1 Introduction

The utilisation of and the industrial/economic interest in non-sulphide zinc ore has changed through time and reflects the ability to process different types of Zn-Pb – ore as well as the industrial capability to use different types of Zn-Pb ores for the winning of zinc and lead. Non-sulphide zinc deposits were the principal source of zinc in the world until the 20th century (LARGE, 2001; BONI, 2003). The dominance in mining of non-sulphide zinc deposits reaches from Roman times up to the 18th century. Different types of non-sulphide zinc ores have been used depending on their availability. Zn-(hydro-)silicates as well as Zn-(hydro-)carbonates or a mixture of these have been used as zinc source for the production of brass (a zinc-copper-tin alloy) (BONI & LARGE, 2003). During the nineteenth and early twentieth centuries, zinc metal was recovered almost entirely from smithsonite-bearing non-sulphide ores in so-called ‘Wälz’ kilns (HITZMAN ET AL., 2003). However, the development of floatation techniques and the ability to process zinc sulphides, such as sphalerite, has resulted in the dominance of sulphide ores in zinc metal production. The (renewed) commercial interest for non-sulphide zinc ore and its associated deposits is due to the availability of improved solvent-extraction methods with coupled electro-winning. This combination of hydrometallurgical techniques provides the possibility to produce zinc with very high purity. Thus, it is possible to produce ‘medical-grade’ zinc with a purity of 99.99 % zinc with relatively low energy input by solvent-extraction and electro-winning processes (SX-EW), generating higher economic value on site (BORG, 2002B).

Non-sulphide zinc deposits combine several important advantages. One of the most important advantages is the high concentration of zinc in several types of non-sulphide zinc ores. Average cost-effective zinc concentrations of carbonate-hosted non-sulphide zinc ores range from 10 % up to 35 % zinc and more. Furthermore, some non-sulphide ore types are characterised by low concentrations of lead, arsenic, cadmium and other toxic and/or unwanted metals. The mining of these non-sulphide zinc ore is highly profitable without detrimental effects on the environment by toxic metals and/or emission of sulphur bearing gasses into the atmosphere (SO₂, sulphuric acid, and associated acid rain) or process residuals that need storage in waste dumps.

Countries, which are mining non-sulphide zinc (-lead) ores, are Brazil, Iran, Namibia, China, and Thailand (WELLMER, 2002, LARGE, 2001). Additional projects in Kazakhstan, Yemen, and Australia will start production in the near future.

The technical progress turned the non-sulphide zinc ores into attractive exploration targets due to a number of advantages such as low metal recovery costs and favourable environmental aspects such as the obvious absence of sulphur (LARGE, 2001, BORG, 2002B, HITZMAN ET AL., 2003). This unusual group of sediment-hosted zinc deposits comprises a number of very significant ore deposits or prospects, compared to both carbonate-hosted and clastic-hosted massive sulphide deposits (DALIRAN & BORG, 2004).

The world zinc production from non-sulphide zinc deposits in 2002 is approximately 2 % (WELLMER, 2002) related to all zinc sources (sulphide zinc deposits). However, the annual production of zinc from non-sulphide zinc ores could in future exceed 10 % of the total global zinc metal production (LARGE, 2001). Non-sulphide zinc deposits contain approximately 11 % of the world’s known zinc reserve (BORG, 2002B). This shows the enormous economic potential of this type of Zn-deposits.
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and reflects its attractiveness for industry and, as a result, the need for a more comprehensive understanding of these zinc deposits. Since the mining of non-sulphide zinc deposits depends on sufficient resources (Wellmer, 2002) improved knowledge about the geochemical characteristics of non-sulphide zinc deposits offer the chance for a more specific and successful exploration of such deposits.

1.1 Non-sulphide zinc deposits in carbonate host rocks

The majority of the known non-sulphide zinc deposits occur in carbonate rocks (Large, 2001; Hitzman et al., 2003). This is a result of the specific geochemical behaviour of the carbonates. The ability to form (solution-) cavities, karst-breccias, and the high pH-values within a carbonate-dominated environment offer ideal conditions for the accumulation, enrichment, and emplacement of both sulphide ore and non-sulphide zinc ore. The highly reactive nature of carbonate rocks favors efficient chemical reactions and accumulation of precipitated minerals.

Non-sulphide zinc deposits have been often (sensu stricto incorrectly) termed as zinc-oxide and/or calamine deposits in historic literature. The term ‘calamine’ comprises all types of non-sulphide zinc ores: carbonates and silicates as well. Non-sulphide zinc deposits have been described by numerous authors, but in depth scientific research started with the economic interest in this type of mineralisation in the last years. Thus, a comprehensive Special Issue of Economic Geology (2003, 98-4) has been published. Numerous authors, such as Borg (2002b), Heyl & Bozian (1960), Hitzman (2001), Hitzman et al. (2003), and Large (2001) described and classified non-sulphide zinc deposits. Basically, two major subclasses of supergene- and one class of hypogene non-sulphide zinc deposits are distinguished according to their geological setting and mineralogical aspects, although Heyl and Bozian (1960, 1962) focused mainly on supergene ore.

