4 Results

4.1 The combined sulphide/non-sulphide Zn-Pb deposit Mehdi-Abad

4.1.1 Introduction and geographic location

The Mehdi Abad Project is located approximately 100 km southeast of the city Yazd and about 500 km southeast of Teheran in central Iran. The mine can be reached by the Yazd-Kerman Highway. Starting from Yazd, after 90 km a gravel road turns off to Bahadoran, and further on to the mine site. The UTM coordinates are 40R 0310158; 3484911. The altitude of this area is about 1850 m. The climate is semi-arid. There is no considerable vegetation within this area, only some bushes and little grass.

The main part of the ore body, the so-called Valley Ore Body (VOB) is located in a depression surrounded by hills and mountains with an altitude of up to 2500 metres (Fig. 8). A second ore body, the Mountain Ore Body (MOB) represents the highest parts of the oxide ore mineralisation (Fig. 9). The altitude of the MOB above the main Mehdi Abad ore body ranges from 2000 up to 2300 metres.

4.1.2 Geological overview

The Mehdi Abad zinc-lead deposit is located in the Central Iranian Shield. Here, Cretaceous limestones and sandstones were deposited over Jurassic rocks. The marine transgression started with the beginning of Cretaceous times with orbitulina-bearing carbonates and shales. Major faults became active during the Kimmerian Orogeny and resulted in horst and graben structures in Central Iran (AZARI & SETHNA, 1994). These grabens acted as sedimentary basins. The sedimentary basin, in which the Mehdi Abad deposit occurs is between the Chapedony fault to the east, and the Nain-
Deshir fault to the west (AZARI & SETHNA, 1994).

Except for the mountains and ridges, the area of Mehdi Abad is covered by alluvial overburden. The Cretaceous strata can be subdivided to the Sangestan Formation as the lowest, the Taft Formation in the middle, and the Abkou Formation on top of this stratigraphic sequence. These formations consist of detrital siliciclastic rocks and carbonates with an increase in carbonates towards the top. Mehdi-Abad has two separate ore bodies.

The VOB is located in a valley and is covered by an alluvial overburden (up to 250 m), whereas MOB locates on a rough mountainside in the northwestern part of the deposit. The MOB is completely oxidised, whereas the main portion of the VOB consist of sulphides. The non-sulphide ore of the MOB is hosted in the Abkouh Formation whereas both the sulphide ore and the non-sulphide ore of the VOB are hosted in the Taft formation (Fig. 10). The fact that the mineralisation of the Mehdi Abad ore body sensu stricto occurs in the Taft Fm. and the calamine ore in the Abkou Fm. documents the large vertical (stratigraphic) extent of the mineralisation.

The Sangestan Formation is the lowest and oldest Formation exposed in the mine area. It consists of shales and siltstones with interlaced calcarenite layers and fine- to coarse-grained quartzitic–feldspathic sandstones, sandy shales, and limestones (with fragments of corals).

The Taft Formation consists mainly of dolomite and dolomitic to ankeritic limestone. The zinc and lead mineralisation occurs within this formation, but the ore body is lateral limited by faults. Outside these terminating faults the same ore bearing Formation shows no notable lead and zinc mineralisation. Generally, the sulphide ore of the VOB is associated with dolomite or ankeritic limestone.

Fig. 10: Stratigraphic column of the Mehdi Abad deposit (modified after GSI, 1988)
The uppermost unit is the Abkou Formation. It can be found in the north, northwest, and west of the mine area (Fig. 11). This sequence overlies the Taft Formation and consists of a succession of limestone, marly limestone, calcareous shales, and dark limestones. The thickness of this formation is about 250 m. The mineralisation of the MOB occurs within the Abkou Formation in brecciated karstic limestones overlying a sequence of limy shales and marly limestones. The mineralisation occurs only in the brecciated limestones, but is repeated by folding (G.S.I., 1988). The folding of this part of the Abkou Formation is due to movements of the two adjoining faults. Besides this location, the Abkou Fm. and other formations are not folded in the area of Mehdi Abad ore body. The same stratigraphic unit within the Abkou sequence shows no mineralisation in other non-folded and non-brecciated regions.

Fig. 11: Geological map of the Mehdi Abad Zn-Pb deposit and the adjoining area. (After Nosratian, 1991)
The structural geology is controlled by three main fault systems striking N-S, NE-SW, and NW-SE. The geologic map of the Mehdi Abad deposit (Fig. 11) shows the position of the main faults in this area. Apparently, these faults represent one of the main controlling factors of mineralisation.

### 4.1.3 The Mountain Ore Body (MOB) of Mehdi Abad

The altitude of the Mountain Ore Body (MOB) (locally also called ‘Calamine Mine’), which is separated by faults from the main sulphide/non-sulphide Valley Ore Body (VOB), ranges from approximately 2000 up to 2300 m and represents the highest parts of the exposed mineralisation of Mehdi Abad. In contrast to the mixed main sulphide/non-sulphide orebody of the VOB, the MOB contains no zinc- and lead sulphides. The MOB consists of numerous adits, which follow the folded and duplicated ore horizon at different levels (Fig. 13). Three adits, on the 2006 m-, 2080 m-, and 2230 m-level have been sampled from W to E and a total of 36 specimens have been analysed by light microscope, XRF, ICP, XRD, SEM, and SEM-EDX.

### Geology of the MOB

The geological map of the Mehdi Abad zinc-lead deposit shows the position of the MOB, wedged-in between two important faults (Fig. 12): limited to the west by the Black Hill Fault, and in the east by the Forouzandeh Fault. The Black-Hill-Fault is one of the main and principal faults of the Mehdi-Abad zinc-lead deposit. The zinc-lead mineralisation occurs exclusively in the strata to the east. The Black Hill Fault is a normal dip slip fault, which strikes NNW-SSE and dips approximately 65°-70° to NE. The Forouzandeh Fault is a dextral strike-slip fault with a strike of approximately 60° to NE and a dip of approximately 50°-80° to the NW. No folding can be recognised away from these two major faults. The enclosed strata within this fault-bounded area are intensively folded. The folding in this area is due to the displacing movement of the two above-mentioned faults and is unique within the area of the Mehdi-Abad zinc-lead deposit.

The non-sulphide zinc-lead ore occurs on mainly three different levels within the Abkouh Formation (Fig. 13), which is the result of fold repetition (GSI., 1988). Overall, the mineralisation is predominantly hosted within the massive limestone of the \( K_{a}^{12} \) member of the Abkouh Formation (Albian) and particularly at the contact of the \( K_{a}^{12} \) to the \( K_{a}^{sh2} \) member. The \( K_{a}^{sh2} \) member consists of yellow to greenish dolomitic and calcareous shales and laminated limestones. The zinc-lead mineralisation consists exclusively of non-sulphide minerals, such as hemimorphite, smithsonite, and hydrozincite. No sulphide minerals have been observed. The MOB is the main location of the Mehdi-Abad zinc-lead deposit, hosted within the Abkouh Formation. In contrast, the predominant portion of the zinc-mineralisation of the VOB of the Mehdi-Abad zinc-lead deposit is hosted in strata of the Taft Formation (Barremian/Aptian) (G.S.I., 1988). The host rocks to the MOB are intensively faulted, brecciated, and locally mylonitised.
Fig. 12: Regional geological map of the Mountain Ore Body, which is located in the northwestern part of the Mehdi-Abad zinc-lead deposit. The ore is hosted within the strata of the Abkou Fm. The rocks between the Black-Hill Fault and the Forouzandeh Fault are folded. The strata and the ore-bearing horizons are stacked by folding, faulting, and thrusting. (Redrawn after Nosratiyan, 1991)

Fig. 13: Schematic NNW-SSE section of the folded and faulted strata at the Calamine Mine area. The ore-bearing strata are stacked in three main units due to folding, faulting, and thrusting. The dotted line indicates reconstructed fold shapes. (Modified after Nosratiyan, 1991).
Examinations of the Mountain Ore Body (MOB)

Three adits on different levels of the MOB have been examined and sampled for the investigation of the metal distribution and genesis of the non-sulphide ore of the MOB. The Fig. 12 and Fig. 13 show the location of these adits. The course, direction and the sample-points of adits no. one and two are given in the appendix (Fig. A. 1 and Fig. A. 2). The total length of the adits decreases on the upper levels. The uppermost adit no. 3 has a length of 20 meters only and is not shown separately due the limited length of from this adit. The underlying principle for the selection of the adits was to get information’s about the spatial distribution of elements, the distribution of metal concentrations, and the different styles of mineralisation within this mine-area.

The base-level adit (no. 1) and mid-level adit No. 2 (Fig. 12, Fig. A. 1, and Fig. A. 2, appendix) are part of a network of several galleries and branches, which lead to big cavities of mined-out non-sulphide zinc-ore. The top-level adit no. 3 is not connected to other tunnels or galleries and represents a locally limited region of historical non-sulphide ore searching – and mining activities.

The level of the adit no.1 is at 2006 m.a.s.l. and starts in strata of medium-thickly bedded, shaley and grey limestone with an average dip-direction of 268/35. The strata consisting of limestone and dolomitic limestone show clearly determinable bedding and an extensively and intensively faulting. Several major intensively and extensively faulted zones are recognisable within these adits. They mainly consist of highly brecciated limestone and/or dolomite with a reddish-brown coloured matrix. The metal concentrations within these fault-zones reaching from no mineralisation or even increased metal-concentrations up to high-grade Zn-(Pb)-concentrations. The strata in between these faults are less brecciated. The stope walls of several fault zones show up to 1 cm thick layers of a coating by white gypsum and a leakage of small amounts of water dripping from the fault. The ICP-analysis of specimen of most of these fault zones give elevated heavy metal contents compared to the wallrock, with zinc showing the highest concentrations (Zn: 2933 ppm, Pb: 90.9 ppm, Sample M02104), but no substantial economic mineralisation. However, several faults as well as highly (karstic-) brecciated areas, which are already mined out, show high Zn-(Pb-) concentrations and the metal bearing minerals occur as a cement of fault- and karst-breccias. Main minerals within these ore-bearing zones are hemimorphite, hydrozincite, calcite, quartz, and iron oxi-hydroxides, such as goethite and hematite.

The mid-level adit no.2 is located on a level of 2027 m.a.s.l. and belongs to another huge and complex system of galleries and caverns, which document extensive mining activities in former times. The entry of this adit is located close to the Black-Hill Fault. The rock, which consists of a mid-grey limestone and dolomites, is massive to highly brecciated on a regional scale and is probably due to karst effects. The fragment-sizes range from cm to dm-scale. Numerous faults cross the rock of this adit, similar to the base level adit. The metal distribution is rather similar to the base level adit. Most of the faults show only slightly increased metal concentrations. However, some of the sampled faults are characterised by high metal concentrations.

The top-level adit no. 3 is the shortest sampled adit with a length of 20 meters on level 2173 m. The limestone of this adit is highly brecciated and is riddled with numerous faults. The non-sulphide zinc ore occurs furthest in the back of this gallery, associated with a fault-system within a range of 8 meters.
Water occurs rarely at all examined levels. Most of them are dry; except several fault related zones with a wettish appearance.

**Ore-mineralogy and style of mineralisation of the Mountain Ore Body**

The non-sulphide zinc ore of the MOB is hosted by limestone and low magnesium dolomitic limestone. The primary sulphide ore is completely oxidised. Based upon the composition of the sulphide ore of the VOB the supposed main sulphide mineral association of the MOB zone was galena-sphalerite-barite-pyrite.

The distribution of the mineralisation and the ore textures are highly dependent on the scale of observation. The occurrence of the ore is strata-bound on a regional scale, but underground the mineralisation is spatially related to faults, fault-breccias, and possibly to localised (karst-) solution collapse breccias. The non-sulphide zinc ore of the MOB can be subdivided into a red zinc ore and a white zinc ore. The red zinc ore is rich in Zn (up to approximately 30%), iron (Fe app. 17%) and other metals such as Pb - (As). The white zinc ore in contrast shows typically high zinc grades (up to 40%) but low concentrations of iron (<7%) and lead and arsenic.

The most important non-sulphide zinc minerals are hydrozincite and hemimorphite. Smithsonite is also common and is detectable by XRD analyses within nearly all non-sulphide ore samples. However, smithsonite occurs only in traces. The most common XRD-detected minerals and their position within the genetic sequence of the non-sulphide ore are (Tab. 6):

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Occurrence</th>
<th>Early</th>
<th>Late</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>(Ca,Mg)CO₃</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>minor/traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barite</td>
<td>BaSO₄</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goethite/Hematite</td>
<td>FeO(OH), Fe₂O₃</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrozincite</td>
<td>Zn₅(CO₃)₂(OH)₆</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smithsonite</td>
<td>ZnCO₃</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hemimorphite-I</td>
<td>Zn₆Si₂O₇(OH)₂·H₂O</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hemimorphite-II</td>
<td>Zn₆Si₂O₇(OH)₂·H₂O</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cerussite</td>
<td>PbCO₃</td>
<td>minor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·H₂O</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coronadite</td>
<td>Pb(Mn(IV),Mn(II))₁₀O₁₆</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hetaerolite</td>
<td>ZnMn₂O₄</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary calcite</td>
<td>CaCO₃</td>
<td>minor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sauconite</td>
<td>Na₀.₃Zn₃(Si,Al)₆O₁₀(OH)₂·4(H₂O)</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mimetite</td>
<td>Pb₅(AsO₄)₂Cl</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The **red zinc ore** (Fig. 14) occurs over the full spatial range of the MOB area as lenses or irregular shaped bodies with varying dimensions that range from several metres up to several 10’s metres. The amount of red zinc ore compared with the white zinc ore increases at the upper levels. Com-
mon minerals of the red zinc ore are Fe-oxyhydroxides, goethite, hematite, hemimorphite, hy-
drozincite, smithsonite, and cerrusite. These minerals occur as a matrix of a carbonate breccia with limestone clasts of a broad size range (cm up to several dm). Hemimorphite, a zinc-hydro-silicate, is one of the most important zinc minerals of this ore-type, although the ore is carbonate-hosted.

The occurrence of the white zinc ore (Fig. 15) is similar to the red zinc ore. The ore zones are irregular shaped and varying form several meters up to several 10’s of metres. The size and occurrence of this ore increases with depth and is most common at the base level adits of the MOB. Most common minerals of this ore type are hydrozincite, smithsonite, and hemimorphite. Iron-bearing minerals are rare compared with the red zinc ore. Hemimorphite is less common compared with the red zinc ore. These minerals occur as a fine-grained cement of a carbonate karst-collapse breccia. The size of the breccia clasts is similar to the red zinc ore and ranges form cm to several dm.

Hemimorphite occurs as two different types: hemimorphite-I and hemimorphite-II. Hemimorphite-I represents sub- to anhedral crystals and masses within the matrix of the breccias. The size of the crystals is up to 200 μm. This hemimorphite-I is highly corroded, partly dissolved, and associated with fine-grained coatings, which mainly consist of hydrozincite, smithsonite and traces of goethite, hematite, and other Fe-oxihydroxides (Fig. 16, Fig. 17, and Fig. 20). Locally, goethite and hematite are absent, and here the highly corroded hemimorphite-I is associated with white, fine-grained hydrozincite and minor amounts of smithsonite. Fe-oxihydroxides (goethite, hematite etc.), associated with hemimorphite-I, show partly high concentrations of zinc (approximately 15 %, SEM-EDX), which is probably the result of high dispersed hydrozincite or due to zinc adsorption by goethite (ANKOMAH, 1992). Several mechanisms are proposed by ANKOMAH for the adsorption of Zn by goe-
thite: (i) the adsorption of the metal on external surfaces, (ii) solid-state diffusion of the metal from external to internal binding-sites, and (iii) metal binding and fixation at positions within the goethite particles.

Hemimorphite-II occurs commonly in veins and open spaces of fault zones and-breccias (Fig. 18

Fig. 14: Red zinc ore from MOB, adit no. 2. The red-
dish-brown colour is due to the high Fe-concentration of this ore type. Common minerals are goethite, hematite, hemimorphite, hydrozincite and traces of smithsonite.

Fig. 15: White zinc ore from the MOB, adit no. 1. Host rock carbonate clasts with fine-grained hydrozincite and traces of smithsonite occur as cement of this breccia.
and Fig. 21), and in the matrix of fault breccias as euhedral crystals, which have grown perpendicular to the underlying surface of fractures and spaces. The size of the hemimorphite-II is up to 300 μm. The occurrence of hemimorphite II is mainly limited to the red zinc ore and hydrozincite and/or smithsonite-mineralised zones and grows preferentially onto these Zn-rich minerals. Thus, hemimorphite is related to relatively late stages of the formation of the MOB.

**Hydrozincite** is another major component within the non-sulphide ore of the MOB and is the main mineral of the breccia matrix within the white zinc ore but is also common in the red zinc ore and occurs commonly as 10 to 100 μm euhedral crystals. Hydrozincite occurs also within the red zinc ore as one of the main zinc minerals and is often associated with highly corroded hemimorphite-I. Additionally, hydrozincite is the predominant zinc mineral within several cm/dm sized faults and fault-related breccia zones. Smithsonite is rare at the MOB. It can be detected with XRD-analyses, but was not found with SEM and microscope. Thus, the occurrence of smithsonite is presumably high-disperse, fine crystalline and occurs only in traces.

**Cerussite and mimetite** are the main lead-bearing minerals of the MOB, whereas segnitite occur-sonly in traces. Cerussite occurs predominantly as crystals related to late-stage precipitations within fractures and pores of the red zinc ore, especially regionally bound and limited to fault- and fracture zones. However, cerussite occurs also rarely within the white zinc ore, preferentially within fractures and pores. Mimetite occurs commonly as yellow needles and aggregates (Fig. 22). Other zinc minerals, such as hetaerolite, coronadite, willemite, or sauconite are rare and are also associated with both ore types. Black coloured hetaerolite forms mm-thick crusts and masses within pores and fractures, suggesting a late stage-related precipitation.

The supergene, non-sulphide ores are characterised by very high Zn-, varying Pb-, and very low Ag-contents (Tab. 7). However, unexpectedly high concentrations of As, Sb, Tl, and Sr within the red zinc ore, point to (a) complex and exotic metal source(s) than expected for typical carbonate-hosted Zn-Pb deposits. A hydrothermal input from a magmatic source appears to be likely.
Fig. 16: SEM-photograph of a boxwork structure, which consists of zinc (hydro-)-carbonates (hydrozincite/smithsonite) and porous goethite. Hemimorphite-I occurs commonly in the centre of the boxwork structures (arrow). Sample M02114.

Fig. 17: SEM-photograph of a boundary between hemimorphite-I (white arrow) and hydrozincite (orange arrow). The boundary surface is irregular and porous and due to as an alteration and replacement of hemimorphite-I with hydrozincite. Sample M02127.

Fig. 18: SEM-photograph of euhedral hemimorphite-II (arrow) growing in vugs and fractures of the breccia matrix, which consists of fine-grained goethite, hydrozincite and hemimorphite-I. (Sample M02108)

Fig. 19: SEM-photograph of a mimetite aggregate (arrow) and small grains of anhedral barite. The mimetite aggregate consists of small euhedral crystals (white arrow). Sample M02124.

Fig. 20: The thin section shows hemimorphite-I (H), which is replaced by goethite, hydrozincite, and smithsonite. Sample M02132, reflected light.

Fig. 21: Hemimorphite-I (black arrow) botryoidally overgrown by layers of goethite and hematite and late stage euhedral hemimorphite-II (white arrow) within a vug. Sample M02133, reflected light.
Results

Fig. 22: SEM-picture of euhedral mimetite, which appears to be partly embedded within a sub-mm thick coating of an unidentified fine-grained (amorphous?) Fe-oxide/hydroxide. A XRD analysis of this Fe-bearing mineral shows no unequivocal results. Sample M02123

Fig. 23: SEM-photograph of linear ordered small, subhedral grains, which consist of barite. The barite is probably weathered and corroded into numerous rounded grains. Sample M02124.

Fig. 24: SEM-EDX element distribution maps of a polished thin-section of sample M02133. Hemimorphite is overgrown by layers of goethite and hematite. The picture, which is marked by “SE”, shows a secondary electron image, and the other two images show element distribution maps of iron (FeKa) and silica (SiKa). The FeKa-picture points to the Fe-bearing layers, whereas the SiKa marked picture indicates the distribution of the Si-bearing hemimorphite. The width of the field of view is 120 μm. Hemimorphite (high Si concentration) in the innermost part of botryoidal-shaped aggregates is probably altered to goethite/hematite (high Fe concentration), which occurs as several, parallel layers. Lighter grey colours indicate a high amount of a specific element. All pictures show the same area.

The minerals and their occurrence suggest several stages of non-sulphide zinc ore genesis, during which formation, dissolution, and re-precipitation appear to have been competing processes with hemimorphite and hydrozincite being the ore minerals.
Hemimorphite-I and hemimorphite-II represent different stages of the ore-forming process of the MOB. After TAKAHASHI (1960) and INGWERSEN (1990), the precipitation of hemimorphite can be described as an equilibrium reaction between hemimorphite and smithsonite/hydrozincite, which is mainly controlled by the partial pressure of CO₂ (P_{CO₂}), pH, and the concentration of H₂SiO₄. Hemimorphite becomes more stable under relatively low P_{CO₂} (< 10⁻² bar) and low pH (< 6.9) conditions. After the formation of a hemimorphite-dominated ore, the geochemical conditions have apparently changed. Hemimorphite became unstable under these new conditions, and was (partly) replaced by hydrozincite. The stability of hemimorphite and the equilibrium reaction between hemimorphite and smithsonite/hydrozincite are shown in detail in chapter 5.4.1 (page 90).

C-O stable isotope geochemistry of carbonates of the MOB

Carbon and oxygen isotope measurements have been applied to samples of the MOB. These samples comprise limestones of the barren host rock, hydrozincite from the non-sulphide zinc ore, and euhedral calcites, which fill open spaces and fractures. The results of the isotopic measurements are presented in Tab. 8 and depicted in Fig. 25. The isotope compositions are expressed as delta values in ‰ relative to V-SMOV for oxygen and relative to V-PDB for carbon.

The diagram (Fig. 25) shows three separate clusters: (1) limestone samples of the host rock, (2) samples of calcite crystals, which occur as fillings in fractures and open spaces of the carbonate host rock, and (3) hydrozincite/smithsonite samples of the MOB. However, the hydrozincite cluster...
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comprises an additional single calcite sample, which plots within in the area of the hydrozincite.

The hydrozincite samples have not a monomineralic composition, since the mineralogy of the zinc-carbonates is relatively complex. Hydrozincite is commonly contaminated by traces of smithsonite and in most cases it is not possible to separate hydrozincite from smithsonite impurity, due to its microcrystalline intergrowth with hydrozincite. Thus, the result of the isotopic measurement of the hydrozincite may be influenced by the isotopic composition of smithsonite.

The analysed limestone samples of the MOB form a separate cluster (Fig. 25) and show a restricted range of both $\delta^{13}$C (between 2.2 and 2.9 $\%$) and $\delta^{18}$O values (between 22.4 and 25 $\%$). The calcite samples form a second cluster. Calcite occurs as euhedral crystals, grew in open spaces and fractures of the limestone. These calcites show an close range of $\delta^{13}$C (between 0.7 and 2 $\%$) and $\delta^{18}$O (between 15.1 and 16.8 $\%$). The third field consists of samples of hydrozincite of the non-sulphide ore from the MOB. The hydrozincite samples show a restricted range of $\delta^{18}$O values between 20.4 and 21.9 $\%$. The $\delta^{13}$C values are more variable and range between -0.4 and -3.8 $\%$. A single calcite sample fits in this field of hydrozincite samples.

The isotope values of the limestone correspond to the range of values, which has been established as typical for marine Cretaceous limestones (VEIZER & HOEFS, 1976).

The calcites of the MOB plot within two distinct regions. Thus, the isotopic composition of the calcites from the MOB suggests two different possible genetic sources. Three samples of calcite show lower $\delta^{18}$O (15.1-16.8 $\%$) and higher $\delta^{13}$C (0.7-2.0 $\%$) compared to a single calcite sample, which is relatively high in $\delta^{18}$O (21.4 $\%$) and low in $\delta^{13}$C (-0.4 $\%$). The $\delta^{18}$O of a carbonate precipitated from water depends on the $\delta^{18}$O composition of the water and the temperature. Increasingly lighter

Fig. 25: Stable carbon and oxygen isotope composition of hydrozincite, late-stage related calcite, and limestone from the MOB of the Mehdi Abad Zn-Pb deposit.
δ\(^{18}\)O values tend to be associated with a decreased salinity and with higher temperatures, whereas the δ\(^{13}\)C composition reflects the source of the bicarbonate, which is dissolved in the water (NELSON & SMITH, 1996). Thus, the only slightly decreased δ\(^{13}\)C values of the calcite veins are due to a buffer effect from the limestone. The negative trend in the δ\(^{18}\)O values of the calcites may reflect precipitation at higher temperatures and is typical for burial (CHOQUETTE & JAMES, 1990; NELSON & SMITH, 1996).

The single calcite sample, which plots within the field of the zinc carbonates, suggests an influence of meteoric water, which delivered isotopically light carbon from the decomposition of organic matter. The δ\(^{13}\)C is moderately depleted and the calcite has been presumably precipitated under the influence of meteoric waters, which are variably buffered by water-limestone interaction (ALLAN & MATTHEWS, 1982; NELSON & SMITH, 1996).

The isotopic pattern of the hydrozincite samples shows a narrow range of δ\(^{18}\)O values and a more variable range of δ\(^{13}\)C data. This behaviour is similar to smithsonite samples, which have been analysed by GILG & BONI (2004) and BONI ET AL. (2003). This probably indicates at least two isotopically different sources of carbon. The roughly constant δ\(^{18}\)O values and the variably low- to medium depleted δ\(^{13}\)C values match the idealised trend of a meteoric carbonate precipitation. Thus, wide variability in δ\(^{13}\)C and narrow variability in δ\(^{18}\)O most likely reflect the influence of meteoric water associated with subaerial exposure (ALLAN & MATTHEWS, 1982, LOHMANN, 1988) and point to the precipitation of the zinc carbonates within the vadose and/or phreatic zone (ALLAN & MATTHEWS, 1982). The isotopically light component of the carbon is the result of dissolved CO\(_2\) derived from the decay of organic matter (CRISS, 1995).

4.1.4 The Valley Ore Body (VOB) of Mehdi Abad

Geology of the Valley Ore Body

The strata of the Taft and Abkou Formation overlie the Sangestan Formation and host the sulphide ore of the Valley Ore Body (VOB) (AZARI & SETHNA, 1994). The Sangestan Formation consists mainly of partly cross-bedded sandstone (Fig. 26), limestone, and shales. The strata of the Taft Formation consist mainly of dolomitic and ankeritic limestone, whereas the Abkou Formation comprises marlstone with conglomeratic intervals, and massive limestone.

The contact zone between the Sangestan and Taft Formation is characterised by an unconformity, which shows an irregular surface with shallow water sediments between the para-reef limestone (Fig. 27) at the top of the Sangestan Formation and the limestone of the Taft Formation. These shallow water sediments consist of red and green mudstone with worm tubes, nodular limestone, and cross-bedded limestone (BRGM, 1993). This zone probably reflects a period of emergence and has been used as a marker horizon in the drill cores. Most of the drill cores of Mehdi Abad stop at this horizon.
Results

The strata of the Taft Formation, which host the main portion of the sulphide ore of the VOB are characterised by an intensive and extensive brecciation. This brecciation is common within most of the VOB drill-cores of Mehdi Abad (BRGM, 1993) and is probably the result of emergence, paleo-carstification, and finally collapse of these strata. The breccia fragments are angular and the fragment-size ranges from a cm- to dm-scale.

The contact zone between the Taft- and the overlaying Abkou Formation is characterised by an unconformity, similar to the contact zone of the Sangestan- and Taft Formation. Here, the cherty limestone of the Taft Formation shows a channelled surface, overlain by a conglomeratic bed, which consists of limestone and chert clasts (BRGM, 1993) and can be interpreted as a renewed period of emergence and probably the stage, during which karstification and collapse of the Taft Formation occurred.

Ore mineralogy of the VOB

Examinations of several samples and detailed investigations of bore holes no. 5308, 5204, and no. 7008 (Fig. 11) show, that the sulphide ore of the VOB consists of several subordinate mineralised zones, which are separated by barren dolomite of the Taft Formation as well as several faults.

The most abundant minerals within the sulphide ore are galena, sphalerite, barite, pyrite, and traces of chalcopyrite. The sulphide ore of the VOB occurs as impregnation of the Taft Formation breccia and fills the interstitial space between the breccia fragments (Fig. 28). Sample examination and literature data as well (e.g. AZARI & SETHNA, 1994) show, that the main sulphide minerals of the VOB are sphalerite, galena, pyrite and traces of chalcopyrite, and other sulphides. Other sulphides, such as marcasite or chalcopyrite in subordinate traces. Disseminated sulphides occur commonly as low-grade mineralisation within the barren dolomite and the adjacent strata. The sulphide mineralisation is not associated with conventional vein-system or with synsedimentary stratiform horizons, but occurs as matrix in a complex fracture and breccia system (Fig. 28). In some cases, the sulphide ore itself occurs as breccia fragments (Fig. 29). Pyrite occurs as angular crystals and masses accompanied with Zn and Pb sulphides or as spherical framboidal pyrite within dolomite and limestone.
It appears that sphalerite and galena have been partly replaced the barite of the dolomite breccia (Fig. 31 and Fig. 32). The sulphide mineralisation occurs as fine-grained crystals in a wide range from euhedral to anhedral crystals. The observed sphalerite/barite ratio changes irregularly but is generally between 1/1 and 2/1, which is in general agreement with the reported ratio of 1 (BRGM, 1993).

**Barite** is ubiquitous within the mineralised dolomite breccia as well as in fractures, veins, and veinlets within the non-brecciated barren dolomite and limestone of the Taft Formation and Abkouh Fm. Additionally, massive barite occurs in the Black Hill area, but only with a slight amount of sulphide mineralisation. In most cases, the barite tends to have grown with a euhedral habit but occurs also as anhedral patches or skeletal crystals. The size of barite crystals varies over a wide range from microcrystalline sub-mm to cm-sized euhedral crystals. The barite grew in pores and open spaces of dolomite. The crystal-size has been probably controlled by the space of the hosting cavities. Locally, barite occurs as broken crystals and is observable in several thin sections. The space between these barite fragments is filled with fine-grained carbonate cement (Fig. 30). The observable barite deformation and the subsequent carbonate cementation of the barite fragments are probably due to a pre- or syn-collapse barite-mineralising event. The barite crystals grew in pores and open spaces of the karstic carbonate and have been deformed and crushed as a result of collapse and compaction of this karst-breccia.

The **dolomite**, which hosts the sulphide ore, is probably secondary and the result of a dolomitisation process. This dolomitisation of the carbonate host rock is possibly either associated with the barite mineralisation or with the sulphide-ore delivering fluids. It is supposed that the dolomitisation was associated with the ore fluids, since the adjacent carbonate strata (Abkou Formation) to the massive barite rock ‘Black Hill’ is not affected to any dolomitisation (Fig. 117 and Fig. 118).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Occurrence</th>
<th>Early</th>
<th>Late</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>(Ca,Mg)CO₃</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>minor/traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barite</td>
<td>BaSO₄</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goethite/Hematite</td>
<td>FeO(OH), Fe₂O₃</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrozincite</td>
<td>Zn₅(CO₃)₂(OH)₆</td>
<td>common</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smithsonite</td>
<td>ZnCO₃</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hemimorphite</td>
<td>Zn₃Si₂O₁₁(OH)₆·H₂O</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cerussite</td>
<td>PbCO₃</td>
<td>minor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·H₂O</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coronadite</td>
<td>Pb(Mn(IV),Mn(II))₅O₁₆</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hetaerolite</td>
<td>ZnMn₂O₄</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary calcite</td>
<td>CaCO₃</td>
<td>minor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mimetite</td>
<td>Pb₅(AsO₄)₃Cl</td>
<td>traces</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 28: Highly brecciated ore-bearing dolomite of bore hole no. 5308 at 212 m. The space between the fragments is filled by a grey coloured matrix of fine-grained sphalerite, galena, and barite and traces of chalcopyrite.

Fig. 29: Angular breccia fragments. The fragments consist of sulphide ore and sulphide ore-mineralised dolomite. (Photograph: G. Borg).

Fig. 30: Barite crystals in dolomite (brown colours) breccia. Some large barite crystals are broken. The space between the barite fragments (white arrows) is filled by small irregular barite fragments and a carbonate matrix. Bore-hole no. 5308 at 226 m. (transmitted light, XN)

Fig. 31: Barite crystals of bore-hole 7008 at 216 m in dolomite (do). Most of barite-crystals (ba) show a euhedral to subhedral shape. In some cases, the barite has been incompletely replaced by galena (ga) and sphalerite (green coloured, sp). Pyrite is rare at this depth and absent in this field of view. (SEM-BSE photograph)

Fig. 32: Barite (ba) is partly replaced by sphalerite (green colour, sp) and galena (ga). Sphalerite and galena are the most common sulphides. Pyrite and other sulphide minerals are generally rare and absent in this thin-section. In some cases, dolomite occurs as euhedral rhombs with crystal sizes up to 200 μm. SEM-BSE photograph of borehole 7008 at 295 m.
4.1.5 Geochemical investigations of the MOB and the VOB

A total of 19 samples of the MOB (hand specimen) and 109 samples of the VOB (drill core and hand specimen) have been analysed by ICP-MS.

Cadmium in the sulphide ore and in the non-sulphide ore

Cadmium is associated with most Pb-Zn deposits (SCHWARTZ, 2000). In particular, the behaviour of Cd during oxidation and the formation of non-sulphide ore are very interesting. The Cd-concentration within the sulphide ore of the VOB was examined in several sulphide mineralised samples. The measured concentration varies in a wide range from 0.3 ppm up to 583 ppm. The relationship of cadmium to other elements has been tested by plotting several graphs, but exclusively the Zn-Cd plot shows a significant positive correlation (Fig. 33). The incorporation of Cd into sphalerite is a common phenomenon (DOMÈNECH et al., 2002) and based on these results, it can be assumed that sphalerite, which is the main zinc-bearing mineral, is the predominant host mineral to cadmium within the sulphide zone. The Cd-Zn (R_Cd/Zn) ratio is nearly constant and gives results of approximately R_Cd/Zn = 0.004 (n=19, stdev = 9.1·10^{-4}). With the molar masses of zinc, sulphur, and cadmium (M_Zn=65.38, M_S=32.06, M_Cd=112.4 g/mol) it is possible to calculate the concentration of cadmium in a simplified (Zn(1-x),Cd_x)S - sphalerite (formula F1).

\[
n \text{Cadmium concentration (Cd)} = \frac{m_{\text{Cd}}}{m_{\text{Zn}} + m_{\text{Cd}}} \times 10^6
\]

This calculation gives an average concentration of 2682 ppm cadmium in sphalerite or 0.27% Cd. However, in most cases the real cadmium concentration of sphalerite is smaller than the calculated value, due to additionally incorporated iron and other elements into the sphalerite crystal lattice. Nevertheless, the calculated (maximum-) concentration of cadmium within the sphalerite is comparable to MVT-type deposits (Tab. 10) (SCHWARTZ, 2000) and fits also within this range even at lower Cd-concentration values. However, this value fits also to a wider spectrum of deposit types within the range of Cd concentrations of each type. According to Tab. 10, Mississippi-Valley type (MVT) deposits show the significantly highest concentrations of Cd in sphalerite (Cd_{sp}). The high Cd_{sp} is caused by the high R_Cd/Zn of basinal brines, which can be considered to be the recent equivalents of MVT fluids (Schwartz, 2000). The Cd-content depends on the R_Cd/Zn ligand activities, and temperature of the ore forming fluid. Thus, exhalative systems with their low R_Cd/(Zn+Cd), and high temperature form deposits with lower Cd concentration in sphalerite (SCHWARTZ, 2000).

The average Cd concentration of the non-sulphide ore of the MOB is similar compared with the sulphide zone of the VOB. However, several extreme values of MOB non-sulphide-related Cd-concentration can be as high as 2004 ppm in whole rock ore samples.
Tab. 10: Basic statistical concentrations for Cd concentration in sphalerite of different deposit types (after Schwartz, 2000)

<table>
<thead>
<tr>
<th>Type of deposit</th>
<th>min</th>
<th>max</th>
<th>mean</th>
<th>median</th>
<th>st. deviation</th>
<th>n of deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td>VMS</td>
<td>100</td>
<td>10000</td>
<td>2360</td>
<td>1890</td>
<td>1.777</td>
<td>87</td>
</tr>
<tr>
<td>SEDEX</td>
<td>50</td>
<td>6250</td>
<td>2560</td>
<td>2200</td>
<td>1735</td>
<td>19</td>
</tr>
<tr>
<td>Skarn</td>
<td>300</td>
<td>9900</td>
<td>3540</td>
<td>3180</td>
<td>2192</td>
<td>54</td>
</tr>
<tr>
<td>Veins in low carbonate rock</td>
<td>15</td>
<td>46480</td>
<td>410</td>
<td>3110</td>
<td>4212</td>
<td>155</td>
</tr>
<tr>
<td>Veins in limestone/dolomite</td>
<td>1000</td>
<td>20000</td>
<td>7260</td>
<td>5000</td>
<td>6256</td>
<td>31</td>
</tr>
<tr>
<td>MVT</td>
<td>390</td>
<td>50000</td>
<td>4850</td>
<td>3630</td>
<td>5668</td>
<td>106</td>
</tr>
<tr>
<td>Sandstone lead-zinc</td>
<td>2570</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Unclass., in limestone/ dolomite</td>
<td>560</td>
<td>21500</td>
<td>4300</td>
<td>2540</td>
<td>4830</td>
<td>27</td>
</tr>
</tbody>
</table>

Cd\textsubscript{sphalerite} concentration in ppm

A possible host mineral for cadmium within the non-sulphide ore is smithsonite. Similar to sphalerite, smithsonite is able to hold up to 45500 ppm Cd (Schwartz, 2000). Smithsonite occurs only in traces in the MOB and, in contrast to Cd within VOB sulphide ore, the cadmium in MOB non-sulphide ore shows no significant correlation with Zn (Fig. 34). One reason might be the high density of faults and the associated alteration, oxidation and mobilisation of zinc minerals, which might have led to a partial separation of zinc from cadmium and, as a result of this process; to a poor correlation. Another possible explanation might be two different generations of Cd-bearing minerals, associated with the major non-sulphide ore types of MOB, the Fe-rich and the Fee-poor ore. Greenockite (CdS) could not be detected as a Cd-bearing mineral that is commonly associated with supergene zinc mineralisation (Takahashi, 1960). The abundance of greenockite within the alteration and non-sulphide zone can be explained by the scavenging of zinc during (re-) crystallisation from non-sulphide zinc minerals, such as smithsonite, hemimorphite, and hydrozincite (Schwartz, 2000).

Fig. 33: Zn-Cd concentration plot of specimen from the sulphide ore of the VOB. The Cd concentration correlates with Zn. and is bound to sphalerite of the sulphide ore. (criteria: sulphide-bound sulphur >3%)

Fig. 34: Zn-Cd concentration plot of specimen from the red zinc ore (red triangles) and white zinc ore of the MOB. In contrast to Fig. 33, no correlation is determinable between the zinc and cadmium contents.
Arsenic in sulphide and non-sulphide ore

Arsenic occurs in the sulphide ore of the VOB as well as in non-sulphide ore of VOB and MOB. The arsenic concentration within the non-sulphide ore of the MOB $\text{CAS-OX-MOB}$ is up to factor 30 higher than concentrations in the non-sulphide ore $\text{CAS-OX-VOB}$ respectively. Similar to cadmium, sphalerite is able to incorporate arsenic into its crystal structure (LEACH ET AL., 1986) but no correlation to sphalerite could be found within the sulphide bearing samples of the VOB. This phenomenon is supported by additional SEM-EDX examinations of sphalerite. The measurements show no arsenic content. Another possibility is the incorporation of As within pyrite. Here, the overall theoretic possible compositional range for arsenic in pyrite is approximately up to 100000 ppm (KOLKER & NORDSTROM, 2001). However, the measurements of sulphide ore samples show bad or no correlation of iron with arsenic. Thus, the arsenic of the sulphide ore is probably bound to pyrite, but with a broad varying range of As-concentrations and is probably also bound to minerals such as arsenopyrite (FeAsS).

The plots of As vs. Pb give a hint of an As-Pb bearing mineral within the non-sulphide ore of the MOB. The ratio $\text{CAS-Ox/C Pb-Ox}=0.18$ of white zinc ore of the MOB is apparently related to mimetite. The $\text{CAS-Ox/C Pb-Ox}$ of mimetite can be calculated by using the formula and the molar masses of As and Pb and is calculated as $\text{CAS-mimetite/C Pb-mimetite}=0.22$. This value is close to the As/Pb ratio of the white zinc of the MOB that suggests mimetite as one As-bearing mineral. In addition with cerussite, which is also detectable in the white zinc one can achieve the lower As/Pb ratio of 0.18 from Fig. 36.

![Fig. 35: Bivariate graph of As vs. Pb of non-sulphide zinc ore, and sulphide ore samples of the VOB. The value of $R^2$ gives no positive correlation between these elements, but a rough trend is visible, especially at samples of the Oxide zone.](image1)

![Fig. 36: Concentration of arsenic in relation to lead of non-sulphide ore-samples from the MOB. The red dots represents specimen, which are characterised by high Fe$_2$O$_3$ (>10%). The black dots represent ore, which is low in Fe$_2$O$_3$ (<5%).](image2)
Results

Fe-concentrations in sphalerite of the VOB

The iron-concentration in sphalerite has been measured in sulphide-ore thin-sections of bore-hole No. 5308 and 7008 by SEM-EDX. All data of bore-hole 5308 show a continuous trend of increasing iron-concentrations with depth (Fig. 37). The highest Fe-concentration has been measured at a level of 275 m of borehole 5308. Here the Fe-content of sphalerite ranges from 6.3 % up to 11.8 % with a mean of 8 %. The iron-concentration at each level of borehole 5308 varies on a wide range of approximately 5 % of the mean.

The iron-concentration pattern of borehole 7008, which intersects the sulphide ore body approximately in its centre, is completely different from borehole 5308. Nearly all samples of borehole 7008 show a low Fe-concentration within sphalerite (Fig. 37) with no apparent visible trend.

The iron content of sphalerite depends on the geochemical parameters of the system pyrite – pyrrhotite – sphalerite and is very sensitive to pressure, sulphur fugacity, and temperature (BARTON & TOULMIN, 1966). As a result of these different variables, this system is only useful in geothermometry for three-phase assemblages of sphalerite – pyrite – pyrrhotite in which the sulphur fugacity is fixed at a given temperature by the coexisting iron sulphides under equilibrium conditions (SCOTT & BARNES, 1971).

Examinations of specimen from bore hole 7008 and 5308 has shown a dominance of galena and sphalerite, but only small amounts of pyrite and no pyrrhotite. Since the Fe-content of sphalerite is quite variable in the absence of pyrite and/or pyrrhotite (CRAIG & SCOTT, 1974), the iron concentration within the sphalerite cannot be used for geothermometry in this case.

The iron concentration within the sphalerite is controlled over a wide range only by the activity of FeS (a FeS). High values of a FeS result in sphalerite with high Fe-concentrations (CRAIG & SCOTT, 1974). This leads probably to decreasing a FeS, which is associated with decreasing Fe concentrations of sphalerite.

Since the Fe-concentration of most ore-fluids increases with higher fluid-temperatures (MARIE ET AL., 2001), the gradient of the Fe-concentration with depth could additionally be the result of decreasing temperature during the hydrothermal pulse of the ore-mineralising event. Lower temperatures (probably more distal to the vent) decrease the Fe-concentration of the fluids and leads to the crystallisation of sphalerite with lower Fe content relative to the more proximal high-temperature
sphalerite.

The increase of Fe-concentration with an increase of depth in borehole 5308 is probably an indication for an upward directed hypogene ore fluid-flow within this ore body. Fe-rich sphalerite crystallised when the Zn-bearing fluids reached the (collapse-) breccia. This led to an iron depletion of the mineralising fluid, associated with the crystallisation of sphalerite at higher levels, which is low in Fe. The same mechanism of Fe-depletion is probably active during the lateral fluid flow. Therefore, the low Fe-concentration in sphalerite in borehole 7008 could point to a lateral mineralisation process with its origin in the western part of the sulphide ore body.

Based on the gradient of the Fe-concentrations within the ore body, a possible source (vent) for the ore fluids might have been located at the western outskirt of the sulphide ore body, probably near the Black Hill Fault.

Another possible explanation for diverse Fe-contents in sphalerite could be different generations of Zn-Pb-Fe delivering fluids that could cause these different Fe-fingerprints of sphalerite. The examined boreholes show completely different Fe-concentration patterns. The Fe-content of bore hole 5308 increases continuously with depth, whereas nearly all samples of bore hole 7008 show very low iron concentrations, which are absent in bore hole 5308. The exclusive occurrence of low-Fe sphalerite in borehole 7008 suggests at least two different fluid generations with a spatially independent occurrence. The controlling factor for the spatial separation could be probably faults.

Occurrence of zinc and lead

The main zinc mineral of the VOB is sphalerite and subordinately non-sulphide zinc minerals, such as hydrozincite, smithsonite, willemite, and hemimorphite. In contrast to the completely oxidised MOB, the VOB comprises both sulphide ore and non-sulphide ore as well. However, the occurrence and the style of the non-sulphide ore are different from that of the MOB. The actual data of the calculated Zn-Pb reserves are (Tab. 11):

<table>
<thead>
<tr>
<th>Tab. 11: Zn-Pb reserves of Mehdi Abad.</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxide reserve</td>
</tr>
<tr>
<td>sulphide reserve</td>
</tr>
<tr>
<td>data: MEHDI ABAD ZINC COMPANY, 2005</td>
</tr>
</tbody>
</table>

Typical zinc and lead concentrations of the VOB are given in Tab. 12. The non-sulphide zinc ore of the VOB reaches Zn concentrations of approximately 8.4 % Zn and 2 % Pb. The zinc concentration of the VOB- non-sulphide ore is neither significantly increased nor is the Zn/Pb ratio significantly changed with regard of the sulphide protore, in contrast to the MOB, where both mentioned effects are observable.
Tab. 12: Element concentrations of the VOB and MOB

<table>
<thead>
<tr>
<th>Element</th>
<th>VOB NS₁ (low grade)</th>
<th>VOB NS₁ (high grade)</th>
<th>VOB¹ Sulphide ore</th>
<th>MOB NS red zinc ore</th>
<th>MOB NS white zinc ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn %</td>
<td>2.8</td>
<td>8.4</td>
<td>7.2</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Pb %</td>
<td>2.5</td>
<td>2</td>
<td>1.6</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>Cu %</td>
<td>0.11</td>
<td>0.03</td>
<td>0.16</td>
<td>&lt;0.01%</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>Ag [ppm]</td>
<td>45.9</td>
<td>23</td>
<td>52</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>As [ppm]</td>
<td>112</td>
<td>305</td>
<td>269</td>
<td>11613</td>
<td>1985</td>
</tr>
<tr>
<td>Cd [ppm]</td>
<td>87</td>
<td>182</td>
<td>1634</td>
<td>307</td>
<td>480</td>
</tr>
<tr>
<td>Fe %</td>
<td>23</td>
<td>21</td>
<td>20</td>
<td>17.5</td>
<td>1.89</td>
</tr>
<tr>
<td>Mn [ppm]</td>
<td>4.6</td>
<td>7.6</td>
<td>3.9</td>
<td>0.07%</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>SiO₂ %</td>
<td>5</td>
<td>5</td>
<td>16.2</td>
<td>15</td>
<td>14</td>
</tr>
</tbody>
</table>

NS = non-sulphide ore, (¹) Data: ITOK INTERNATIONAL, 2005

The occurrence of zinc within the sulphide zone of the VOB is generally similar to and associated with that of lead, but concentrations are of a higher magnitude. In borehole no. 5308, zinc and lead concentrations increase generally from a depth of 450 to 256 m (Fig. 38) to a maximum of approximately 10000 ppm. The Zn-Pb content increases rapidly within the sulphide zone up to approximately 100000 ppm for zinc and 31000 ppm for lead. With the transition to the gossan zone, the similar trends stops and lead concentration increases much more than those of zinc do. Here, the graph can be interpreted as retention of (relatively immobile) lead and arsenic and a remobilisation or loss of (soluble) zinc. This is probably an effect of a diverse mobility of these elements during alteration processes and is well known for gossan zones in general (BOYLE, 1993). The most common zinc-bearing mineral within the sulphide zone is sphalerite, but in the non-sulphide, and gossan zone hemimorphite, smithsonite, and hydrozincite are the most common Zn-minerals. Lead occurs as
galena within the sulphide ore, and within cerussite, mimetite, and minor amounts of coronadite in non-sulphide ore.

The non-sulphide zinc ore overlays the sulphide ore (Fig. 38) and is mainly restricted to fault-zones (BRGM, 1994) or is well developed at these zones. The concentration of zinc within these oxidised zones is low compared to the equivalent ore type of the MOB. The non-sulphide ore of the VOB is predominately Fe-(Mn)-rich and shows no distinct tendencies of metal-separation and differentiation into a red zinc ore and a white zinc ore.

The geochemical data of borehole no. 5204 show an unusual pattern (Fig. 39). Here, the concentration of zinc is consistently higher than the concentration of lead, despite the presence of a continuously oxidised zone without sulphide intercalations.

Fig. 40: Schematic cross section of drill core no. 5204 and its related strata. The meteoric water is guided along the oxidised, ‘gossanous’, and porous contact zone between the Taft Fm. and Sangestan Fm.. Zinc has probably been dissolved in the upper parts and (re-) precipitated in lower portions of the gossanous horizon.

Fig. 41: Cross-section of the VOB. Boreholes and the Zn (sulphide and oxide) and Pb concentrations are plotted to illustrate the occurrence of the sulphide and non-sulphide ore types. The non-sulphide mineralised zone overlays the sulphide ore. The overall Zn-concentration of the non-sulphide zinc ore is limited to relatively low Zn-concentrations (2-8% Zn) compared with the MOB. (modified after BRGM, 1994)
This effect of increasing Zn concentrations and a lead-zinc ratio Zn/Pb>1 within the gossan can be explained by the geologic position of this bore hole (Fig. 40). The gossan is restricted to the contact between the Taft Formation and the subjacent Sangestan Formation. The gossan and the contact zone dip to the west. It can be assumed, that meteoric water migrated along this path through the porous gossan. Thus, it is proposed that the dissolved zinc has been transported from upper parts of the gossan to lower regions where it became re-precipitated. This supergene process led to an enrichment of zinc within the lower parts of this gossan section and is probably an important factor for Zn-enrichment in similar regions of this deposit. The geochemical conditions of zinc mineral dissolution and precipitation in carbonate host rocks are described in detail in Chapter 5.4 (page 90).

The non-sulphide ore of the MOB shows no level-dependent systematic vertical trend in its Zn/Pb distribution. The ratio remains relatively constant at approximately Zn_Pb = 15-20 except for few extreme values. Under the assumption of a decreasing mobility of the metals Zn >> As >> Pb (BOYLE, 1993) and a Zn/Pb ratio of a supposed sulphide protore Zn_sulph/Pb_sulph = 2, the non-sulphide ore of MOB must have been affected by an enrichment process for zinc, which has led to a contemporaneous decreasing concentration of Pb and Fe_2O_3 (Fig. 42). The result of this process is a non-sulphide ore with a wide range of Fe_2O_3, but small amounts of lead only.

The Zn-rich zinc-rich cluster of Fig. 42 marks a non-sulphide ore, which is probably the result of Zn-mobilisation, displacement and reprecipitation, whereas iron remained as a relative immobile element.

**Copper**

The copper concentration in the examined drill core samples of sulphide ore is much higher than in non-sulphide ore samples of the MOB. The concentrations within the non-sulphide ore of the MOB range up to 200 ppm. These values are very low, compared to the gossanous zone of the VOB, which shows Cu concentrations up to 2.000 ppm. In contrast to the low Cu content of non-sulphide MOB ore, the examined drill core of sulphide ore contains up to 2400 ppm Copper. The copper
within the sulphide zinc ore is commonly related to chalcopyrite and the carbonate mineral malachite, whereas copper of the gossan zone seems to be bound to malachite.

**Occurrence of silver in the sulphide ore of MOB**

The sulphide ore of the Valley Ore Body (VOB) of Mehdi Abad shows silver concentrations up to 350 ppm. In contrast to these relatively high concentrations, the non-sulphide ore of both the VOB as well as the non-sulphide ore of the Mountain Ore Body (MOB) show only minor or background concentrations of silver. The occurrence of silver is intimately associated with the sulphide ore of the VOB, whereas the non-sulphide zone of the VOB only shows small concentrations related to the sulphide ore (approximately 10 ppm Ag). Since no specific silver bearing minerals was detectable, the purpose of the actual study was to investigate the geochemistry and the mineralogy of this silver.

Silver is common in a wide range of concentrations in different types of massive-sulphide deposits, such as MVT-, SHMS-, Irish-type and others. In these deposits, Ag occurs as Ag-bearing minerals or is predominantly associated and incorporated in sphalerite, marcasite, pyrite, and/or galena (Hangi & Paarberg, 1996; Matthies, 1996).

The analyses of sulphide ore samples of the VOB show a moderate positive correlation of the silver concentrations with lead (galena) (Fig. 44).

![Fig. 43: SEM-EDX element distribution maps of sample 5308-226. Bright areas indicate the presence of a specific element. The low Ag concentration results in a higher background noise within the Ag-element distribution map. However, silver is associated with the occurrence of lead, indicated by light colours within the galena.](image)
The diagrams, which are shown in Fig. 44, Fig. 45, and Fig. 46 indicate a binding of silver to both Pb (galena) as well as Sb and not to As. but the detailed interelement correlation plots (Fig. 4 & 5) show only for Sb a good correlation. Arsenic correlates nor or probably within a small range with silver and is highly variable. Based on these results one can assume that silver is probably bound to a Sb (and As ??) bearing mineral, such as argentian tetrahedrite ((Cu,Fe,Ag,Zn)\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13} and/or freibergite (Ag,Cu, Fe)\textsubscript{12}(Sb,As)\textsubscript{4}S\textsubscript{13}. Freibergite forms a series with tetrahedrite (Cu,Fe,Ag,Zn)\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13} with a variable Sb/As ratio. This could be one reason for the highly variable Ag/As ratio within the sulphide ore. Most of these Ag-Sb-(As) minerals probably occur within galena as μm-sized inclusions within the galena (ZENG ET AL., 2000). This explains the visible correlation of Ag with Pb in Fig. 44.

