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:
Materials and methods

These samples and data provide the basis for the research activities of this thesis. The samples were prepared for further investigations at the Martin-Luther-University Halle-Wittenberg. This comprises the cutting and formation of rock samples for the preparation of thin sections for light microscopy, SEM and SEM-EDX analyses. Additionally, crushing and milling of the specimen have been carried out for XRD, RFA, and ICP-MS analyses.

2.2 Methods

2.2.1 Sampling and sample preparation

The drill cores have been selected and cut either to half-sized or to quarter-sized cores by usage of a rock saw. One part remained on site, whereas the other part was used as sample for further analytical work. The sample sizes of drill cores reach from 10 up to 30 cm in length and were taken after a careful examination of the drill core from both geochemically relevant zones and wall rocks.

Hand specimens have been geo-referenced by using a GPS or by the use of geo-referenced maps of local adits and shafts of the sampled mines. Mineral paragenesis and relevant sediment structures have been studied in detail in selected core segments and have been documented using a digital photographic camera.
2.2.2 XRD analyses

X-ray diffraction (XRD) measurements were performed at the Institute for Geological Sciences of the Martin-Luther-University Halle-Wittenberg on a Bragg-Brentano-Diffractometer of the type Siemens D 5000, with a Cu X-ray tube (CuKα) and Ni monochromator operated at 40 kV and 30 mA. The diffraction patterns were compared with a set of standard patterns compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). A full description of the X-ray diffraction methodology, analytical settings, and applications can be found in BRINDLEY & BROWN (1980) and MOORE & REYNOLDS (1997).

Powder samples were prepared from the same slabs of rock used to make thin and double polished sections. Rock pieces of vein minerals and host rock were initially crushed by hand using a metal hammer to reduce the samples to cm-sized fragments. Finally, the material has been ground with a tungsten disc mill to approximately 600-μm grain size. The powder obtained was scanned in the 2θ range from 10° to 60° with increments of 0.04° 2θ. Counting time was 2 seconds.

2.2.3 SEM and SEM-EDX analyses

Scanning electron microscope investigations were made on both Au- and C-coated samples using a JEOL JSM-6300 scanning electron microscope. This SEM is coupled with an X-ray energy dispersive spectrometer. Analytical EDX settings were 20 kV beam voltage and count time of 60 seconds (peaks).

2.2.4 Light microscopy

From most representative samples of sulphide ore, non-sulphide ore and the host rocks polished and unpolished thin sections were prepared. The thin sections were studied under transmitted and reflected light. Photographs of the thin sections were made by using the Microscope Zeiss Axiophot and the coupled digital camera Nikon DS-5M.

2.2.5 ICP-MS analysis

Whole-rock analysis of the major, trace, and rare earth elements by ICP-AES and ICP-MS were done by Acme Analytical Laboratories, Vancouver, British Columbia (Canada). The raw samples were milled by using a tungsten carbide shatter box, involving tungsten contamination during sample preparation. Therefore, the tungsten data cannot be used for geochemical interpretation.

Elements are expressed as common oxides for each element (i.e. Al₂O₃, CaO, Cr₂O₃, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, TiO₂). Other element concentrations are given in ppm. Total abundances of the major oxides and several minor elements are based on a 0.2 g sample analysed by ICP-emission spectrometry following a lithium metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition has been determined by weight difference after ignition at 1000°C.
2.2.6 Stable isotope analyses

The term 'stable' refers to isotopes, which are not radioactive. Radioactivity is an evidence for nuclei affected by decaying processes. Thus, stable isotopes show a long-term stable behaviour and are not influenced by decaying processes. In most cases, one stable isotope is predominant and other isotopes only occur in traces.

The different masses of the isotopes of each element lead to differences in physicochemical properties of each isotope. The chemical properties of molecules differing only in isotopic substitution are qualitatively the same, but quantitatively different. These differences in chemical properties can lead to considerable isotope effects in chemical reactions. The partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios is referred to as isotope fractionation.

