A FLUID INCLUSION AND STABLE ISOTOPE STUDY OF SECONDARY OXIDATION MINERALS FROM THE TSUMEB CU-PB-ZN DEPOSIT, NAMIBIA

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Introduction

The Tsumeb Pb-Zn-Cu(-Ag-As-Ge-Cd-V) deposit is hosted by a pipe-like karstic structure filled with feldspathic sandstones and carbonate breccias in folded dolostones of the Neoproterozoic Otavi Group at the northern edge of the Damara Belt in NE Namibia (Lombaard et al., 1986). Primary sulfide mineralization consists mainly of galena, tennantite, sphalerite, bornite, enargite, pyrite, and various Cu sulfides forming carbonate replacements and breccia in-fills. The minor gangue minerals are dominated by dolomite, calcite, and quartz. The primary epigenetic sulfide ores were deposited from saline hydrothermal fluids expelled during the Pan-African orogeny probably from internal zones of the Damara Belt (Chetty, Frimmel, 2000). However, a significant part of the original sulfide ore bodies has been oxidized. A first supergene sulfide oxidation zone extends to a depth of about 350 m below the surface. Secondary oxide minerals compose ~50% of the mined ore in the first oxidation zone (Lombaard et al., 1986). At a depth of about 800 m below the surface, a second oxidation zone appears and reaches discontinuously to the deepest explored levels of the mine (~1700 m below the surface). The overall extent of sulfide oxidation in this second oxidation zone is less than in the first oxide zone. The deep-reaching sulfide oxidation can be related to a downward movement of oxygen-rich surface waters along fractures, e.g., the North Break Fracture Zone, and a complex karst system within the dolomitic host rocks. This specific geological situation and almost hundred years of continuous mining has made Tsumeb one of the world's most famous mineral localities with more than 250 different mineral species and exceptionally beautiful, crystallized specimens. The majority of the rare, sometimes unique minerals at Tsumeb come from oxidized ores that are generally dominated by smithsonite, cerussite, malachite, azurite, duftite, mottramite, anglesite, willemite, dioptase, wulfenite, and mimetite. We describe here for the first time fluid inclusions in some secondary Pb-bearing oxidation minerals and present preliminary microthermometric measurements, as well as stable oxygen and carbon isotope data of various supergene base-metal carbonates, to determine the conditions during sulfide oxidation at Tsumeb.

Fluid Inclusions

Fluid inclusions have been found in wulfenite, cerussite and anglesite. Primary fluid inclusions occur in growth zones of yellowish tabular wulfenite ($PbMoO_4$) crystals from the second oxidation zone. The fluid inclusions range in size from few micrometers to 10 millimeter in the largest dimension and have usually highly irregular shapes. They consist at room temperature of two fluid phases (liquid+vapor) or more rarely of a single liquid phase. The degree of fill in two-phase inclusions within growth zones is very consistent at ~0.98. Smaller inclusions in such growth zones are often monophase, probably due to failure of bubble nucleation. Microthermometric measurements have been obtained on fragments of two thin transparent and unpolished natural wulfenite crystals. Very low heating rates were applied (<<0.1°C per minute) using a LINKHAM THMSG 600 stage. All two-phase fluid inclusions of both samples homogenize into the liquid phase in a very narrow temperature range between 48.5 and 50°C (n=10). Pressure corrections are small for the studied samples (~6°C). The temperatures of wulfenite crystallization are determined at ~55°C. The vapor bubbles, however, did not renucleate in these inclusions during cooling or even after storing the sample for a week in a freezer at ~ -15°C. Thus, homogenization measurements could not be repeated.

Primary, up to 10 millimeter large fluid inclusions have also been detected in several clear cerussite ($PbCO_3$) crystals. Two specimens contain abundant two-phase (liquid + vapor) inclusions with a consistent and high degree of fill (~0.98) similar to wulfenite and very characteristic negative crystal shapes. Few inclusions with a lower and more variable degree of fill are crossed by fractures and probably have leaked. Very rarely tubular secondary monophase inclusions have been observed along healed fractures. Another sample contains highly irregular primary, exclusively monophase liquid inclusions. We have not yet obtained microthermometric data on the two-phase fluid inclusions in cerussite as the host crystals too large and thick for the sample chamber of the heating stage and preparation of conventional doubly polished thick sections may cause homogenization or fracturing of the large fluid inclusions. We plan to determine homogenization measurements of fluid inclusions in these up to 10 centimeter large cerussite crystals using a thermally controlled water bath and a stereomicroscope.

