5 Data interpretation and numerical modelling of carbonate-hosted non-sulphide zinc deposits

5.1 Limitations of the geochemical model

This geochemical model describes the most important processes of formation of carbonate-hosted non-sulphide zinc deposits and the results of these theoretical assumptions and processes are in agreement with observations that have been made at Mehdi Abad and Irankuh. The model and the assumptions are limited exclusively to a carbonate host rock environment.

The mechanisms of metal separation and the formation of two distinct types of non-sulphide zinc ore are highly dependent on the iron/pyrite content of the sulphide protore. Sulphide ore without pyrite would result predominantly in 'white zinc ore'. On the other hand, a sulphide ore, which fulfills the ideal conditions and consists of pyrite and sphalerite/galena but is influenced by a slow oxidation process, associated with large quantities of water will most likely result in a 'red zinc ore'-dominated non-sulphide deposit. Slow oxidation leads to a limited armoring process and the neutralisation occurs faster – probably just within the oxidation zone. In this case no mentionable metal transport and separation will occur.

Iron is assumed to be immobile within the oxidation zone for the presented general model of metal separation and non-sulphide ore formation: once precipitated as HFO it should remain within this zone. However, the neutralization of the acidic solution leads to a subsequent formation of various amounts of hydrous iron-oxide colloids (RUNNELLS AND RAMPE, 1989). Here, the most important mechanism for transport within the aqueous solution is the mechanical transport of iron as suspended colloidal particles (KIMBALL ET AL 1995). This behaviour is also known from processes similar to the sulphide oxidation, such as the oxidation of sulphide mine tailings and others (FERRERIA DA SILVA ET AL., 2005). The HFO colloid particles are able to transport adsorbed metals (As, Pb, Zn and other) into adjacent regions of the host rock. It is difficult to estimate this effect with regard of the final composition of the white zinc ore.

Thermodynamic data of hemimorphite are not available in literature. Willemite is the exclusive zinc-silicate mineral included in these calculations. Willemite occurs within a wide variety of geological environments and conditions. It can be formed under low-temperature conditions during alteration and oxidation processes of zinc sulphides, and can be found also in supergene non-sulphide zinc deposits (BONI, 2003), e.g in arid environments such as Goodsprings district in Nevada (TAKAHASHI, 1960) as well as under humid climates (JEONG & LEE, 2003), and is also associated with magmatic-hydrothermal processes (BRUGGER ET AL., 2003).
5.2 Important geochemical processes related to the oxidation-zone

The oxidation of the sulphide protore and the related geochemical reactions are highly complex. The most important process is the direct oxidation of solid sulphides by molecular oxygen. Another important process of sulphide (and especially pyrite-) oxidation is the reaction of sulphides with Fe(III)-ions and/or -complexes. Here, Fe(III) acts as an electron acceptor instead of oxygen. Fe(III) is generated by the oxidation of Fe(II) by oxygen or by microbially-driven oxidation of Fe(II) to Fe(III). Finally, other oxidants may be present in the sulphidic mineralised rocks, such as nitrate or manganese (IV) (HERBERT, 1999). However, other oxidation processes than oxygen-driven reactions may occur, but are negligible due to the commonly low concentrations of these other oxidants.

5.2.1 Oxidation of pyrite

The oxidation rate of pyrite is well documented in the work of numerous authors, which studied the oxidation processes of pyrite under different conditions, such as DOMENECH et al. (2002). These authors have studied the dissolution rate of pyritic sludge with flow-through experiments. WILLIAMSON & RIMSTIDT ET AL. (1994) presented a dissolution rate law of pyrite as a function of oxygen concentration and pH using data of other authors and studied the dissolution of pyrite by Fe$^{3+}$ (ferric iron).

The oxidation of pyrite and the subsequent hydrolysis of ferric iron play an important role in the genesis of non-sulphide ore deposits. The reaction of oxygen with pyrite generates the highest portion of the sulphuric acid, according to the chemical reactions R1 and R2, whereas the oxidation of sphalerite will generate only minor amounts of sulphuric acid (dependent on the Fe-concentration within the sphalerite, according to reaction R9 (BERTORINO ET AL., 1995)) and the oxidation of galena will produce no acidity at all. Thus, the oxidation of pyrite is the most important factor and source for low pH values within the active oxidation zone of a sulphide ore body.