These two major classes of non-sulphide zinc ore are: Group A: Supergene deposits, which formed by supergene oxidation, and Group B: hypogene deposits. Group-A supergene non-sulphide zinc deposits are the most common type and are associated with hydrated zinc-silicates and carbonates such as hemimorphite ($\text{Zn}_2\text{Si}_2\text{O}_7\text{(OH)}_2\cdot\text{H}_2\text{O}$) and hydrozincite ($\text{Zn}_5\text{(CO}_3\text{)}_2\text{(OH)}_6$) or other carbonates (mainly smithsonite, ZnCO₃). Group-B hypogene deposits in contrast, consist dominantly of anhydrous zinc silicates and oxides, such as willemite (Zn₂SiO₄), zincte (ZnO), franklinite (ZnFe₂O₄), and others, locally with minor amounts of sulphide minerals. Group-B mineralisation is considered to be of primary hydrothermal origin and has been formed at low sulphur and high oxygen activities (Boni & Large, 2003; Hitzman, 2001). Thus, silicates dominate the mineralogy of group-B hypogene deposits, with a typical prevalence of willemite. The (rare) metamorphosed non-sulphide zinc deposits (Franklin Furnace and Sterling Hill, New Jersey) probably belong to this class as well (Boni & Large, 2003), and are characterised by metamorphic non-sulphide zinc minerals such as franklinite and gahnite.

Beside these classifications of non-sulphide zinc deposits several authors have studied the broad field of geochemical aspects associated with the genesis of non-sulphide zinc deposits, starting from the sulphide protore up to the oxidation and the preservation conditions. However, most of these studies focus on specific detail, but lacking in the implication of these specific geochemical reactions into a broad model for the genesis of (supergene) non-sulphide zinc deposits in a car-
bonate environment and their preservation is lacking.

1.2 Aims and objectives of this study

The aim of the present thesis is an improved understanding of the mechanisms of the formation and preservation of carbonate-hosted non-sulphide zinc deposits. The concentration and the limitation of this study to carbonate environments and host rocks is the result of completely different behaviours of geochemical processes within carbonate rocks compared to siliceous host rocks.

One part of this thesis focuses on geological, mineralogical, and geochemical aspects of this type of deposits considering as example the non-sulphide and sulphide combined zinc deposits Mehdi Abad and Irankuh. Variations in mineralogy, geochemistry, and the distribution of the non-sulphide zinc minerals as well as their relationship to the sulphide protore have been analysed with respect to supergene oxidation processes of the sulphide protore, transportation and separation processes of metal ions, and the precipitation of the non-sulphide minerals. The second half of this thesis combines the results of these examinations and develops a general geochemical model for the genesis of carbonate-hosted non-sulphide zinc deposits. This implies the investigation and numerical simulation of the related geochemical processes and the development of a generalised geochemical model.

1.3 Outline of this study

The thesis has been divided into 6 chapters. The first and second chapter addresses the basic fundamentals of non-sulphide zinc deposits and the methods that have been used for this study. The third chapter introduces the regional geological setting of Iran and the examined areas. The fourth chapter presents the results of the examination of two non-sulphide zinc deposits: Mehdi Abad and Irankuh. The main geological and geochemical features have been examined with a special focus on non-sulphide ore related processes.

Chapter 5 presents a general geochemical model for the genesis of carbonate hosted non-sulphide zinc deposits, which includes the results of the observations of both deposits and theoretically geochemical modelling. The model is used to explain the formation of the non-sulphide ore of Mehdi Abad and Irankuh.

The final chapter six summarises the outcome of this research and the appendix includes analytical results from ICP-MS analysis.

1.4 Study area

Iran hosts numerous important non-sulphide and mixed sulphide/non-sulphide zinc deposits, such as Angouran, Mehdi Abad, Kuh-e-Surmeh, and Iran-Kuh, which are well exposed and relatively easily accessible. Either the examined deposits are active mines with well-developed open pits and
adits (Iran-Kuh, Mountain Ore Body –MOB- of Mehdi Abad) or extensively drilled exploration projects (Valley Ore Body –VOB- of Mehdi Abad).

Thus, Iran is the ideal region to study different non-sulphide zinc deposits for a detailed geochemical and mineralogical analysis and comparison of variations among them.

2 Materials and methods

2.1 Sample material

Samples have been obtained and collected from Irankuh and Mehdi Abad zinc deposits. Here, the first step of the field campaign was the comprehensive geological examination and evaluation of each deposit as a condition precedent for an effective sample collection. The fieldwork comprised both surface- and underground work.

The geochemical analyses are based on samples from both drill cores and hand specimen. The drill cores were obtained from the local mines/exploration camps and were selected according to their geological position and potential geochemical relevance. The lithological descriptions of the sedimentary host rocks and local core logs have been used on site for the selection of samples. In addition, hand specimen from selected adits, trenches, and surface outcrops have systematically sampled.

Field work in Iran was from May 24th to June 19th 2002. The purpose of this visit was to establish a general overview of the geology of Iran and to visit and sample the main Iranian Zn-Pb deposits Mehdi-Abad and Irankuh. The work comprised general geologic fieldwork and sampling. An additional visit at Teheran has been made in December 2003 (December 13-21, 2003). The purpose of this visit was the scientific exchange with the Geological Department of the Shahid Beheshti University of Teheran and to give talks about the results of this research project. An additional visit was made at the Geological Survey of Iran.

A total number of 202 specimens with a total weight of approximately 130 kg have been sampled during the field campaign from May 24th to June 19th 2002. The following tables Tab. 1 and Tab. 2 show the specific number of samples: