1 Introduction

1.1 Non-sulphide Zinc Deposits Worldwide

With the development of solvent-extraction (SX) and electro-winning (EW) processes, there has been a renewed economic interest for non-sulphide zinc deposits, also called 'zinc oxide deposits' throughout the world (e.g. Large 2001, Boni & Large 2003, Borg et al. 2003, Hitzman et al. 2003).

The commercial exploitation of "zinc oxides" deposits has rapidly become an important source of metallic zinc. Within the foreseeable future the annual production of zinc from oxide ores could reach about 11 % of the global zinc metal production (Fig. 1). The attraction of these deposits includes the scale economy, as individual projects mostly exceed 1.000.000 tons zinc metal (Fig. 2), and the projected low processing costs for the production of zinc metal or high-grade zinc oxide on site (Large 2001).

The majority of the non-sulphide zinc deposits have formed mainly by the oxidation of zinc sulphide deposits in a near surface environment. Besides these supergene deposits there are a few hypogene non-sulphide zinc deposits known, which are characterised by a hydrothermal origin. Fig. 3 shows the location of the most important supergene and hypogene non-sulphide zinc deposits worldwide.

![Fig. 1: The proportion of global zinc metal from non-sulphide and sulphide ores, Zn [Mt]. Data from BGR and several internet pages (2002).](image1)

![Fig. 2: Tonnes of zinc metal in non-sulphide zinc projects. Data from several internet pages, 2002.](image2)
Tonnages of non-sulphide zinc deposits range from less than 1 Mt to more than 200 Mt with grades of 7 % to more than 40 % Zn (Fig. 4). Deposits of this size include Skorpion (Namibia), Mae Sod (Thailand), Lan Ping (China), Angouran (Iran), Mehdi Abad (Iran), Shaimerdan (Kazakhstan), Jabali (Yemen), Sierra Mojada (Mexico) and Franklin/Sterling Hill (USA). In addition, there are a number of other mines producing relatively small tonnages of non-sulphide zinc ores in Vietnam (Cho Dien), Turkey, China, Morocco and Egypt. For completeness, one should add to the total the high tonnages recovered in formerly exploited districts, like SW Sardinia, Belgium and Ireland, as well as in the areas where the non-sulphide zinc concentrations are not considered a resource, like in Upper Silesia (Poland) (Boni & Large 2003).
1.2 Purpose and Scope of this Study

The study commenced in July 2000. At that time the genesis of the non-sulphide Skorpion deposit was controversially discussed. Two opposing main genetic models existed envisaging as either supergene oxidised primary Zn-sulphides or hypogene primary Zn-non-sulphides. Corrans et al. (1993) assumed a supergene origin for the non-sulphide ores, however, without carrying out any further detailed investigations of the metallogenesis. Therefore, the present metallogenic study has been undertaken in order to investigate the origin of the non-sulphide ore body in detail.

The present study is focused mainly on ore petrology, geochemistry, and metallogenesis of the Skorpion deposit, based on data from drill core of Anglo American’s exploration drilling programme in 1999, but also on some limited surface outcrop samples prior to a more extensive exposure of the ore body in the open pit. The study also uses geochemical information from Anglo American’s long-term exploration programme of the area, which was provided by Anglo American in a Microsoft Access database. Additionally, geochemical results from the drilling campaign of the Skorpion Mine in 2004 have entered into the present study.

The investigations carried out on drill core samples as well as on surface outcrop samples include microscopic techniques, e.g. light-microscopy and SEM-EDX technique, as well as geochemical methods, e.g. XRF, ICP-MS, XRD and electron microprobe techniques.

Between July 2000 and September 2002 three field campaigns were undertaken in order to get familiarised with the regional geology, to sample drill core from the Skorpion deposit and to study the uppermost part of the Skorpion ore body after the mining had commenced in October 2001.

The early stages of investigation during this research project had revealed that the Skorpion ore body must have formed by supergene weathering of a primary sulphide deposit. Therefore, it is not the aim of this study to discuss the opposing main genetic models mentioned above. The overall aim of the present study is to formulate a metallogenic model for the supergene Skorpion non-sulphide ore body and particularly focus on the petrographical and geochemical characteristics of ores and their host rocks in order to elucidate the processes, which led to the formation of the supergene ore body. Additionally, the thesis seeks to provide a discussion about the timing and definition of the ore-forming events.

1.3 Outline of this Study

The thesis has been divided into four chapters. The first chapter introduces the study presenting the Skorpion deposit within a global framework and including previous work done on non-sulphide zinc deposits worldwide. Aim and purpose of the present study are formulated and the methodology is described.