An association of silver and silver bearing minerals with sphalerite and/or pyrite could not detected by using SEM-EDX and as a positive correlation in a Zn-Ag diagram.

The silver grade of the VOB ranges from 330 ppm (borehole 5308) down to approximately 30 ppm in several other boreholes. This value is highly dependent from the galena content of the sulphide ore. However, BRGM investigations (MONTHEL, 1994) have shown up to 300 ppm Ag for the western and central part of the VOB and up to 92 ppm for the eastern part.

Fig. 44: Ag-Pb variation diagram for the sulphide ore of the VOB. Silver is associated with the occurrence of lead/galena within the sulphide ore and shows a moderate correlation.

Fig. 45: Ag-Sb variation diagram for the sulphide ore of the VOB. Silver shows a moderate correlation to Sb, which is probably due to a Sb-Ab bearing mineral.

Fig. 46: Ag-As variation diagram for the sulphide ore of the VOB. Silver shows no correlation of Sb related to Ag within the range from 0 to 180 ppm Ag.
Results

**TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and Zr in the Valley and Mountain Ore Body**

Regardless to their origin, all samples show nearly the same Ti/Al ratio (Fig. 48). This constant ratio applies to both samples of the MOB as well as samples of the sulphide- and the oxide-zone of the VOB.

Zr correlates with both Ti and Al (Fig. 47). All element pairs of Zr, Al, and Ti show a positive significant interelement correlation within the sulphide as well as the non-sulphide zone of VOB and MOB. The interelement correlation is probably the result of the occurrence of a Zr-Al-Ti bearing mineral. These elements are characteristically present in detrital aluminosilicate minerals, such as clays (Peter & Goodfellow, 1996), which could be a component of the siliciclastic sediments, carbonates, and limestones of Taft- and Abkou Formation. There is no correlation with SiO\textsubscript{2}, which is probably the effect of multiple sources of SiO\textsubscript{2} within the limestone, dolomite, siliciclastics, and the Zn-Pb ore such as quartz grains, chert, zinc-silicates (hemimorphite) and other minerals.

Since Ti, Al, and Zr are highly immobile elements in most alteration zones (Maclean & Barret, 1993; Jun et al., 1996), these elements could be residuals of a Ti-Al-Zr mineral. The Ti/Al/Zr ratio remained constant during and after the alteration of this precursor mineral, which is due to the immobility of these elements.

---

Fig. 47: The inter-element correlation between Zr and Al\textsubscript{2}O\textsubscript{3} is similar to the TiO\textsubscript{2} - Al\textsubscript{2}O\textsubscript{3} diagram. The concentrations of nearly each specimen from both the VOB (blue dots) and MOB (red triangle) show a significant positive correlation. This probably reflects the clastic component in the chemical sediments (limestone).

Fig. 48: The concentration of TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} show a highly significant correlation. All samples from the MOB as well as the VOB show nearly the same Ti/Al ratio. This is probably due to the occurrence of a Ti-Al bearing mineral or it is a relict pattern of a former Ti-Al bearing mineral. (blue=VOB, red=MOB)
Thallium content in VOB and MOB

Thallium occurs within different types of Zn-Pb deposits as a trace element and is commonly associated with sphalerite (Leach et al. 1986), pyrite, marcasite, and other sulphides (Duchesne et al., 1983), of hydrothermal mineralisation. The thallium concentration of the Mehdi Abad deposit varies on a wide range (Tab. 13). The highest concentration can be found within the non-sulphide ore body of the MOB. Here the concentration of Tl reaches up to 348 ppm whereas the concentration of Tl within the non-sulphide ore of the VOB shows values of about 1 ppm (Tab. 13). Thallium seems not to be associated with zinc or Iron – but is probably linked with As. As Domènech et al. (2002) has shown Tl is probably also associated with galena, which indicates its inclusion as trace element into the mineral galena.

Tab. 13: As and Tl mean values and their standard deviation for different ore types of Mehdi Abad.

<table>
<thead>
<tr>
<th>Ore-Type and Location</th>
<th>As [ppm]</th>
<th>As stand.dev.</th>
<th>Tl [ppm]</th>
<th>Tl stand.dev.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOB: sulphide ore</td>
<td>176</td>
<td>408</td>
<td>2.6</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>VOB: non-sulphide ore</td>
<td>145.9</td>
<td>153.9</td>
<td>5.0</td>
<td>6.6</td>
<td>8</td>
</tr>
<tr>
<td>MOB: red ore</td>
<td>11623.7</td>
<td>11042.6</td>
<td>105.9</td>
<td>125.1</td>
<td>7</td>
</tr>
<tr>
<td>MOB: white ore</td>
<td>2034.4</td>
<td>2576.1</td>
<td>37.9</td>
<td>16.3</td>
<td>9</td>
</tr>
</tbody>
</table>

Fig. 49: Thallium concentrations of the non-sulphide zone of the MOB and sulphide- and non-sulphide ore of the VOB. Both ore bodies are highly distinguishable by their Tl and As concentrations, which form three clusters. The Tl and As concentrations of the MOB are approximately 80 times higher than the concentrations of the VOB. The As-(Tl-) concentrations of the white ore of the MOB are low with regard to the red zinc ore. In contrast to that, the non-sulph. ore and the sulphide ore of the VOB show no differentiation in As and Tl.
The samples of the MOB and the VOB plot at least within three different clusters (Fig. 49). These three clusters are due to highly different Ti- and As-Sb-Cd concentrations within these two non-sulphide ore bodies. To explain this effect one can assume three different models:

(i) The source of both Ti and As of these non-sulphide ore-bodies was a sulphide protore, which was formed during one mineralising event for both the protore of the VOB as well as the protore of the MOB. During the oxidation of the sulphide ore As and the Ti remained as immobile elements within the MOB and have been concentrated during the process of carbonate dissolution and sulphide oxidation. However, calculations of this process, which are based on values of Tab. 13 give a factor for the As-accumulation of approximately 26 and the factor for the Ti enrichment is about 19. These rates are obviously too high to be realistic and they are in contrast with investigation of the As- and Ti concentrations of the oxide-zone of the VOB. Here, calculations have shown that there is no obvious enrichment in these elements (Fig. 49). Due to this fact, a highly immobile behaviour of As- and Ti during the oxidation of the protore of the MOB is improbable.

(ii) Both ore bodies, the MOB and the VOB are the result of at least two different mineralising events. These events were associated with different As and Ti concentrations.

(iii) Both ore-bodies are the result of one mineralising event, but the MOB was influenced by an earlier or later stage hydrothermal As- and Ti-delivering event.

Further investigations have to focus the source and the mechanisms, which are responsible for the different As and Ti concentrations of the MOB and the VOB.

**REE elements**

All REE data of the ore samples have been normalised to chondrite composition (data source: TAYLOR & MCLENNAN, 1985) except the data of the carbonate host rock, which is normalised to NASC (data source: HASKIN ET AL., 1968). The chondrite-normalisation for both non-sulphide and sulphide mineralised samples has been chosen to make these graphs comparable with other authors, which mostly use chondrite normalised data to describe sulphide mineralised samples (MVT, SHMS, VMS, and other styles of mineralisation). A normalisation of the REE data by using a CaCO₃ reference (e.g. a marble) would be possible, but is only useful for a regional comparison of the samples among themselves.

The REEs are relatively immobile during weathering, low-grade metamorphism, and hydrothermal alteration (ROLLINSON, 1993) and offer a good possibility for comparing and analysing the host rock and its mineralisation, which has been partly affected by intensive and extensive alteration processes. Sample analyses, which show REE values under the detection limit, have been estimated by using the method of half detection limit (HAAS & SCHEFF, 1990). All values below detection limit are assigned a value of the detection limit divided by 2. This procedure becomes necessary for some purposes, such as calculation of Eu/Eu* anomalies. Only two samples of an unaltered dolomitic host rock of MOB has been analysed yet. Because of this reason, these data will represent the unaltered and unmineralised carbonate host rock of both the sulphide ore of VOB and the non-sulphide ore of MOB. The criterion, which is used for a classification, as an unaltered host rock, is self-determined. The criteria for the classification as an unaltered and unmineralised carbonate
host rock are (i) a distance of at least 5 meters to ore-bearing rocks, (ii) a widely spaced fracture pattern and thus a minimised influence of alteration/meteoric fluids, and (iii) an apparent local background of Pb-Zn, Pb, and Fe. Four samples have been chosen to represent the limestone host rock (Fig. 50). The REE patterns of these specimen show roughly parallel trends with an erratic change of element concentrations. Elevated light REEs (LREE) relative to lower heavy REEs (HREE) can be recognised. Both specimen show a Eu/Eu* ratio, which ranges from 0.95 to 2.47. The Eu/Eu* anomaly is calculated by using the formula F 2 (McLennan, 1989):

\[ \text{Eu/Eu*} = \frac{\text{Eu}_N}{\sqrt{\text{Sm}_N \cdot \text{Gd}_N}} \]

\( (N = \text{normalised}) \)

**REE patterns of samples from the VOB**

The REE pattern of the VOB sulphide ore (Fig. 51) shows higher REE concentrations, in relation to the unmineralised carbonate host rock (Fig. 50). The trend of lower HREEs is visible within most sulphide ore samples. The LREE contents are highly variable within the sulphide ore and La/Lu ranges from 84.2 to 19.7. A significant negative Ce/Ce* anomaly is not visible. Most of the sulphide ore samples show a strong positive Eu/Eu* anomaly.

The REE pattern of all examined oxide zone samples of the VOB are similar to patterns from the VOB sulphide ore (Fig. 52). Most gossan samples of the boreholes show a positive Eu/Eu* anomaly. The less mineralised samples of the sulphide and gossan zone of the boreholes show a characteristic high values of LREEs, and relatively constant and low values within the HREE range, which effects an nearly x-axis parallel graph (Fig. 50). The sulphide ore samples show a distinctive positive Dy/Dy* anomaly (Fig. 51) which ranges from 1 to 5.3. This anomaly seems to be limited to the sulphide ore-bearing strata. The non-sulphide ore as well as the dolomite and the limestone as well seems to be not affected by a Dy/Dy* anomaly.
Fig. 51: Chondrite-normalised REE patterns for sulphide-rich dolomites of the VOB with [Zn]$>2\%$, [Fe$_2$O$_3$]$>10\%$. Most of these dolomites show a distinct Eu/Eu* anomaly.

Fig. 52: Chondrite-normalised REE pattern of samples from the oxidised zone of the VOB with [Zn]$>3\%$, [Fe$_2$O$_3$]$>6\%$. All samples show high Fe concentrations and thus, belong to the class of the ‘red zinc ore’. A well developed positive Eu/Eu* anomaly is visible in all samples of the oxidised zone.

Fig. 53: Chondrite-normalised REE pattern of dolomites of the VOB. Most of the samples show a characteristic positive Eu/Eu* anomaly and are high in LREEs, whereas HREEs decreasing.

**REE pattern of non-sulphide ore from MOB**

In contrast to the oxidised zones of the examined drill cores from the VOB, the specimen of the non-sulphide ore of MOB can be divided into two specific types. These types are based on their concentration of Fe$_2$O$_3$, and Zn. The main non-sulphide ore-types are (i) an ore with high concentration of Fe$_2$O$_3$ (>10\%) and Zn (red zinc ore) and (ii) an ore, low in Fe$_2$O$_3$ (<7\%) and high in zinc, the white zinc ore. Both types of non-sulphide ore show completely different REE patterns (Fig. 54 and Fig. 55). The REE patterns of the red zinc ore of the MOB are comparable to the oxidised zone overlying the main sulphide ore body of the VOB. The samples show the characteristic high contents in LREEs with lower HREEs (Fig. 54), but no distinct Eu/Eu* anomaly. Except one sample, the La/Lu ratio shows high values, which ranges from 3.6 to 11.8 (mean=8.4, n=7).
The samples of the white zinc ore show relatively low values of LREEs and HREEs with regard to the red zinc ore samples. The values vary around 12 for the LREEs and 1.2 for the HREEs. The La/Lu ratio ranges from 0.8 to 40 (mean=10, n=9). Another marked feature is a significant Eu/Eu* anomaly (mean =0.55). The typical and good determinable positive Dy/Dy* anomaly that is detectable at the sulphide ore and in the overlying oxidised zone of the VOB, is missing here. (Dy/Dy* mean=1.02, n=9).

Fig. 54: Chondrite-normalised REE pattern of high-Fe non-sulphide ore samples from MOB. (These samples are characterised by Fe$_2$O$_3$ > 10% and Zn > 5000 ppm values). All samples show a characteristic decreasing value toward the HREEs.

Fig. 55: Chondrite-normalised REE patterns of the white zinc ore from MOB. (The plotted samples are Fe-poor with Fe$_2$O$_3$<7% and zinc-rich with Zn values >50000 ppm). The graphs show an x-axis parallel pattern and, referred to the Fe-rich ore, low REE values.

Fig. 56: Chondrite-normalised REE patterns of low-Fe non-sulphide ore samples from MOB. (The plotted samples are Fe-poor with Fe$_2$O$_3$<4% and zinc-rich with Zn values >100000 ppm). The graphs show an x-axis parallel pattern and, referred to the Fe-rich ore, low REE values.
Discussion and interpretation of the REE patterns

The limestone, dolomite and the sulphide ore show a distinct enrichment in light REE when normalised against chondrite. This pattern is typical for marine chemical sediments and platform carbonates (MAZUMDAR ET AL., 2003). The dolomitisation process should not necessarily influence the REE composition of the precursor limestone and the pattern of the limestone should be visible at the dolomites after the dolomitisation process (MIURA & KAWABE, 2000; QUING & MOUNTJOY, 1994). Thus, it is probable that the similar REE pattern especially the enrichment of the LREE and the decreasing values towards to the HREEs is due to the original limestone.