The following reactions show the oxidation of pyrite by oxygen (reaction R1) and the oxidation of pyrite by ferric iron (reaction R2) (DOLD, 2003):

$$\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$  \hspace{1cm} \text{R1}

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$ \hspace{1cm} \text{R2}

The oxidation of Fe$^{2+}$ by O$_2$ (R3) has to precede reaction R2 and is an important part of the iron redox-cycle (SALMON, 2003). Ferric iron leads to the precipitation of Fe-oxihydroxides (reaction R4 and R5) due to a hydrolysis reaction, which, in turn, is coupled with the release of 3 mole H$^+$ related to 1 mole Fe(III).

This acid-generating step of the oxidising process is followed by a neutralisation reaction, in which the released protons react with the carbonate of the dolomite and/or limestone or with other minerals, which are capable to neutralise acidic solutions (e.g. feldspar). The elimination of most of the protons will shift the hydrolysis equation R4 and R5 to their right side and will thus stabilise the precipitated Fe-oxihydroxides.
Ferric iron is also a strong oxidant of pyrite. At low pH (< 4.5) Fe$^{3+}$ oxidises pyrite faster than oxygen (HERBERT, 1999). The oxidation of pyrite by ferric iron might be an important factor for the oxidation processes at deeper (O$_2$ undersaturated or O$_2$ free) levels of a sulphide ore body. The Fe$^{3+}$ can be transported (dissolved as a complex or colloid) to these deeper levels where it probably leads to a widening of the oxidation front. However, this process is highly dependent on the availability of oxygen for the oxidation reaction of Fe$^{2+}$ to Fe$^{3+}$ and the limiting factor for the oxidation of pyrite by both the oxidation by ferric iron and the oxidation by oxygen is the availability of oxygen.

The transport of gasses, especially O$_2$ dissolved in water, is much less effective than the gaseous transport due to diffusion processes. The diffusion of oxygen is the main parameter governing the dissolution/oxidation of pyrite and other sulphides and the release of metals. Thus, ore bodies, which are influenced by hydraulically unsaturated conditions, are characterised by high metal concentrations within the aqueous solutions (SAALTINK ET AL., 2002). Examinations of oxidation processes of mine tailings have shown that dissolved oxygen may be completely consumed by passing through an organic-rich cover by microbial respiration and organic matter oxidation (HERBERT, 1999). In that case, the oxidation of the sulphides is limited to anoxic microbial activity or the oxidation of pyrite by Fe$^{3+}$, which slows down the rate of oxidation dramatically.

Another important factor for the oxidation of pyrite is the presence of oxidising bacteria, such as *thiobacillus ferrooxidans*. The presence of these and similar bacteria can increase the oxidation rate of sulphides by several orders of magnitude in an acidic environment. Under low pH (<4) the oxidation of pyrite by acidophilic, chemolithoautotrophic Fe(II) and sulphur/compound oxidising bacteria predominates over chemical oxidation, above pH 4 metal sulphides are chemically oxidised predominantly by O$_2$. The organisms are not attached onto the mineral surface, but the sulphides are being oxidised via the electron shuttle Fe(II)/Fe(III) (SCHIPPERS, 2003). At a pH below 4, Fe(III)-hydroxides become soluble and Fe(III) ions or complexes act as an effective electron acceptor for the oxidation of pyrite. The oxidation of Fe(II) to Fe(III) by micro-organisms is highly dependent on the presence of O$_2$, which is the predominant primary electron acceptor for all the oxidation processes within the sulphide ore body.

5.2.2 Oxidation of sphalerite and galena

Sphalerite and galena are, beside pyrite, the most important Zn- and Pb-bearing minerals within most types of carbonate-hosted Zn-Pb sulphide deposits. In contrast to the oxidation of pyrite,
which generates the largest volumes of sulphuric acid, the oxidation of galena and sphalerite produces no or only subordinate amounts of protons/acidity. However, during the oxidation process of sulphides, the concentration of $\text{SO}_4^{2-}$ ions is highly increased due to the oxidation of galena, sphalerite (reactions R6 to R9) and the associated generation of sulphuric acid due to the oxidation of pyrite (reaction R1).

