occur in the immediate vicinity of the Hämmerlein deposit (Dreiberg and Zweibach), and the shale-hosted part of the Hämmerlein deposit, the total inferred Sn resource amounts to 101,500 t, with 2149 t of indium and 200,200 t of zinc (Treliver Minerals, 2015).

Soon after discovery of the deposit in the late 1970 s, 49100 t of ore from the Hämmerlein skarn orebody were mined and processed experimentally in a pilot plant, but the concentrate grade of Sn remained below expectations. Schuppan and Hiller (2012) name three reasons for poor recovery:

(1) Complex mineralogy, often fine-grained
(2) Variety of Sn-bearing minerals (cassiterite and various Sn-bearing silicates)
(3) Variability in grain sizes of valuable minerals (grain sizes of cassiterite range from $>$ 500 μm to $<$ 1 μm; Fig. 1)

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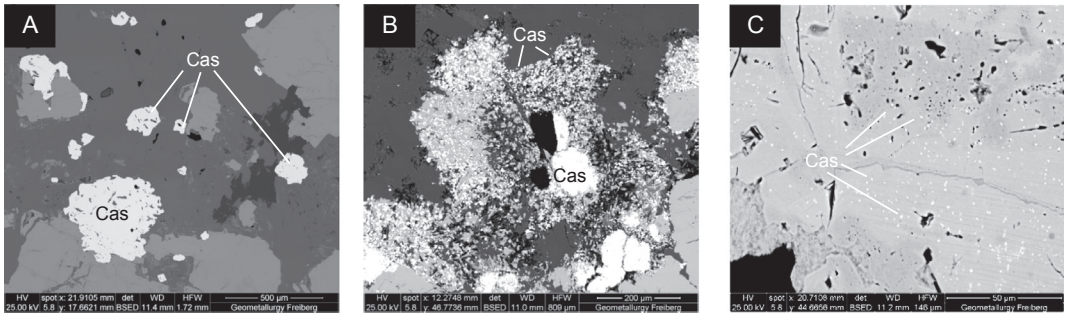

Fig. 1. Variability of grain sizes of cassiterite in three different samples from the Hämmerlein deposit. (A) Up to 500 µm; (B) between 5 and 100 µm; (C) Smaller 1 µm.

According to Pawlek (1983), only concentrates with at least 60 wt. % Sn meet commercial requirements. This renders cassiterite (with a stoichiometric content of 78.8 wt.% Sn) the only Sn ore mineral. Consequently, it is insufficient to assess the inherent value of Sn skarn ores such as the Hämmerlein deposit by determining the grade of Sn by chemical assay (e.g. by X-ray fluorescence spectrometry, XRF) only. Rather than the Sn determined by whole rock chemical assay, the Sn contained in cassiterite should be the determinant used. Agterdenbos and Vlogtman (1972) and Kinealy and Eadington (1983) tried to solve this issue by using a sequence of fluxes that selectivley dissolve stanniferrous silicates and eventually cassiterite. However, this method did not achieve a high accuracy and offers limited information about mineralogy and the deportment of Sn-bearing minerals.

Within the context of a publically-funded research project dedicated to the beneficiation of complex Sn ores of the Erzgebirge, it was decided to develop a novel approach for the quantification of the recoverable Sn content of the Hämmerlein orebody by automated mineralogy. Previous studies have illustrated the potential of this approach to calculate the deportment of resources like e.g. gold (Goodall, 2008; Goodall and Butcher, 2012), rare earth elements (Smythe et al., 2013), or indium (Frenzel et al., 2015).

The conventional approach of automated mineralogy (Fandrich et al., 2007; Gu, 2003) is expanded in this study to include minerals with Sn contents close to the detection limit for energy-dispersive X-ray spectroscopy (EDX). Furthermore, the distinction of fine-grained minerals and compositionally zoned minerals is improved. Data from electron probe microanalysis (EPMA) complement automated mineralogy information. X-ray powder diffraction (XRD) and bulk geochemical analysis are used for data verification and quality control.

2. Methods

This section deals with the applied methods from sample preparation to analytical techniques. The part on automated mineralogy is extended with a paragraph on the link between mineral grain sizes and the fraction of recorded mixed spectra in a sample. A graphic example illustrates the differences between the conventional and our modified approach.

2.1. Sampling and sample preparation

Twenty-five samples from six different lithological units of the +590 m level of the Hämmerlein orebody were examined following detailed stope mapping. The six lithological units were classified according to suggestions from the Robertson (1999) for naming metamorphic rocks (Table 1). Hand specimens (Ø = 10–20 cm) were collected from the six lithological units. Suitable parts of the hand specimens were chosen for the preparation of 15 polished thin sections with a thickness of 30 µm. The petrography and mineralogy of these samples were studied in detail (Kästner, 2016). Six of the 15 samples were selected for more detailed investigation. These samples were comminuted sequentially by hammer (< 3 cm fragment size), jaw crusher (< 0.5 cm fragment size) and impact mill (approximately 95% passing 400 µm). The samples were homogenized and split into several subsamples. 30 mm grain mounts were prepared by mixing 5 g aliquots with the same volume of graphite and epoxy resin. While the epoxy cures, a gravity-related settlement effect may be expected due to the discrepancy in densities between cassiterite (ρ = 6.99) and silicates minerals, such as quartz (ρ = 2.65). To prevent bias caused by settling, the grain mounts were cut into vertical slices (B-sections) and prepared as suggested by Heinig et al. (2015). For XRD analysis, 2.5 cm^3 aliquots were milled in a McCrone micronizing mill (Retsch) to a grain size of approximately 4 µm.

2.2. Analytical tools

Samples were characterized using a number of analytical methods, including scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS)-based image analysis (*aka* automated mineralogy), electron probe microanalysis (EPMA), X-ray powder diffraction (XRD), and bulk geochemical analysis. XRD and bulk geochemical analysis was used to reconcile data regarding modal mineral content and bulk geochemistry calculated from automated mineralogy data. Similar approaches for the characterization of complex ores have previously been used by e.g. Smythe et al. (2013), Parian et al. (2015) and Osbahr et al. (2015).

2.2.1. Automated mineralogy

Automated mineralogy (Fandrich et al., 2007; Gu, 2003) supplies quantitative mineralogical and textural data that is extracted offline from particle maps. It identifies minerals and calculates information such as modal mineralogy, bulk geochemistry, and mineral associations of the analyzed sample as a function of the density, mineral chemistry and the measured surface (Hoal et al., 2009). A choice of platforms are available on the market, including TIMA (Tescan), IncaMineral (Oxford Instruments), MinSCAN (Zeiss), QEMSCAN or MLA (both from FEI). For this study, analyses were performed on a Mineral Liberation Analyzer (MLA) equipped with an FEI Quanta 650 F field emission SEM (FE-SEM) with two Bruker Quantax X-Flash 5030 energy-dispersive X-ray (EDX) detectors.

MLA grain-based X-ray mapping (GXMAP) method was selected as the measurement mode for the analyzed ore. The discrimination of the minerals by their greyscale (BSE mode), with a closely spaced grid of X-ray points (X-ray mapping) ensures that minerals are reliably identified (Fandrich et al., 2007). Data processing was done using the software package MLA Suite 3.1.4.686 including the tools *MLA Image Processing*, *MLA Mineral Reference Editor* and *MLA Dataview*. SEM and MLA operating conditions are listed in Table 1.

The identification of minerals detected during data acquisition by MLA requires the compilation of a mineral reference list. The approach to compile this reference list was significantly modified for this study. Therefore, the conventional approach – as well as the modifications – are described in detail below.

The modification to the well-established conventional approach to