The isotope fractionation is caused by isotope exchange reactions and kinetic processes. These processes depend on the reaction rates of (isotopic) molecules. Other factors may be the chemical composition or the crystal structure.

The detection of different isotopes of a specific element is based on the different masses of each isotope. The most effective way to detect isotopes is a mass spectrometer, which separates the isotopes due to the behaviour of their charged ions within magnetic fields.

The δ-values reflect the fractionation mechanisms and processes predominant for each specific element during geological evolution. The oxygen isotope ratio $\delta^{18}$O provides a useful tool for the study of water/rock interaction in carbonate minerals and rocks, as this ratio shifts for both phases away from their initial values during interaction. The carbon isotope ratios $\delta^{13}$C can be used to trace the carbon source and the carbonate evolution during diagenesis and very low-temperature metamorphism. Thus, the carbon and oxygen isotope studies on carbonate minerals of the non-sulphide zinc ore and the carbonate host rock have been used to determine the conditions of non-sulphide ore formation and the source of the fluids and the carbonate ions.

For a more complete description of the theoretical background, analytical techniques, and common applications of stable isotopes the reader is referred to HOEFS (1997), SHARP (1999), VALLEY ET AL. (1986), and ATTENDORN ET AL. (1997).
2.2.7 Geochemical modelling and calculations

The results of the examined deposits have been tested by using the PHREEQC code (PARKHURST & APPELO, 1999). PHREEQC is a well established modelling program and has been successfully used by numerous authors, such as SALMON & MÄLMSTRÖM (2002), APPELO ET AL (1998), and others to describe, simulate, and solve hydro-geochemical problems. PHREEQC is capable to model equilibrium reactions of aqueous solutions. These solutions can interact with other phases, such as minerals, gases, or model processes like sorption and non-electrostatic surface-complexation processes. The calculations are based on an extensible database and give results for saturation indices, as well as pH, redox calculations and 1-D transport simulations as well. Thus, this program is an excellent tool to test geochemical assumptions and to calculate parameters of equilibrium reactions.

The PHREEQC calculations are based on the thermodynamic database ‘thermo.com.V8.R6.230’ compiled at the Lawrence Livermore National Laboratory, USA. PHREEQC was used for the calculation of equilibrium reactions and data, the calculation of the 1-D transport/titration model and the calculation of metal sorption effects onto ferrihydrite. The calculation of the metal sorption uses the generalised two-layer model of DZOMBAK AND MOREL (1990). The equilibrium constants for the adsorption of all species onto ferrihydrite were derived from adsorption experiments on ferrihydrite (DZOMBAK AND MOREL, 1990).

The adsorption calculation is based on a hypothetical (Fe-Zn-Pb) metal-rich aqueous solution, which includes the mobile elements and corresponding precipitated immobile Fe-oxihydroxides, which remained immobile within the oxide zone. The metal concentration values are based on values from acid mine drainage (AMD) waters. These waters are the result of an oxidation process of sulphides and one can assume that the metal concentration and the pH values of non-neutralised AMD waters are similar to an initial metal-rich fluid, which originated from oxidising sulphide ore. The range of metal concentrations for AMD waters is given in Tab. 3:

<p>| Tab. 3: Typical metal concentrations of AMD [mg/l⁻¹] (values from GAZE A ET AL., 1996). |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>Fe</th>
<th>Zn</th>
<th>Pb</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/l⁻¹</td>
<td>8.5 – 3200</td>
<td>0.04 – 1600</td>
<td>0.02 – 90</td>
</tr>
<tr>
<td>mol/l⁻¹</td>
<td>1.5·10⁻³ – 5.7·10⁻²</td>
<td>6.1·10⁻⁷ – 2.41·10⁻²</td>
<td>9.6·10⁻⁸ – 4.3·10⁻⁴</td>
</tr>
</tbody>
</table>