In case of sphalerite, Fe is able to substitute Zn within the sphalerite up to 15 mol %. This Fe-bearing sphalerite will be an additional source for the generation of acid due to the hydrolysis reactions (R9).

$$\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4$$ \hspace{1cm} R6

$$\text{PbS} + \text{HCO}_3^- + 2\text{O}_2 \rightarrow \text{PbCO}_3 \downarrow + \text{SO}_4^{2-} + \text{H}^+$$ \hspace{1cm} R7

$$\text{ZnS} + 2\text{O}_2 \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-}$$ \hspace{1cm} R8

$$4(\text{Zn}_{0.75}\text{Fe}_{0.25})\text{S} + 8\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{FeO(OH)} \downarrow + 3\text{Zn}^{2+} + 4\text{SO}_4^{2-} + 3\text{H}^+$$ \hspace{1cm} R9

[Reactions R6 to R9 after BERTORINO, 1995]

5.2.3 Neutralisation reactions and precipitation of secondary minerals

The acid generated during the oxidation process is able to react with other minerals, such as carbonates and several silicates. This dissolution can lead to "acid hyper karst" and generates significant secondary permeability and thus pathways for fluids. Important minerals for the neutralisation of the acid are carbonates such as calcite and dolomite. In many carbonate-hosted deposits, both minerals occur closely intergrown with sulphide ore minerals. However, silicate minerals such as feldspar, muscovite, pyroxene, and amphibole) are rare and thus lead only subordinately to mineral dissolution and the generation of secondary porosity and, subsequently, an enhanced permeability.

Without any neutralisation, the acid, which is produced during the oxidation of pyrite and other sulphides, would result in pH values ranging between 1 and 4 and lower (SEAL ET AL., 2002). However, rare non-sulphide ore deposits do exist, in which the neutralisation has been mainly controlled by the neutralisation reactions from the break-down of feldspar and mica. One prominent example of such type of non-sulphide deposit is the Skorpion deposit in Namibia. Here, the non-sulphide ore is hosted by arkosic meta-arenites and the acid-neutralising break-down reaction of feldspar and mica has formed non-sulphide ore, which consists mainly of sauconite (a zinc-smectite) (KÄRNER & BORG, 2001; BORG ET AL., 2003)

Neutralising reactions result in a pH-increase within the pore fluids and the release and re-precipitation of metal cations from the carbonate host rock, such as $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and minor amounts of $\text{Fe}^{2+}/3^+$. These cations commonly participate in the formation of secondary minerals. The in-
crease in pH is accompanied by the precipitation of various (metal-bearing) minerals. Additionally, the newly formed minerals interact in several ways with the metal-bearing aqueous solution. Firstly, the precipitates are able to buffer the aqueous solutions within different ranges of pH (Blowes & Ptacek, 1994) (Tab. 17) and secondly, the precipitates inhibit the acid-neutralisation reaction with the carbonates of the host rock due to an ‘armouring’ of the carbonate minerals (Humicki, 2004; Humicki & Rimstidt 2004). Although an immediate neutralisation by highly reactive carbonate host-rocks (pH of 7 and above) might be expected, the oxidation of sulphides and the ‘armoring’ of the carbonate minerals result in an oxidation front, which shows a stabilised low pH, ranging approximately from pH 4 to pH 6 (Yanful & Orlandea, 2000).

Carbonate minerals and H⁺ ions are consumed as a result of the neutralisation, releasing dissolved cations (Ca²⁺ and Mg²⁺) and mainly bicarbonate HCO₃⁻ (reactions R16 and R17) into the solution. The carbonate and bicarbonate may react and bond with metal ions such as Cd²⁺, Mn²⁺, Zn²⁺, Pb²⁺, and others and precipitate these elements as secondary minerals. However, the precipitation of secondary carbonates is highly dependent on the pH of the aqueous solution and requires high pH values.

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad \text{R16}
\]

\[
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad \text{R17}
\]

Tab. 17: The hydrolysis of different secondary Fe(III)-phases releases different amounts of H⁺-ions into the aqueous solution and act as a buffer to the geochemical system within the oxidation zone.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Equation</th>
<th>Moles H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>am. Fe(OH)₃(s)</td>
<td>( \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3^+ + 3\text{H}^+ )</td>
<td>3</td>
</tr>
<tr>
<td>ferricydrite</td>
<td>( 10\text{Fe}^{3+} + 60\text{H}_2\text{O} \rightleftharpoons \text{Fe}_5\text{O}_9\downarrow + 30\text{H}^+ )</td>
<td>3</td>
</tr>
<tr>
<td>goethite</td>
<td>( \text{Fe}^{3+} + 2\text{H}<em>2\text{O} \rightleftharpoons \text{FeO(OH)}</em>\downarrow + 3\text{H}^+ )</td>
<td>3</td>
</tr>
<tr>
<td>hematite</td>
<td>( 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 \downarrow + 6\text{H}^+ )</td>
<td>3</td>
</tr>
<tr>
<td>schwertmannite</td>
<td>( 8\text{Fe}^{3+} + \text{SO}_4^{2-} + 14\text{H}_2\text{O} \rightleftharpoons \text{Fe}_5\text{O}_8(\text{OH})_6 \downarrow + 22\text{H}^+ )</td>
<td>2.75</td>
</tr>
<tr>
<td>jarosite</td>
<td>( 3\text{Fe}^{3+} + \text{K}^+ + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightleftharpoons K\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 \downarrow + 6\text{H}^+ )</td>
<td>2</td>
</tr>
</tbody>
</table>