The chapter two familiarizes the reader with the regional geological setting of southern Namibia and serves as an introduction to the geology of the Skorpion area.

The Skorpion deposit itself is presented in chapter three. This chapter forms the main part of the thesis. The ore body and its host rocks are described petrographically and geochemically and ore-forming processes are discussed. This chapter also reviews the geomorphological evolution of southern Namibia and applies regional published data to the Skorpion area.

The final chapter summarises the outcome of this research and presents ideas for future work.

Two appendices, which are filed on a CD, conclude the study. Appendix one includes borehole logs as well as maps showing the location of boreholes and surface samples.
Analytical results, such as XRF and ICP-MS data, but also electron microprobe- and SEM-EDX analyses are contained in appendix two. Appendix two also includes a sample list.

1.4. Methodology

1.4.1 Sampling

A first field campaign has been undertaken in July 2000 in order to sample drill core from diamond cored boreholes of the Skorpion deposit. After consulting the exploration geologists working on the Skorpion deposit at that time (K. Hart, K. Hartmann), drill cores of 10 representative boreholes from different parts of the Skorpion ore body have been selected, namely SD03, SD07, SD08, SD20, SD24, SD39, SD48, SD65, SD80, and BH70 (App. 1, map 1). The drill cores from the selected boreholes were already geologically logged. Thus, the geological information, which is included in the borehole logs (App. 1) correspond to the lithological interpretation of the Anglo American's exploration geologists at that time. Some 300 samples were taken ensuring that the different lithological units and their mineralised horizons are covered (App. 1). Intervals containing the rather unobtrusive non-sulphide zinc mineralisation were identified using a zinc indicator solution, called 'Zinc Zap' (Tab. 1). The sample numbers refer to certain intervals, which are depicted in the lithological borehole logs. These logs also contain information about analytical methods that were applied to each sample.

Tab. 1: Zinc Zap reaction according to Skorpion Zinc Mine.

<table>
<thead>
<tr>
<th>Zinc Zap reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non</td>
<td>Solution stays clear or turns green (no or almost no zinc present)</td>
</tr>
<tr>
<td>Weak</td>
<td>Solution turns light orange (about 4 – 9 % Zn)</td>
</tr>
<tr>
<td>Moderate</td>
<td>Solution turns orange-red (about 9 -13 % Zn)</td>
</tr>
<tr>
<td>Good</td>
<td>Solution turns red (about 13 – 20 % Zn)</td>
</tr>
<tr>
<td>Blood red</td>
<td>Solution turns dark red (about &gt; 20 % Zn)</td>
</tr>
</tbody>
</table>

Another two field campaigns have been undertaken in February 2001 and September 2002 in order to collect reference samples from surface outcrops of the wider Skorpion area and samples from the uppermost part of the Skorpion ore body after the mining had commenced. A corresponding sample list is included in the appendix (App. 2). Taken all samples into account including drill core samples and surface samples, the present study is based mainly on the investigation of 150 thin sections and some 180 XRF-, 70 ICP-MS (19 by courtesy of Anglo American Corporation)-, 100 XRD-analyses and several SEM-EDX-, electron microprobe-, and stable isotope analyses.

1.4.2 Analytics

Light Microscopy
Polished thin sections covering the various lithological units and different mineralisation styles were prepared for petrographic observations. Thin sections were investigated using light microscopy techniques under both reflected and transmittal light.
X-ray Fluorescence Spectrometry
Major and minor element concentrations in bulk rock samples were determined using conventional X-ray fluorescence spectrometry (XRF) at the Geological Department of the Martin-Luther-University Halle-Wittenberg.
Rock samples were crushed and then pulverised. The grinding equipment was cleaned between each sample by using SiO₂-sand as well as acetone in order to avoid contamination of sample material. However, at this point it also has to be stressed that those samples, which were ground with wolfram-bearing grinding equipment, display contaminations of wolfram and minor cobalt.
Samples were analysed as pressed powder resin pellets by Siemens-XRF SRS 3000, after determination of loss of ignition (LOI). Crystals used for refraction were LIF(200), PET and TIAP, measuring time was 20 seconds per line (approx. 90 minutes for a complete spectrum) at a minimum acceleration voltage of 20 kV and 10 mA currency. Calibration was performed by using certified international standards. LOI was determined by roasting each sample at 1000°C for 2 hours.

ICP-MS
Trace, including rare earth, element concentrations have been analysed by Activation Laboratories Ltd. using ICP-MS techniques.