However, at least one process, the dolomitisation process or the ore mineralising event should be accompanied with the generation of the distinct positive Eu/Eu* anomaly. Most samples of the sulphide ore, of the oxidised zone overlying the sulphides, and of the dolomite samples of VOB show this marked Eu/Eu* anomaly and has its highest peaks within the sulphide ore, but also with significantly positive values in oxide zones and dolomite of the VOV. The MOB in contrast does not show such a Eu/Eu* anomaly. Here, most samples show a slightly negative Eu/Eu* anomaly, which is also common in marine carbonates (MAZUMDAR ET AL., 2003).

A possible explanation for the characteristic REE fractionation pattern, reflected by relatively high La/Lu ratios, is the preferential removal of LREEs from the fluid by carbonates, due to a replacement of Ca within the crystal structure of the carbonate (DAVIES ET AL., 1998). Accordingly, carbonate minerals should be more enriched in LREEs than in HREEs and La/Lu\textsubscript{carbonate}>La/Lu\textsubscript{fluid} (DAVIES ET AL., 1997). Hydrothermal fluids are enriched in LREEs and show a low content of HREEs (PARR, 1992). These fluids could increase La/Lu by regional mixing with seawater. Because of this reason, hydrothermal fluids are another important factor for the La/Lu ratio of seawater, which could influence the REE pattern toward to high HREEs and decreasing LREEs of the carbonates.

A positive Eu/Eu* anomaly can be due to an enrichment of Eu\textsuperscript{2+} related to Eu\textsuperscript{3+} (PARR, 1992). The stability of Eu\textsuperscript{2+} and Eu\textsuperscript{3+} is dependent on the pH and Eh. An anomalously high concentration of total Eu in chondrite-normalised samples may reflect hydrothermal fluid temperatures of above 250 °C and reducing hydrothermal conditions (PARR, 1992). Additional to the high La/Lu ratio, the marked positive Eu anomaly in both Zn-Pb sulphide and non-sulphide ore of the VOB supports the thesis of a hydrothermal (T>250 °C, and reducing conditions) genesis of the sulphide ore (PARR, 1992). One possible explanation for the wide-ranging Eu/Eu* anomaly could be changes in proximity to an active hydrothermal vent.

However, the Eu/Eu* ratio within the sulphide ore and the oxide zone of the VOB is an indication of a hydrothermal signature. The lacking Eu/Eu* anomalie at the MOB might document an vent-distal position during the ore mineralising event. Another explanation could be the influence of two separate ore delivering events.

The observed phenomenon of relatively low LREE and HREE values of the white zinc ore of the MOB related to the red zinc ore and the carbonate host rock of MOB (Fig. 56) is probably a result of zinc mobilising, transport and reprecipitation. REE are immobile for most types of weathering and alteration processes (ROLLINSON, 1993) and remain in the original rock and the oxidation zone from where the zinc has been remobilised or dissolved. Thus, the high REE values of the red zinc ore are an effect of REE-enrichment within the oxidation zone (red zinc ore) due to carbonate dissolution and zinc mobilisation. The migrating Zn-rich fluids are poor in REEs and thus the resulting
white zinc ore shows lower REE values compared with the barren host rock.

**Barium and strontium**

Barium is an abundant element in both the samples of drill cores and specimen of MOB. Barite is the chief host of barium in non-sulphide ore of MOB as well as sulphide and oxide zones of VOB. The highest concentration of barium occurs within the sulphide ore, but elevated values occur also within oxidised zones of the main sulphide ore body as well as the non-sulphide ore of MOB. The bivariate plot of Barium versus Strontium correlates positively over a wide range (Fig. 57). This is due to the Sr-compatibility in the barite crystal lattice. It appears that the Zn-Pb mineralisation is at least regional associated with high concentrations of barite, which is characterised by high contents of strontium. The sample of a felsic intrusive body shows also high Ba and Sr concentrations. The Ba/Sr ratio is similar to the samples of the Mehdi Abad ore. This fact supports the thesis of a hydrothermal overprint derived from the emplacement of a felsic magmatic rock. A second possible explanation might be a separate event, which has delivered barite to both the felsite and Mehdi Abad.

![Bivariate plot of Barium versus Strontium of all samples](image)

*Fig. 57: Bivariate plot of Barium versus Strontium of all samples (numbers indicate different bore holes, which has been sampled, all other specimen are grab samples). Both calamine specimen as well as drill core samples correlate over a wide range, which is characterised by high Ba and Sr concentrations. A poorly correlated field of samples can be assumed for low concentrations of Sr (10 to 300 ppm), and even lower concentrations of Ba (15 to 2000 ppm). The sample of a felsic intrusion plots perfect in the linear trend.*

**Mass balance calculations**

A mass balance calculation can give an estimation either if the non-sulphide ore of VOB was formed by oxidation processes of a sulphide ore without additional Zn sources, or if an additional Zn-source was necessary. The model, which has been developed for the oxidation process of the
sulphide protor comprises several chemical assumptions as follow:

- The oxidation of the sulphide protor of MOB is due to the influx of oxygen, which acts as an electron donator. Iron and sulphur are electron acceptors and were oxidised.
- Other components that exclusively delivered to the sulphide ore were H₂O and CO₂.
- The sulphide ore system looses calcium, sulphur, and carbonate, which is due to solution processes.
- The mass-balance calculation comprises for quantitative results the elements Ca, Pb, Zn, Fe, Ba, C, O, and S, but ignores elements that occur in traces.

The LREE's La and Ce has been used for an estimation of the mass-loss factor of the non-sulphide ore. Both elements are immobile within a wide range of geochemical conditions (CHRISTIDIS, 1998, MIDDLEBURG ET AL. (1988), CRAMER & NESBITT, 1983, FEDO ET AL. (1995)).

The applicability of the system La – Ce is given if the ratio between these phases is constant and not affected by dissolution and/or weathering effects. The La – Ce ratio of relevant samples (sulphide ore and non-sulphide ore) of Mehdi Abad VOB are plotted in Fig. 58 to prove this assumption. The graph shows a linear correlation between the sample data regardless of their origin within the ore body. The La-Ce system agrees with the required stability and will be used here as reference for further calculations.

![La-Ce plot of both sulphide and non-sulphide ore samples of Mehdi Abad VOB.](image)

**Fig. 58: La-Ce plot of both sulphide and non-sulphide ore samples of Mehdi Abad VOB.** The red marked cluster represents samples from both high-grade sulphide ore (app. 8 % Zn) and high-grade non-sulph. ore according to Tab. 12. The magenta coloured cluster is build by surface-near and surface gossan samples. All data show a linear correlating trends with $R^2=0.97$ and $R^2=0.94$. Both interpolated graphs overlaying each other with low variation only. Thus, no effect of selective mobility of either La or Ce can be estimated.

The here used method describes the non-sulphide ore of the MOB as a restit of the sulphide protor. This restit was formed by dissolution and oxidation processes, which include element influx and escape. However, immobile elements such as La or Ce remain in the restit and were not additionally supplied to this system. Therefore, the enrichment of La-Ce within the ‘restit’ should be inversely proportional to its mass reduction respectively directly proportional to the difference of the protor-mass and ‘restit’-mass. This factor is necessary for further mass balance calculations.
The surface and surface-near gossanised samples plot into separate cluster. Here, the alteration process was associated with a significant mass loss. The mass-loss factor $f_{ml}$ has been determined by using the graph of Fig. 58. The quotient $C_{\text{nonsulph}} / C_{\text{sulp}}$ results in $f_{ml} = 2.8$, whereas the La values gives an value of $f_{ml} = 2.3$. Thus, the average mass-loss factor can be estimated as $f_{ml} = 2.5$.

The data of the sulphide and non-sulphide ore overlying each other and form a single cluster at the La-Ce diagram (Fig. 58). Thus, the usage of the La-Ce data of both the sulphide and non-sulphide ore of the VOB is not appropriate to calculate a specific mass loss factor, but hints to an $f_{ml}$ that is near 1. An mass loss factor around 1 would suggests that the non-sulphide zinc ore of the VOB is the result of an in-situ oxidation of the protore and the non-sulphide zinc ore as been presumably formed without an additional Zn-source. This hypothesis is supported by similar metal concentrations of both ore-types; especially the high-grade non-sulphide ore and the sulphide ore show similar values of Zn, Pb, and Fe concentrations.
4.2 The non-sulphide Zn-Pb Kolahdarvazeh deposit at the Irankuh district

The Irankuh district comprises several zinc-lead deposits. They are located in the Irankuh Mountain Range, 20 km south of Esfahan (Fig. 4) in West-Central Iran. The elevation of the mines is approximately 1700 m. Similar to Mehdi Abad, this region is influenced by a hyper-arid climate with a low-levelled rainfall and high temperatures. There is virtually no vegetation within this area.

The Irankuh district comprises several Zn-Pb deposits: the Goushfil pit (sulphide ore), the Kolahdarvazeh pit (non-sulphide ore), the small Tappeh-Sorkh pit, and some others. The UTM coordinates of the Goushfil pit are 40R 558444; 3598117 and the coordinates of the Kolahdarvazeh pit are: 40R 559169; 3597867.

The summarised ore reserve of these mines is estimated at approximately 10 million tonnes with 7.5% zinc and 2.4% lead (Tab. 14). The ratio is relatively high with an average of approximately 0.76 (GHAZBAN ET AL., 1994). The Mines within this district produce both a sulphide concentrate as well as an oxide concentrate.

The main difference between the Goushfil- and the Kolahdarvazeh pit is the chemistry of their ores. The ore of the Goushfil pit is characterised by high amounts of sulphide ore and a minor amount of non-sulphide zinc ore only. The Kolahdarvazeh mine is an open pit mine, which produces a concentrate of non-sulphide zinc ore and shows only small amounts of sulphides.

The origin of the ore has been discussed by several authors. ZAHEDI (1976) attributed the dolomitisation and mineralisation of the Esfahan area to the Alpine orogeny. However, the first study attributed to the Irankuh district deposits itself was written by RASTAD ET AL. (1980) and RASTAD, E. (1981). These studies consider that the ore mineralisation is a part of a Cretaceous transgressive series and interpret the ore emplacement as sedimentary and diagenetic. More recent isotope based examinations on the sulphides of RASTAD ET AL. (1980) suggest an epigenetic model for the Irankuh deposit. Their model is supported by regional geological observation, such as the discordant nature of the sulphide ore and its emplacement along the Iran-Kuh Fault as well as by isotopic data.

The Goushfil pit (Fig. 59) is the most important Zn-Pb deposit within this area, which produces a sulphide concentrate. Beside the mined sulphide ore, they have approximately two million tons of tailings with a low-grade non-sulphide ore. This ore contains approximately 8 % Zn hosted in dolomite rocks. However, the non-sulphide ore of the Goushfil pit is not utilisable for the solvent extraction process, since the concentration of zinc is too low for the acid leaching process that is used for the extraction of zinc from the ore.
Fig. 59: View of the Goushfil pit at the Iran-Kuh district. Cretaceous dolomite in the south and Jurassic shales in the north are separated by a W-E trending fault. The vertical zonation (marked by the blue line) separates a non-oxide zone (dark grey colours) in the lower parts of the deposit and an oxide-zone (brown colours) in the upper parts. The sulphide ore is mainly hosted in the dolomite (blue arrow). The non-sulphide ore occurs within the oxide zone as secondary mineralisation predominantly in the vicinity of faults and fractures (yellow arrows).

The Kolahdarvazeh pit is under exploration and mining since 1962 and produces a high-grade non-sulphide zinc concentrate. The industrial mining has stopped and only some small adits are currently mined by artisan miners.

Tab. 14: Important Zn-Pb mines of the Irankuh district, west-central Iran

<table>
<thead>
<tr>
<th>Mine</th>
<th>sulphide ore &amp; mean grade (% Zn)</th>
<th>non-sulph.-ore &amp; mean grade (% Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tappeh-Sorkh</td>
<td>5.046.431 (5.4%)</td>
<td>825.142 (6.6%)</td>
</tr>
<tr>
<td>Goushfil</td>
<td>4.299.500 (11.6%)</td>
<td>713.479 (10.8%)</td>
</tr>
<tr>
<td>Kolahdarvazeh</td>
<td>no reserve</td>
<td>mined out, approximately 30 %</td>
</tr>
</tbody>
</table>
Fig. 60: Schematic geological map of the Irankuh mining district. (modified unpubl. geological map, BAMA Mining Corp.)
4.2.1 The Kolahdarvazeh Mine

Stratigraphic setting

The regional stratigraphic sequence of the Irankuh area (Fig. 62) starts with Lower Jurassic shales at the lowermost position, followed by Lower Cretaceous strata (Barremian-Aptian), Upper Aptian sediments, and on top of this sequence sediments of the Oligo- and Miocene. Two major stratigraphic gaps can be found within this stratigraphic sequence. The first separates the Lower Jurassic shales from the Lower Cretaceous strata. The second gap is located between the Cretaceous- and the Oligocene strata (RASTAD, 1981).

The oldest rocks of the Irankuh area are the Jurassic shales, which are exposed in the north-western part of the area, near the Goushfil pit. These strata are composed of dark grey shales with intercalations of silt- and sandstone (MOMENZADEH, 1976).

The sediments of the Lower Cretaceous overlying unconformably the Jurassic shales and form a continuous sequence beginning from the Barremian up to the Upper Aptian sediments. The total thickness of this sequence is approximately 800 m. These Cretaceous strata comprise mainly dolomite, limestone, and minor amounts of shales and marbles.