am. Fe(OH)₃ = amorphous ferric hydroxide, Reactions R10 to R15 after Dold et al. (1999A)

R16 and R17 after Freeze & Cherry (1979)
5.3 Important processes of metal-fractionation

The process of the formation of non-sulphide zinc ore has been examined, with a particular focus on the metal separation process that is a crucial factor in the formation of red and white zinc ore. The results of our investigations show that multiple processes occur simultaneously during the formation of these different ore types: (1) the armoring effect of minerals (reaction inhibition of galena and calcite), (2) metal sorption onto HFO, and (3) different mineral solubilities and stabilities of various Zn- and Pb-minerals.

5.3.1 Armoring of galena

Observations from the Iranian deposits of Mehdi Abad and Irankuh have shown a preferential corrosion and oxidation of pyrite and sphalerite compared to galena. In most cases, galena is rimmed by anglesite containing abundant sub mm-sized galena inclusions. The size of the anglesite-coating is commonly up to 150 μm and more. These minerals are commonly associated with cerussite, which occurs in the immediate vicinity to- or is partly intergrown with the anglesite. In contrast to galena, other sulphides are less common within the oxidation zone of a sulphide ore body and their occurrence is commonly dependent on the stage of oxidation. Under the assumption that the sulphide ore consists mainly of a pyrite-sphalerite-galena paragenesis, the exclusive occurrence of galena or different oxidation stages of the sulphides suggest different reactivities within the oxidation process. Thus, the relative reactivity for these minerals at Mehdi Abad and Irankuh can be qualitatively characterised as:

\[
\text{pyrite} > \text{sphalerite} > \text{galena}
\]

These empirical field observations are similar to those of other authors, such as MEGAW ET AL. (1996) and laboratory experiments with varying pH values from 2 to 6 (JAMBOR, 1994). The pH-values used in these laboratory experiments are characteristic for a proposed oxidation zone of carbonate-hosted sulphide Zn-Pb deposits. Thus, the observations of samples from oxidised ores of several Iranian deposits are in agreement with these laboratory results of KAKOVSKY & KOSIKOV (1975).

The reactivity of pyrite, galena and sphalerite is highly variable and shows differences between the theoretically proposed and the observed reactivity. This reflects the different conditions under which oxidation occurs (e.g. gossans, abiotic, biotic, saturated-, unsaturated zone) (JAMBOR, 1994).

Under the presence of sulphate ions and low-ph conditions (Fig. 97) Pb\textsuperscript{2+}-ions precipitate as anglesite. Anglesite has a low solubility especially in SO\textsubscript{4}\textsuperscript{2-}-bearing aqueous solutions (K\textsubscript{s}=1.53·10\textsuperscript{-8} mol\textsuperscript{2}·l\textsuperscript{-2}, FAURE, 1998) and forms (more or less in situ) a coating onto undissolved galena and protects galena from an intensive direct contact with oxidising reagents (Fig. 98). This “protective” coating is probably one explanation for the apparent resistance of galena during the oxidation process. The solubility of zinc sulphates, such as zincoelite, in contrast, is much higher and the related zinc- and sulphate concentrations would not be reached with the considered hypothetical initial solution. The precipitation of insoluble lead minerals starts with anglesite at low (acidic) pH values and changes to insoluble carbonates, such as cerussite or hydrocerussite. The formation of cerussite or hydrocerussite is determined by the partial pressure of CO\textsubscript{2}. The formation of hydroce-
russite is limited to relatively low $P_{CO_2}$ (log $P_{CO_2}$< -1.85 kPa, INGWERSEN, 1990), at higher pH values (approximately at pH 6.2). Thus, lead forms insoluble minerals over the full relevant range of pH, and $P_{CO_2}$, which occur in the acidic oxide zone of sulphide deposits and the basic environment of carbonate host rocks.