The zinc concentrations are based on values given by GAZE A ET AL. (1996). The composition of the model-solution is based on the zinc concentration of Tab. 3. Zinc concentrations are assumed to be on the higher side of the typical range to take into account the high sulphide concentration within sulphide ore compared to mine dumps. The initial hypothetical solution comprises only the metals Fe³⁺, Zn²⁺, Pb²⁺ and SO₄²⁻ ions at an initial pH=2 and the elements should be in their highest oxidation state, according to an oxygen-path oxidation process. Ferric iron Fe(III) is mostly immobile at pH=2 due to the precipitation of insoluble Fe-oxihydroxides. Thus, the value of iron within the supergene fluid is presumed to be relatively low with 1.7·10⁻³ mol·l⁻¹ according to the solubility of HFO.

The predominant portion of the iron remains immobile within the oxidation zone as insoluble Fe-
oxihydroxides. As a first approximation, the amount of the immobile iron can be estimated by using the relative amounts of Fe, Zn, and Pb in the sulphide protore. The amount of iron (mainly associated with pyrite) within the sulphide protore have been estimated by using analyses of the sulphide ore of the Mehdi Abad, Valley Ore Body. The mean mass% for selected elements within the sulphide ore are: 7.2 % Zn (in sphalerite), 2.3% Pb (galena) and 20% Fe (pyrite) with a ratio of Zn/(Zn+Pb) of 0.75. Calculations (using the molar masses: $M_{\text{Zn}}=65.39, M_{\text{Pb}}=207.2$, and $M_{\text{Fe}}=55.85$ g*mol$^{-1}$) show the relative molarities between these metals:

$1_{\text{Fe}}:0.38_{\text{Zn}}:0.028_{\text{Pb}}.$

Pyrite is the most reactive mineral with respect to oxygen-path reactions (JAMBOR, 1994, KAKOVSKY & KOSIKOV, 1975) but zinc is also highly reactive and soluble at pH=2. The amount of oxidised pyrite can be estimated by using the relative molarity of these minerals under the assumption of a sulphide ore with homogeneously distributed pyrite, sphalerite and galena. Thus, the assumed oxidation of sphalerite and the concentration of $2.4 \cdot 10^{-2}$ mol·l$^{-1}$ Zn within the metal-rich fluids is associated with $6.3 \cdot 10^{-2}$ mol oxidised pyrite ($=6.3 \cdot 10^{-2}$ mol Fe(III)), from which the biggest portion precipitates as HFO and is thus removed from the solution.

The calculated concentration of cation-associated sulphate ions is similar to those values given in numerous analytical results of AMD systems (FORSTNER & WITTMANN, 1983, FERREIRA DA SILVA ET AL. 2005, and other authors).

The calculations include the geochemical behaviour of the zinc minerals smithsonite, hydrozincite, and willemite. Hemimorphite is not included although it is the most common zinc silicate mineral in the examined Iranian deposits. However, it is difficult to determine the field of stability of hemimorphite, since presently no thermodynamic data are available for this mineral. Several authors (e.g. INGWERSSEN, 1990) attempted to estimate the thermodynamic data from solubility curves (provided by TAKAHASHI, 1960 and others). These results were not used due to high experimental uncertainties of these data. These uncertainties are caused by the usage of acetate-buffered solutions during the pH-dependent hemimorphite solubility experiments. The presence of acetate leads to the formation of zinc-acetate complexes. The binding of zinc as acetate complexes decrease the activity of free Zn cations within the solution (VOEGELIN ET AL., 2003). This phenomenon should increase the solubility of hemimorphite and thus distort the solubility curves of hemimorphite towards to an apparently higher solubility.

Tab. 4: Hypothetical acidic solution on which the modelling is based upon. Most of the iron is bound to HFO, which remains within the oxidation zone.