The strata of the Barremian and Lower Aptian sediments are the host rocks of the sulphide/non-sulphide ore mineralisation, which forms two discrete ore-bearing horizons within the K3 unit: the Goushfil-Kolahdarvazeh Horizon and the Goushfil-Gowdezendane Horizon (RASTAD, 1981). The K3 unit mainly consist of yellowish to brownish coloured dolomite and grey limestone. The limestone is medium to thick bedded with fossils, whereas the dolomite is massive to thick bedded.

The general structural setting of the Kolahdarvazeh pit is similar to the Goushfil pit. A sub-vertical, NW-SE trending fault (Kolahdarvazeh fault), which is located in the southern most part of the deposit, separates Cretaceous black shales from Cretaceous dolomites and limestones (Fig. 63). The main difference between the Kolahdarvazeh- and the Goushfil pit are the age of the shales (Kolahdarvazeh Mine: Cretaceous shales, Goushfil: Jurassic shales).
The ore of the Kolahdarvazeh mine is hosted within the strata of the Cretaceous K3d unit, which is cut by the sub-vertical Kolahdarvazeh- and Tofangchiha faults. The Kolahdarvazeh fault restricts the occurrence of mineralised rocks and the deposit to the South, whereas the Tofangchiha fault limits the deposit to the North. The most portions of the non-sulphide (and subordinate amounts of sulphide ore) occur between these two Faults.

The limestone and the dolomite of this area dip approximately 17° - 30° to the South. The whole area shows an intensive and extensive faulting.

The Irankuh district is mainly controlled by three different fault systems. The Kolahdarvazeh-, the Tofangchiha- as well as the Irankuh fault. Most of these faults as well as the folded strata of this region show a parallel trend to the Zagros Fold Belt and the Zagros Thrust zone, which is the result of the convergence of the Arabian and the Iranian plates.
Fig. 63: Overview of the Kolahdarvazeh mine. Non-sulphide zinc ore (‘zn-ox’) (mainly hydrozincite/smithsonite) occurs in the oxide zone (‘ox’) of the Cretaceous rocks (above the blue line). The non-sulphide zinc minerals precipitated as a matrix of karst-breccias within dolomite and limestone and as mineralisation in faults and fractures. Mainly sphalerite, galena, and pyrite can be found within a small area in the sulphide-zone of the shales (close to the main fault) and in the ore lens between the main fault and the dolomite unit.

Style of mineralisation

The sulphide ore

Both the sulphide mineralisation as well as the non-sulphide ore of the Kolahdarvazeh mine occurs within Cretaceous dolomite and limestone. Sulphide mineralisation occurs in a number of locations in the proximity or especially at the contact to the shales. Most of the detectable sulphide ore occurs discordant to the hosting dolomite within the not oxidised zone near to- or directly at the contact to the shales. The most portion of the dolomite hosted precursor sulphide protor is oxidised and sulphide sulphides occur rarely within the dolomite. Unoxidised dolomite-hosted sulphide ore from the Kolahdarvazeh mine is only visible at drill cores and rarely at several adits.

In most cases, the sulphide ore is partly oxidised and only local relics of sulphides (mainly galena) are visible. The primary sulphide mineralisation consists of sphalerite, galena, subordinate amounts of pyrite, traces of marcasite, and chalcopyrite. Associated minerals are barite and calcite mainly as veins and fillings of fractures. The majority of the sampled sulphide ore is at least partially oxidised. In an advanced state of oxidation most of the sulphide minerals are oxidised and only galena
is present as the most oxidation-resistive mineral. The reddish to yellowish sphalerite occurs in minor amounts as fillings in fractures and spaces. The most portion of the sphalerite occurs as semi-massive replacements of the dolomite. Galena and pyrite are relatively minor and are associated with the occurrence of sphalerite. However, pyrite occurs in traces also as sub-mm sized frambooids within the dolomite without any other (Zn-Pb-) mineralisation.

Sulfides, in particular sphalerite and galena, have replaced barite. Barite has probably formed both prior to and during the main period of sulfide mineralisation. Later barite crosscuts early sulphides and shows no corrosion or replacement by sulphides.

The mining district of the Irankuh area and especially the Kolahdarvazeh mine is characterised by low Fe concentrations. Pyrite as the main important Fe-bearing mineral is a minor component of the sulphide ore reflected by the arithmetic mean values of Fe$_2$O$_3$ = 1.5 % (Tab. 15).

The occurrence of dolomite-hosted sulphide ore is restricted to small zones, which ranges from dm to several metres (rare). These sulphides occur preferentially in the proximity of overlying shales or within massive and undisturbed dolomites (Fig. 73), which are not influenced by faults.

*The non-sulphide ore*

The majority of the non-sulphide ore is associated with karst-breccias within the dolomite and limestone (Fig. 66), but non-sulphide mineralisation occurs also within faults and fractures. In contrast to the Goushfil pit, which shows mainly sulphide mineralisation, the amount, and especially the grade of the non-sulphide zinc-ore of the Kolahdarvazeh pit is very high and the fraction of sulphide-ore is much smaller. Smithsonite, hydrozincite, hemimorphite, cerussite, malachite, calcite, goethite, hematite, limonite, and barite are the main minerals in the oxide-zone.
The non-sulphide ore occurs predominantly as a matrix of karst- and fault breccias (Fig. 68). Most of these breccias consist of angular fragments (2 cm up to several metres in diameter) set in a fine- to medium grained matrix. In some breccias, the fragments can be seen to match along their opposed sides, indicating only modest disturbance. The matrix mainly consists of zinc- (lead-) carbonates, such as smithsonite, hydrozincite, cerussite and minor amounts of zinc-silicates and zinc-manganese minerals: hemimorphite or coronadite Pb(Mn⁴⁺,Mn²⁺)₈O₁₆, and others. Goethite, hematite, and iron (hydro-) oxide minerals are not common, but occur in most samples as traces. The occurrence of high concentrated iron-bearing minerals is regionally limited.

Most of the breccias within the Kolahdarvazeh region seem to be karst-breccias with varying size and dimensions. The diameter of these karst-breccias varies from some meters up to 10 meters and more (Fig. 67).

Non-sulphide zinc-(lead-) mineralisation is common as a filling of fracture planes and fault-zones and occurs in the region of the Kolahdarvazeh pit as well as in the Goushfil pit and their vicinity.
The non-sulphide Zn-(Pb-) minerals occur as mainly four types and styles at the Kolahdarvazeh mine. The first type (Type-A) occurs as filling of (more or less) planar faults and fractures (Fig. 69). The contact between the non-sulphide ore and the barren rocks is commonly sharp. Most of the secondary (non-sulphide) minerals grew normal to the fault- and fracture planes. Iron-oxide minerals, such as goethite and others are rare, which is according to their immobile behaviour during weathering and alteration processes. The grade of this type of non-sulphide zinc ore is relatively low, which is due to the limited surface- and fracture-size. Common minerals are secondary calcite, hydrozincite, smithsonite, hemimorphite, cerussite, traces of manganese minerals (coronadite), and traces of Fe-oxides and Fe-hydroxides.

The second type (Type-B) of non-sulphide zinc mineralisation occurs as a matrix of fault- and karst-breccias and is characterised by fine-grained cement. The fragments of the breccia are angular and show a sharp contact between the dolomite fragments and the cement (Fig. 70). Similar to Type-A, the common minerals are hydrozincite, smithsonite, hemimorphite, cerussite, and minor concentrations of Mn- or Fe-bearing minerals. However, this type of breccia is not common and occurs regionally limited as small karst-breccia systems or as fault-breccia.

One possible interpretation of this ore-type is a rapid mineralisation process. During this process, the breccia fragments had no time to interact with the ore-delivering fluids. The breccia fragments have not been altered chemically and/or mechanically. The edges remained sharp and angular. This hypothesis is supported by the fact of a fine-grained cement, which is probably also due to a rapid mineralisation and precipitation process. Another reason for these sharp edges of the breccia clasts could be the inert behaviour of some types of dolomite to the mineralising fluids.

The third type, Type-C, of non-sulphide zinc mineralisation is similar to Type- B. The non-sulphide ore occurs as a matrix of fault- and karst-breccias. However, the fragments of this type of breccia are not angular but (sub-) rounded. They lost their sharp contact between the non-sulphide matrix and the dolomite/limestone fragments. The matrix consists of fine-grained to coarse-grained (layered) crystals/masses, which commonly show a (concentric) zonation (Fig. 71). The size of these zones varies from a sub-mm scale up to several cm and dm. Common minerals are hydrozincite, smithsonite, hemimorphite, cerussite. Manganese and iron-bearing minerals are rare.

This type of breccia is common within the Kolahdarvazeh pit. In contrast to the formation of Type-B ore, here the mineralisation was probably a long lasting process. An intensive period of interaction between the breccia-fragments and the ore delivering fluids led to a (partial to total) dissolution and replacement of calcite and/or dolomite of the breccia-fragments. The edges of the dolomite/limestone fragments became round and irregular.

The Type-D non-sulphide ore consists of both non-sulphide minerals as well as varying amounts of sulphides. Within this ore-type, galena is the most common sulphide mineral (Fig. 72). This is probably the result of a higher reactivity of sphalerite during the oxidation process. The spaces between the breccia fragments are filled with hydrozincite, smithsonite, and cerussite. The adjacent regions of the galena bearing mineralisation are rich in cerussite and leadhillite Pb₄(SO₄)(CO₃)₂(OH)₂. This type is common at deeper levels of the Kolahdarvazeh mine and can be investigated exclusively in drill-cores.
Detailed investigations on sulphide and non-sulphide ore samples of the Kolahdarvazeh mine have been performed on borehole DDH64 and DDH40 (Fig. 73 and Fig. 74) and on several samples of the Kolahdarvazeh mine and artisanal-mined adits. The sampled boreholes are located within the area of the Kolahdarvazeh pit. The position of the DDH64 is (UTM 3598421.092; 553313.532) at an elevation of 1670 m. The total depth of DDH64 is 129.2 m with an inclination of 80° and a dip-direction of 251°. The DDH40 is located at position UTM 3598484.102; 553174.822 at an elevation of 1620 m. The depth of DDH40 is 151.2 m and a dip of 65° to a dip-direction of 70°. The boreholes cross dolomites of the Cretaceous K3 unit and Cretaceous shales of the K5 unit.
Results

Fig. 73: Profiles of boreholes DDH 64 and DDH 40. The borehole DDH40 is located nearby the main vertical fault that limits the Kolah Darvazeh mine to the south. The shales of borehole DDH40 are fault-related and regionally sheared in the carbonates. (unpubl. data of the Bama Mining Co., Esfahan)

Fig. 74: Schematic cross section of the Koladahrvazeh mine and the location of the bore holes DDH40 and DDH64. (Modified after internal and unpublished data of the Bama Mining Co., Esfahan)
Results

Fig. 75: Dolomite of DDH64 at 12 m. The dolomite is gray to dark grey coloured. Fractures are coated with Fe-hydroxides.

Fig. 76: Photomicrograph of a thin-section of a typical dolomite of borehole DDH64. The crystals show a perfect 120° angle at the triple-points, that points to a dolomitised limestone. (xn) Sample IK02134

Fig. 77: Typical drill core sequence of borehole DDH64 with a zone of high-grade non-sulphide ore at 110 m (red marked). The non-sulphide ore consists mainly of cm-sized dolomite fragments that show a replacement by mainly smithsonite and hydrozincite, which also build the matrix of this breccia.

Fig. 78: DDH64 at 111 m. The dolomite is brownish-reddish coloured. The brownish dolomite clasts are (if visible) and remnants of them are highly altered and show diffuse edges due to replacement by smithsonite and hydrozincite (the dark red coloured area is caused by Zinc Zap, an indicator for non-sulph. zinc minerals).

Fig. 79: Detail of a non-sulphide ore mineralised zone of DDH64 at 50 m. Breccia clasts (green arrow), consisting of dolomite surrounded by cement of smithsonite and hydrozincite (blue arrow). Goethite occurs in a microscopically scale as concentric botryoidal shaped layers (orange arrow) and as a constituent of the breccia matrix.
Fig. 80: Photomicrograph of a concentric growth banding due to the precipitation of hematite/goethite and smithsonite/hydrozincite (blue arrow) on dolomite fragments (Dolo) of a (karst-) breccia. A deformation of the bands and an unusual contact to the dolomite (red arrow) are probably due to a late stage movement of the dolomite clasts. IK02135 (xN), borehole DDH64

Fig. 81: The Photomicrograph shows smithsonite crystals (red arrow) in which hydrozincite (Hy) has developed and replaced smithsonite along crystallographically preferred planes (blue arrow). The dolomite (Dolo) is highly fractured and brecciated. The fragments are cemented by hydrozincite. IK02135 (xn), borehole DDH64

Fig. 82: BSE-image showing smithsonite and its replacing along preferred planes. Breccia fragments of dolomite (Dolo) and barite (Ba) have been cemented by hydrozincite (Hy) and smithsonite (SM). The space between the dolomite crystals is filled by hydrozincite smithsonite. IK02135 (xN), borehole DDH64

Fig. 83: BSE-image of a layered sequence of smithsonite (black arrow) and a Fe-Mn bearing mineral (probably Mn-bearing hematite) (white arrow). Due to the perpendicular contact of the layers to the smithsonite (red line) it can be assumed that this sequence is probably subsequent brecciated or has been intergrown with smithsonite and hydrozincite (SM). IK02135 (xN), borehole DDH64

The dolomite host rock shows grey to brownish colours and has a medium grain size of approximately 0.2 mm. The grains are tightly interlocking. Most of the dolomite crystals show a perfect 120° angle on their triple points, which indicates a recrystallisation, probably due to a dolomitisation process of a pre-existing limestone (Fig. 77 and Fig. 76). Pyrite is rare and occurs as sub- to euhedral crystals (< 50 μm) and masses (Fig. 64). The fractures of the dolomite are filled by calcite and/or minor amounts of Fe-hydroxides, hydrozincite, and smithsonite. Barite occurs as veins within the dolomite.
The examination of the drill cores DDH40 and DDH64 has shown several zones (approximately 10 to 30 cm) with high concentrations of non-sulphide ore (predominantly Zn-minerals) with subordinate amounts of lead minerals (Fig. 78 & Fig. 79). One of these zones has been sampled at a depth of 50 m. The most abundant Zn-minerals are hydrozincite and smithsonite. Lead occurs as cerussite and iron precipitated as fine-grained coating on fractures, and as intergranular filling of the non-sulphide ore minerals as well as concentric grown Fe-hydroxide aggregates (Fig. 80). Other minerals are barite, dolomite, and calcite. The non-sulphide ore-bearing zone at 50 m is probably a regional limited fault related breccia or a debris-filled karst-conduit. A collapse breccia would be improbably with regard of the limited dimension of this zone.