Fig. 97: Stability fields of Anglesite and Cerussite (25 °C, 100 kPa, calculated with Phreeqc). The lines show the phase boundary for different CO$_2$ partial pressures. Anglesite is stable even at low sulphate concentrations and at low pH. (atmospheric $P_{CO_2}$ = 3.16·10$^{-2}$ kPa)

Thus, the relative resistivity of galena within the oxidation process is best explained by armouring effects. Armored galena have been observed on samples from Mehdi Abad, Irankuh, and Ku-e-Surmeh and have also been described for other oxidised sulphides by several other authors as well, e.g. JEONG & LEE, (2003). The immediate precipitation of anglesite under acidic conditions results in two effects: i) the reaction inhibition by ‘armoring’ and thus prevention of a fast oxidation of galena, and ii) the concentration of Pb$^{2+}$ ions within the aqueous solution is limited by the solubility of anglesite (log$_a$ Pb$^{2+}$ < -3.5 mol*l$^{-1}$).

5.3.2 Armoring of calcite

The neutralisation of sulphuric acid by calcite, as described in reaction R9, leads to the precipitation of gypsum, accompanied by the precipitation of Fe-oxihydroxides due to raised pH values. In general, this leads to a strongly adhesive encrustation of calcite and/or other minerals and to a partially or almost totally suppressed reactivity of the encrusted minerals (HUMICKI, 2004; HUMINICKI & RIMSTIDT 2004; WILKINS ET AL., 2001).

Recent investigations of HUMICKI (2004), HUMINICKI & RIMSTIDT (2004), WILKINS ET AL. (2001), YANFUL & ORLANDEA (2000) and others have focussed on the reaction between sulphuric acid and carbonates and the effects of precipitation of gypsum coatings on the surface of calcite. Experiments that have measured the rate of calcite dissolution in conjunction with gypsum and/or iron hydroxide precipitation on the surface of calcite show that gypsum rather than iron hydroxide coatings may influence the neutralisation in slowing down the dissolution rate of the limestone in a car-
bonate host rock (Fig. 99). The isolation of calcite from further reaction by gypsum prevents the limestone from generating any additional alkalinity in the system (HAMMARSTROM, 2002).

Fig. 99: The rate of calcite dissolution (measured as proton consumption) decreases rapidly with time. This is an effect of the CaSO₄-coating of calcite. The oxidation of a sulphide ore body is a long lasting process, which is reflected in high values on the time-axis of this diagram - associated with low H⁺ consumption rates of the calcite. (after Huminicki, 2004)

These observations are highly relevant for any oxidation- and metal-fractionation model of non-sulphide zinc deposits. As a result of the decreased reactivity of gypsum-coated carbonates, the pH-value of the metal-bearing aqueous solutions increase along the fluid path over a long distance. This provides the possibility for the metals to fractionate and precipitate spatially separately, depending on the pH of the solution.

The concentration of SO₄²⁻ ions is highly increased during the oxidation of sulphides (oxidation of galena, sphalerite, reactions, R6 to R9) and the associated generation of sulphuric acid due to the oxidising of pyrite (reaction R1 and R2). The solubility of gypsum in these acidic SO₄²⁻-rich fluids is much less than in pure water due to the common ion effect (Le Chatelier’s Principle) (formula F 3). Under these conditions, gypsum is insoluble and forms a stable coating.

After the oxidation of the sulphides, the SO₄²⁻ concentration decreases rapidly, gypsum becomes much more soluble and is transported out of the (karst- and non-sulphide zinc) systems. The solubility of gypsum under normal aqueous conditions (K_sp=1.9·10⁻⁴) is higher than the solubility of calcite and dolomite.

\[
CaCO₃ + 2H^+ + SO₄^{2-} + 2H₂O \rightarrow CaSO₄ \cdot 2H₂O \downarrow + H₂CO₃(aq) \quad \text{after WILKINS ET AL. (2001), R9}
\]

\[
K_{sp} = \frac{a_{Ca^{2+}} \cdot a_{SO_4^{2-}}}{a_{CaSO_4}} \approx \left[Ca^{2+}\right] \left[SO_4^{2-}\right] = 1.9 \times 10^{-4}
\]

An additional mechanism for the armoring of limestone is the precipitation of Fe-oxihydroxides. The mechanisms, by which Fe-oxihydroxides armour limestone is still poorly understood. However, the reactivity of Fe-armoured limestone has been estimated to range from 4% to 62% compared to the reactivity of ‘fresh’ limestone (SUN ET AL., 2000).
The difference in the effectiveness for the armoring of carbonate minerals by either gypsum- or ferrihydrite-coatings is due to the geochemical origin and genesis of both types of coatings. Gypsum precipitates close to or immediately onto the carbonates as a result of a neutralisation reaction, whereas ferrihydrite has to be transported as insoluble particles towards the calcite to be available for armoring. A combination of both armoring mechanisms is presumably particularly effective to maintain a stable acidic environment within the oxidation zone of a carbonate-hosted sulphide ore body. Thus, the dissolution of primary and the precipitation of secondary minerals and the metal transport within the active oxidation zone is modelled for these most common conditions.