X-ray-Diffractometry
Powder XRD technique was applied on whole rock samples in order to investigate the mineralogy of host rocks and ore paragenesis. Samples were crushed and milled and bulk powder specimens were prepared. In some cases, minerals were hand-picked from the whole rock samples in order to investigate rare mineral phases in detail. The separated mineral specimen was ground and placed on a silicon plate. The specimens were analysed on a Philips X-ray diffractometer using Cu-Kα radiation measuring from 3° to 90° (2 teta) at the Geological Department of the Martin-Luther-University Halle-Wittenberg.

SEM-EDX
Scanning electron microscopy technique coupled with an energy dispersive spectrometer has been carried out on selected samples using a GEOL JSM6300 at the Geological Department of the Martin-Luther-University Halle-Wittenberg. Minerals, which could not be identified under the light microscope due to their size, were analysed semi-quantitative using SEM-EDX technique. Thin sections and rock samples were coated with carbon before they were placed in the vacuum chamber of the scanning microscope. Additionally, high resolution backscattered images as well as secondary electron images have been taken in order to show ore textures.

Electron Microprobe Technique
The analyses of samples using the electron microprobe technique have been carried out at the Federal Institute for Geosciences and Natural Resources, Hanover.
Focus of the study was the determination of major and trace elements in both primary sulphides and secondary non-sulphides and sulphides. The measurements have been carried out by using a CAMECA SX 100. This microprobe is equipped with 5 wavelength dispersive (WDS) spectrometers and fully integrated energy dispersive spectrometer. The WDS spectrometers have been used to conduct quantitative analyses on individually selected points, but also on traverses and point grids. High resolution backscattered images have been taken in order to show ore textures.
**Stable Isotope Analyses**

Carbon and oxygen isotope studies have been carried out at the Technical University of Munich, Germany by A. Gilg in order to determine their concentrations in samples of smithsonite from the metasiliciclastic host rock and of calcite from the marble unit. The extraction of CO₂ from carbonates has been done at 72°C with water-free phosphoric acid in individual reaction tubes (GasBench II; ThermoFinnigan). The measurements of isotope ratios have been carried out by using a ThermoFinnigan Delta plus-mass spectrometer with a ‘continuous flow’ system that uses helium as carrier gas. The correction of the oxygen isotope fractionation between CO₂ and smithsonite, released from the reaction with phosphoric acid, has been done according to Gilg et al. (2001). All C and O isotope compositions are reported in δ-notation in per mil (‰) relative to the PDB and V-SMOW standards, respectively, and show an absolute error of 0.1 ‰.

Sulphur isotope analyses have been undertaken by H. Strauss at the University Of Munster, Germany in order to determine their concentrations in sulphide samples from felsic metavolcanic rocks that occur in the footwall of the non-sulphide Skorpion deposit. The sulphides minerals were hand-picked from the crushed whole rock samples and analysed by coupling of mass spectrometer and elementary analyser. All S isotope compositions are reported in δ-notation in per mil (‰) relative to the V-CDT standards, and show an absolute error of 0.3 ‰.

**1.4.3 GIS work**

The GIS ArcView 3.2 has been used as a database for storing borehole and sample information as well as geochemical data. Regional geological data were provided by Anglo American. Maps containing sample and borehole locations (App. 1) are generated by ArcView 3.2 using Anglo American's geological information as background data. Additionally, the Spatial Analyst extension for ArcView 3.2 was used in order to discover and understand spatial relationships in geochemical data. The Spatial Analyst was used to create cell-based raster data from geochemical vector data of the Skorpion ore body. The vector data from the Skorpion ore body include geochemical data produced in the course of the present study, but also geochemical results from several drilling campaigns by courtesy of Anglo American Corporation and Skorpion Mine. Grids interpolated from vector data include maps showing the palaeo-morphology of the Skorpion area, the present morphology of the Skorpion area, the thickness of young cover sediments (overburden), but also the lateral metal distribution patterns within the Skorpion ore body for base metals (Zn, Cu), Mn and Fe. Additionally, grids of single-metal distribution patterns were contoured and metal contours were laid on top of each other in order to elucidate the spatial relationships between them. Lithological and structural data from the Skorpion open pit (as of June 2004), compiled by Dirks (2004), have been used as background information for the metal distribution maps in order to understand the relationship between metal distribution, lithology and structure.