<table>
<thead>
<tr>
<th>pH</th>
<th>2</th>
<th>Fe$^{3+}$</th>
<th>$1.7 \cdot 10^{-3}$ mol·l$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pe</td>
<td>4</td>
<td>Zn$^{2+}$</td>
<td>$2.4 \cdot 10^{-2}$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
<td>Pb$^{2+}$</td>
<td>$1.6 \cdot 10^{-4}$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.0 mol·l$^{-1}$</td>
<td>SO$_4^{2-}$</td>
<td>$3.7 \cdot 10^{-4}$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>HFO</td>
<td>$6.1 \cdot 10^{-2}$ mol</td>
<td>insoluble, remains within the oxide zone</td>
<td></td>
</tr>
</tbody>
</table>

The hypothetical continuous reaction/neutralisation of the initial acidic aqueous solution with the carbonate host rock was modelled by applying up to 200 reaction steps to the aqueous solution
Materials and methods

At each reaction step a specific and constant amount of 0.01 moles of limestone or dolomite (or a mixture of both) were added irreversibly to one litre of solution. Then the solution equilibrated with local mineral assemblages and gas phases. After equilibrium reaction and precipitation, the resulting solution was used again to react in a further reaction step.

The solution reacts with the wall rock minerals (dolomite and/or calcite) in 200 incremental steps. The change in pH and saturation indices of different minerals and the metal- and anion concentration within the aqueous solution have been studied and analysed over these steps. The following minerals were included to precipitate from the solution: anglesite, cerussite, hydrocerussite, hydrozincite, smithsonite, willemite, gypsum, goethite, ferricydrite, hematite, calcite, dolomite, schwertmannite, magnesite and aragonite. These minerals represent the most common and relevant secondary minerals within carbonate-hosted non-sulphide zinc deposits and show stabilities, which may be realistically reached during the numeric simulation.

As a consequence, all or one of these minerals are allowed to precipitate if they become thermodynamically stable and the saturation index $Si_{[\text{mineral}]}$ of these phases is reached (a value of 0). If the saturation index $Si_{[\text{mineral}]} < 0$ then the solution is undersaturated, with respect to this specific mineral and, consequently, it would not precipitate from the solution. If $Si_{[\text{mineral}]} = 0$ then the concentration has reached the maximum value and the specific mineral will precipitate. A saturation index $Si_{[\text{mineral}]} > 0$, which indicates oversaturated solutions, is not allowed in this modelling process. A mineral, once precipitated, becomes removed from the fluid and does not participate in further reactions. This simulates a one-dimensional irreversibly progressing fluid migration through reactive limestone.

![Fig. 1: Titration model used for neutralisation- and precipitation reactions of acidic fluids within carbonate host rocks and precipitation of secondary minerals. An initial solution reacts in "n" steps with a specific amount of additional reactants (e.g. limestone), the system equilibrates and, after reaching the equilibrium, is followed by the next reaction.](image-url)
The geological and especially the tectonic style of Iran is highly influenced by the development and history of the Tethyan region (Fig. 2). The tectonic events, which occurred around the Iranian Plate margins, are related to rifting processes of Gondwana and subsequent collision with the Arabian plate from the WSW. These important processes affected the Iranian Plate and the adjacent plates, such as the African, Indian, Arabian, and Eurasian Plates, during Mesozoic to Tertiary times (ALSHARHAN ET AL., 2001; ALAVI, 2004).

The Tethyan region, which includes the Iranian Plate and the adjacent areas, underwent three major evolutionary stages. The first stage was the closing of the Paleo-Tethys and rifting of the Neo-Tethys from early Permian to late Triassic times. With the second stage, the subduction process of the Neo-Tethys and the collision of the Indian Plate with the Eurasian Plate from the Jurassic to the early Lower Tertiary began. The third and last stage is associated with the collision between the Arabian plate and the Eurasian plate from early Tertiary to the present (SHUFENG, 2002).

The first step, the Gondwana break-up, was associated with tensional basins and basement highs. The central Iranian segment separated from the Arabian plate along the line of the present High Zagros Zone (ALSHARHAN ET AL., 2001). The result of this process was the opening of the Neo-tethys. The closure of Neotethys started with the Late Cretaceous and proceeded into Cenozoic times. This phase is marked by the emplacement of a number of prominent ophiolithes in Oman, Iran, Syria, and southeast Turkey.