The layered sequence of iron-hydroxides and smithsonite shows fractures and indicates a subsequent brecciation after its precipitation (Fig. 83). These fragments are intergrown by euhedral smithsonite. This smithsonite is probably affected by alteration- and corrosion-processes, in which the smithsonite was partly replaced by hydrozincite (Fig. 82). Hydrozincite cements the breccia fragments and fills vugs and open spaces of this examined sample. Here, hydrozincite represents the final stage of the mineralising and cementation process (Fig. 84).
The occurrence of sulphides and their concentration increase with depth of borehole DDH64. Sphalerite and galena is commonly associated with pyrite (Fig. 65). The sulphides occur as fillings of the interstitial spaces of the dolomite crystals as well as cement of dolomite clasts. Most of the examined sulphide zones show a more or less extensive oxidation.

The oxidation of galena is associated with the formation of cerussite (Fig. 86) and small amounts of leadhillite, $\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$. Sphalerite has been oxidised to smithsonite, which is altered/transformed at a later stage to hydrozincite.
Results

The oxidation of sphalerite is associated with the forming of massive anhedral smithsonite and acicular shaped hydrozincite. Hydrozincite overgrew most of these minerals, fills pores, and open spaces of the oxidised ore and the adjacent regions. Similar to other samples of this borehole, it can be assumed that hydrozincite is associated with the last stage of oxidation and non-sulphide ore forming processes.

Geochemical investigations on samples from the Kolahdarvazeh mine

The calculation of the Zn/(Zn+Pb) ratio from sulphide ore samples of the Kolahdarvazeh mine (Tab. 15) gives a Zn/(Zn+Pb) value of 0.84. This value is similar to values for this mining district, which are given by Ghazban et al., 1994. They calculated a Zn/(Zn+Pb) value of 0.76. However, the Zn/(Zn+Pb) ratio is relatively invariant. The values of both the sulphide ore and the non-sulphide ore are similar with Zn/(Zn+Pb)$_{sulph}$=0.84 = Zn/(Zn+Pb)$_{ox}$=0.82 and are an evidence for a lacking metal separation process between Zn and Pb.

Tab. 15.: ICP-MS data of selected metals. Comparison between sulphide- and non-sulphide ore samples of the Irankuh-district/Kolahdarvazeh mine. (Sulphide ore: n=7, non-sulphide ore n=14)

<table>
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<tr>
<th></th>
<th>Cu$_{sulph}$</th>
<th>Cu$_{ox}$</th>
<th>Pb$_{sulph}$</th>
<th>Pb$_{ox}$</th>
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<th>Zn$_{ox}$</th>
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<th></th>
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<th>Ag$_{ox}$</th>
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The red zinc ore is a common type at Mehdi Abad and other non-sulphide zinc deposits (e.g. Sierra Mojada), but observations at the Kolahdarvazeh mine and the examination of drill cores have shown that here the “red zinc ore” is absent. Most of the non-sulphide zinc ore samples of the Koladahrvazeh mine are poor in iron. The colour of the non-sulphide ore is bright white to yellowish- and brownish white and even the oxidised sulphides do not show a deep red colour but brown to ochre colours. The ternary diagram in Fig. 90 also reflects the above-mentioned dominance of zinc and lead, especially related to iron. In contrast to Mehdi Abad, the Fe-Zn-Pb values show no clear differentiation process. The white zinc ore is dominating at the Kolahdarvazeh mine. Both the sulphide protore and the non-sulphide ore show similar characteristics in these elements.
The cadmium concentration of the sulphide ore is approximately 641 ppm. In contrast to Mehdi Abad, where Cd correlates with Zn, the sulphide ore of the Kolahdarvazeh mine shows not such a relationship between these elements. Without a positive correlation between Zn and Cd it was not possible to calculate the Cd in sphalerite. In fact, cadmium is probably not only incorporated in sphalerite, but also occurs probably with other minerals.

C-O stable isotope geochemistry of carbonates from the Kolahdarvazeh mine

Carbon and oxygen isotope measurements were applied to hydrozincite and dolomite samples of the Kolahdarvazeh mine and the results of the isotopic measurements are presented in table Tab. 16 and depicted in Fig. 91. The same limitation as used in Mehdi Abad is also valid for hydrozincite samples from the Kolahdarvazeh mine. The hydrozincite samples have not a monomineralic composition. XRD analyses point to an additional phase within the hydrozincite samples, which was detected as smithsonite. However, according to SEM (-EDX) analyses smithsonite occurs only in traces and should not influence the data of the hydrozincite importantly.

Tab. 16: $\delta^{13}$C and $\delta^{18}$O values of selected samples of the Kolahdarvazeh mine

<table>
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<th>Sample</th>
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The hydrozincite samples plot in a similar region as the hydrozincite data from Mehdi Abad. The hydrozincite samples show a range of $\delta^{18}O$ (SMOW) values between 21.9 and 22.9 ‰. The $\delta^{13}C$ values range between -3.8 and -7.1 ‰. The dolomite samples intersect with the cluster of limestone samples from Mehdi Abad.

The isotopic pattern of the hydrozincite samples show close-ranged $\delta^{18}O$ values and a more variable range of $\delta^{13}C$ data. The $\delta^{13}C$ values are up to 3.3 ‰ lower than those from hydrozincite of Mehdi Abad. This behaviour of hydrozincite samples to tend to homogeneous $\delta^{18}O$ values and varying values of $\delta^{13}C$ is similar to the hydrozincite samples of Mehdi Abad and leads to a similar interpretation. At least two isotopically different sources of carbon are assumed for the formation of hydrozincite. The formation of the hydrozincite should be potentially influenced by an isotopically light component of carbon as a result of dissolved CO$_2$ derived from the decay of organic matter. However, the hydrozincite of the Kolahdarvazeh mine shows lower $\delta^{13}C$ values than its pendant from Mehdi Abad. This suggests a more important role of organic and meteoric CO$_2$ than in Mehdi Abad. A possible reason is a variable contribution of carbonate carbon from the limestone and/or the dolomite host rock and reduced organic carbon derived from the overlying soils and is comparable to pedogenic carbonates (CERLING 1984, CONIGLIO ET AL., 1996).

The isotopic values for smithsonite from different locations, especially from Sardinia (GILG & BONI, 2004) and Skorpion/Namibia (BORGHÉSE ET AL., 2003; KÄRNER, 2006) shows a similar behaviour as the hydrozincite samples from Mehdi Abad and the Irankuh/Koladarvazeh mine. The interpretation of the smithsonite data points also to a supergene genesis and the influence of meteoric water combined with dissolved CO$_2$ derived from the decay of organic matter. However, the $\delta^{18}O$ values of smithsonite are shifted to higher values. This might indicate a different isotope fractionation factor between hydrozincite and CO$_2$ related to the smithsonite and is secondly related to the additional amount of water within the crystal structure, which also influences the $\delta^{18}O$ to lower values.

Fig. 91: Stable carbon and oxygen isotope composition of carbonates and hydro-carbonates from Irankuh compared with smithsonite isotope compositions worldwide. Data: Sardinia and Angouran: GILG & BONI (2004); Skorpion: KÄRNER (2006)
Rare earth elements (REE) were determined for the dolomite host rock, the carbonate hosted sulphide ore and the non-sulphide ore. The REE distribution of the Koladahrvazeh mine is characterised by low to extremely low REE/C1 values. Numerous samples show that the concentration of different REE are below the detection limit and thus they are not plotted in the diagrams. The lowest REE concentrations are detectable in the dolomite host rock. The data show no enrichment in LREE’s or HREE’s. The sulphide ore in contrast shows slightly higher REE values. The LREE’s are slightly enriched compared to a moderate depletion of HREE’s. However, the number of values below detection limit is still high and thus no clear statement about an Eu anomaly is possible.

The data of the measured samples show a relative high fluctuation. The barren dolomite host rock only gives relatively low values for REE/Chondrite varying around 0.5 (Fig. 93). However, the samples of the sulphide ore and the non-sulphide ore show around up to 3 times higher REE values, but they also show a high variation (Fig. 94). Thus, the presence of sulphide-mineralised dolomites is associated with increased REE element concentration with a tendency to higher LREE concentrations and decreasing values towards the HREE. The non-sulphide ore samples plot apparently within the same region as the non oxidised sulphides (Fig. 95). The graph of the non-sulphide ore is also influenced by a high variability of the REE values. A minor decrease in REE concentrations can be probably read and interpreted from the mean value diagram Fig. 96.

Most samples of the dolomite host rock show La, Ce and Lu values below the detection limit. In contrast to these dolomite samples, the majority of the sulphide ore as well as the non-sulphide ore samples have detectable La, Ce, and Lu values and thus are clearly distinguishable from the barren host rock. The nearly identical REE concentrations of the sulphide ore and the non-sulphide ore of the Koladahrvazeh mine suggest that the non-sulphide minerals replaced the sulphides. Only a minor fraction of the non-sulphide ore is probably the result of a metal dissolution– transport– and subsequent precipitation process.

This process is associated with decreasing REE-concentrations due to their immobile behaviour (as shown for Mehdi Abad). In addition, the La-Ce plot for sulphide- and non-sulphide samples indicates no enrichment/depletion process, which should be a possible indication for a restit high in REE and a new formed distal non-sulphide ore that is low in REE. However, the close position of the REE data of the sulphide-, the non-sulphide, and the dolomite complicate the interpretation. According to the measured REE data two scenarios are possible. Firstly, the non-sulphide ore could have been formed in situ as a direct replacement of the sulphide protor or secondly the non-sulphide ore has been precipitated after an aqueous transport and thus as a distal precipitation.

**Fig. 92:** La-Ce plot showing both sulphide and non-sulphide ore samples from the Koladahrvaze mine. All samples plot within one cluster which suggests a direct replacement of the sulphide protor with the non-sulphide minerals that form the non-sulphide ore.
Fig. 93: REE data of the dolomite host rock from the Kolahdarvazeh mine. Not plotted data are below detection limit.

Fig. 94: REE data of the sulphide ore from the Kolahdarvazeh mine. The dashed line is a sulphide ore that is hosted in black shales.

Fig. 95: REE data of the non-sulphide ore of the Kolahdarvazeh mine.

Fig. 96: Mean values of each REE classes: dolomite host rock, sulphide ore, and non-sulphide ore.
4.3 Comparison of the Kolahdarvazeh Mine and Mehdi Abad

The examination of both the Kolahdarvazeh mine and the Mehdi Abad deposit shows similarities as well as differences between them.

**Similarities:**

In both cases, the sulphide ore as well as the non-sulphide ore are hosted in Cretaceous limestone and dolomite. The occurrence of dolomite is predominantly spatially associated with the sulphide ore and is most likely due to a dolomitisation process during the Zn-Pb-(Cu) mineralisation. The location of sulphide- and non-sulphide ore is controlled and limited by faults (Kolahdarvazeh fault at Irankuh, and Black Hill Fault in Mehdi Abad).

The emplacement of the sulphide protore is laterally limited by faults. Outside these terminating faults the same ore bearing formation shows no notable lead and zinc mineralisation.

The exclusively non-sulphide ore of the Mountain Ore Body in Mehdi Abad, is hosted within topographically higher and exposed located Cretaceous strata, without an alluvial overburden. The non-sulphide ore of the Mountain Ore Body occurs as a matrix of a karst- and fault-breccia as well as a filling of fracture planes. These features are similar to the Kolahdarvazeh ore body, in which a high percentage of the sulphide ore has been oxidised. The mineralised area of the Kolahdarvazeh pit is located on the southern flank of the Irankuh Mountains and is not overlain by an alluvial overburden.

The non-sulphide ore body of both the Koladarvazeh mine as well as the ore body of the MOB at Mehdi Abad is underlyn by less or not permeable strata (MOB: shaly limestone, Kolahdarvazeh: shales).

**Differences:**

The sulphide ore of Mehdi Abad shows high concentrations of iron and arsenic, which are still present within the oxidised ‘red zinc ore’, due to the immobile behaviour of Fe and As. In contrast to the ‘red zinc ore’ of Mehdi Abad the in-situ oxidised non-sulphide zinc ore of the Kolahdarvazeh pit shows only subordinate amounts of arsenic and iron. A typical non-sulphide ‘red zinc ore’ is absent at the Kolahdarvazeh mine.

The main non-sulphide zinc minerals of the Kolahdarvazeh mine are smithsonite and hydrozincite. Hemimorphite occurs only in subordinate amounts, whereas the non-sulphide ore of the Mehdi Abad MOB consists of both high amounts of hemimorphite and smithsonite/hydrozincite as well.

The MOB of Mehdi Abad shows two main types of non-sulphide ore. The red zinc ore as a result of an in-situ oxidation of a sulphide ore. The ‘white ore’ is the result of a complex dissolution, remobilisation, and reprecipitation process of zinc, which led to a white non-sulphide zinc ore with traces of iron and arsenic. At the Koladahrvaze mine the white zinc ore dominates.

The data and observations of both deposits will be used in the following chapters to develop a comprehensive geochemical model of carbonate-hosted non-sulphide zinc deposits.