At this point, it should also be pointed out that regional maps have been created using UTM coordinates (map datum WGS84). However, maps showing the Skorpion open pit area are generally created using the local mine grid, which is offset 29° west of true north and 18.3° west of magnetic north, respectively. The different ways of data presentation are the result of the different databases, which entered into the present study.
1.5 Previous Work

Since non-sulphide zinc deposits have recently become technically and economically important again, the research on non-sulphide zinc deposits was reinforced and focused on several economic deposits throughout the world. An attempt of a general compilation of data on non-sulphide deposits worldwide based on their mineralogy and geological characteristics, including some sketchy information on Skorpion, has been published by Large (2001). He subdivided non-sulphide zinc occurrences into:

- **Type I** characterised by MVT or CRD/manto Zn mineralisation with smithsonite, hemimorphite, and hydrozincite, e.g. Mehdi Abad, Mae Sod, Lanping
- **Type II** associated with major structures in Late Proterozoic – Early Cambrian sedimentary successions with willemite, hemimorphite, and smithsonite, e.g. Vazante, Beltana, Kabwe, (Franklin and Sterling Hill)
- **Type III** oxidised sulphide ores, preserved by an overlying cover with sauconite, hemimorphite and smithsonite, e.g. Skorpion, Shaimerden.

A more genetic classification has been published by Hitzman (2001) and Hitzman et al. (2003) based on Heyl & Bozion (1960). The classification includes:

- **Supergene** zinc oxide deposits, e.g. Mehdi Abad, Mae Sod, Lanping, Skorpion, Shaimerden
- **Hypogene** zinc oxide deposits, e.g. Vazante, Beltana, Kabwe
- **Metamorphic** zinc oxide deposits, e.g. Franklin, Sterling Hill

As mentioned above, the pioneering work regarding non-sulphide zinc deposits was carried out by Heyl & Bozion (1960). They published first a classification of non-sulphide zinc deposits including hypogene, supergene, and metamorphic non-sulphide zinc deposits. Furthermore, they subdivided the group of the supergene deposits into three main types according to their formation processes as follows:

- direct replacement deposits,
- wall rock replacement deposits, and
- saprolitic accumulations.

Direct replacement types are formed by in-situ oxidation of primary zinc ores essentially in place, without major migration of the zinc in solution. The host rocks of the precursor sulphide ore body are also host to the supergene non-sulphide ore body. Direct replacement deposits are more complex and richer in precious metals than deposits formed by the replacement of wall rock.

Wall rock replacement deposits are the result of leaching of primary ores, migration of zinc in solution, and redeposition of zinc by replacement of nearby carbonate or siliciclastic wall rocks.

Saprolitic accumulations are typically a mixture of (i) thoroughly decomposed earthy but untransported rock and oxidised zinc minerals, (ii) residual masses of clay, smithsonite, and hemimorphite that have slumped vertically and collected in solution pockets of decomposed limestone between buried pinnacles of unweathered limestone, and (iii) zinc carbonates and silicates that were deposited near the limestone walls in the bottoms of the solution pockets.
by reaction of descending zinc-bearing solutions that formed from the weathering of the mineralised pinnacles and leaching of the saprolites above.

The classification of supergene non-sulphide zinc deposits is very helpful in order to explain genetic processes. However, it has be taken into account that a supergene deposit can form by more than one of the processes described above, and thus hybrid systems are likely to occur.

During the last few years, research on non-sulphide zinc deposits including hypogene, metamorphic and supergene deposits, was mainly focussed on the major economic occurrences worldwide, e.g. Shaimerden, Kazakhstan (Schaffalitzky & Boland 2001, Boland et al. 2003, Kärner 2003a), Beltana, Australia (Muller 1972, Groves et al. 2003, Hitzman et al. 2003), Angouran, Iran (Hirayama 1986, Daliran & Borg 2003, Gilg et al. 2003), Vazante, Brazil (Monteiro et al. 1999, Hitzman et al. 2003), but also on older mining districts containing smaller, historically exploited deposits, e.g. Kabwe, Zambia (Kortmann 1972, Kamona & Friedrich 1994), Franklin/Sterling Hill, New Jersey (Frondel, C. & Bam 1974, Johnson & Skinner 2003) and Sardinia (Boni et al. 2003, Boni & Large 2003).

Geological information from the Skorpion deposit sensu stricto has been scarce (e.g. Corrans et al. 1993, Borg et al. 2003) due to restricted access to Namibia’s Diamond Area No. 1, the ‘Sperrgebiet’, where the deposit is situated and because of a competitive local exploration environment. However, the general geology of the region and the regional geochemistry of the supracrustal magmatic rocks have been described in detail by authors such as Söhnge and Villiers (1947), McMillan (1968), Davies and Coward (1982), von Veh (1993), Alchin (1993), Frimmel et al. (1996a, b), and Frimmel (2000a, b). Additionally, a regional-scale data compilation and interpretation of the distribution patterns of base metal occurrences and their relationship to early crustal structures within the branches of the Pan-African fold belts of Namibia, including limited information from the Gariep belt, has been compiled by Borg (2000).