A 5 cm large and 8 millimeter thick fragment of a zoned tabular anglesite ($PbSO_4$) crystal from level 28 (890 m below the surface, second oxidation zone) contains only pseudosecondary monophase liquid inclusions. A colorless, but inclusion-rich (clay minerals?) core is cut by early pseudosecondary fluid inclusion trails that end at the border to the outer, yellowish inclusion-free rim. Other late pseudosecondary fluid inclusion trails end close to the outer crystal faces. Both generations of pseudosecondary fluid inclusions often display negative crystal shapes, necking-down features and are up to one millimeter in the longest dimension.

Carbon and oxygen isotopes

Preliminary stable carbon ($^{13}C/^{12}C$) and oxygen ($^{18}O/^{16}O$) isotope data have been obtained for smithsonite, cerussite, azurite and malachite. The isotope compositions are expressed as delta values in permil relative to V-PDB and V-SMOW, respectively. The carbon isotope values range from -8.6 to -4.6 permil for smithsonite (n=11), from -20.0 to -7.7 permil (n= 15) for cerussite, from -10.9 to -1.6 permil (n=4) for azurite and from -12.5 to -7.9 permil (n=6) for malachite. The wide range of carbon isotope values in oxidation minerals indicate variable contributions of at least two isotopically distinct sources of carbon. The isotopically heavy carbon is mainly derived from dissolution of dolomite host rocks or gangue minerals related to primary sulfide mineralization (Chetty, Frimmel, 2000) by acids generated during sulfide oxidation and/or less likely from atmospheric carbon dioxide. Reduced organic matter from overlying soils or even bacterial action during oxidation provided the ^{13}C-depleted carbon in the oxidized fluid and consequently in the secondary base-metal carbonates.

In contrast to carbon, oxygen isotope values show relatively limited variability for each mineral (smithsonite: 19.9 to 24.2 permil; cerussite: 11.3 to 15.9 permil; azurite: 24.0 to 25.5 permil; malachite: 22.1 to 23.8 permil). This indicates that both the temperatures during formation of each carbonate mineral and the isotope composition of the oxidation waters did not change much. Assuming that the oxygen isotope composition of the oxidation water is identical to that of present-day mine waters at Tsumeb (-10 permil; Ch. Külss, pers. comm.), we can calculate temperatures of secondary mineral formation using the fractionation equations provided by Melchiorre et al. (1999, 2000, 2001) and Zheng (1999). The calculated oxygen isotope temperatures range from ~30 to 50°C for both smithsonite and cerussite. Slightly lower temperatures of 20 to 30°C are calculated for the basic copper carbonates azurite and malachite. It is noteworthy that smithsonite and cerussite occur generally early in the paragenetic sequence relative to azurite and malachite (Keller, 1984), although some of our analyzed cerussites crystallized on or together with azurite and malachite. The maximum formation temperatures of Pb and Zn carbonates obtained from oxygen isotope data is identical to homogenization temperatures of fluid inclusions in wulfenite, another early mineral in the paragenesis, and is also consistent with the presence of two-phase fluid inclusions in cerussite. Further detailed studies are necessary to decide whether the observed temperature differences in the base-metal carbonates at Tsumeb are real and related to either cooling or geothermal gradients or possibly related to errors in some of the assumptions involved in oxygen isotope thermometry.

Conclusions

The preliminary data of our study show that useful geothermometric information can be obtained from both fluid inclusions and stable isotope compositions of secondary oxide zone minerals at Tsumeb. Microthermometric measurements in combination with stable isotope studies of inclusion fluids and host minerals can potentially be used to calibrate new oxygen isotope thermometers.

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