Contrary to expectations, which would suggest an immediate neutralisation within the highly reactive host carbonates (pH of 7 and above), the oxidation of sulphides and the armoring of the carbonates results in an oxidation front, which shows stable low pH values, ranging from approximately pH 4 to pH 6. Observations of sulphide- and carbonate-bearing mine tailings show, that the oxidation of sulphides leads to low pH values within a carbonate-dominated environment due to armoring effects (YANFUL & ORLANDEA, 2000). Long-term experiments by several authors, such as YANFUL & ORLANDEA, (2000), have shown the effects of limestone armoring to the neutralisation of acid mine drainage (ARD). The added limestone lost its effectiveness for neutralisation after a couple of years, as a result of the precipitation of secondary minerals onto the limestone particles.

5.3.3 Metal sorption onto ferrihydrite

Cu, Cd, Pb, Zn and As can be adsorbed onto Fe-oxyhydroxides (goethite, ferrihydrite) and this process of cation–adsorption onto hydrous ferric oxides is highly dependent on the pH level of the aqueous solution (MARTINEZ & MCBRIDE, 2001; DZOMBAK & MOREL, 1990). The chemical behaviour and mobility of metal cations are largely controlled by their interaction with these iron-oxides (TRIVEDI ET AL., 2003). Ferric hydroxides have specifically high surface areas (up to 600 m²g⁻¹) (Lee & Saunders, 2003). This high surface area, associated with the affinity of ferric iron hydroxides to Me(II)-ions, results in a highly effective adsorption process controlled by pH and metal concentration.

Lead and zinc show different degrees of absorption onto ferrihydrites as shown in. The quantitative binding of Pb(II)-ions onto ferrihydrite reaches its maximum and the saturation of the ferrihydrite at approximately pH 5.5 (DYER ET. AL, 2003; RUTHERFORD, 2002). In contrast to lead, quantitative zinc adsorption starts at higher pH values, ranging from approximately pH 5.5 to 7.5 (DZOMBAK & MOREL, 1990). This is an additional, important reason for the metal separation and fractionation of lead and zinc within non-sulphide ore bodies. Most of the lead within the oxidation front is adsorbed under acidic condition onto hydrous ferric oxides. Under these acidic conditions however, zinc remains mobile in the aqueous solution and is, consequently, transported further (vertically or laterally) to distal areas. The pH increases slightly due to the neutralisation inhibition by the CaSO₄ and Fe-oxyhydroxide armoring of the carbonate host rock. As a result, zinc precipitates in distal (commonly deeper) portions of the supergene system, which are commonly free of hydrous ferric oxides and lack any substantial secondary lead accumulations.

Fe-oxyhydroxides occur as nanometre-sized colloidal precipitates. These colloidal precipitates can be transported in aqueous solutions into spatially deeper or to more distal levels (RUTHERFORD, 2002) dependent on the (acid-) karst system, fault systems and the general porosity and perme-
ability of the host rock. Thus, it is important to note that the occurrence of red Fe-oxides alone is not a sufficient indicator of a sulphide (proto-) ore that existed originally at this position.

The sorption of metal-ions as well as carbonate-ions onto hydrous ferric oxides (HFO) is a function of pH (DZOMBAK AND MOREL, 1990). HFO is also called amorphous ferric hydroxide, or amorphous iron hydroxide and is a precipitate, which forms upon rapid hydrolysis-precipitation from ferric iron solutions. Hydrous ferric oxide is a poorly crystalline, highly porous solid with a large surface area from 200 m²g⁻¹ to approximately 750 m²g⁻¹. The mineral-to-water interface of HFO has a pH-dependent charge and is highly reactive (HOFMANN ET AL., 2004). The reactive surfaces of metal oxides, such as hydrous ferric oxide in natural waters are predominantly covered by carbonate species (CO₃²⁻, HCO₃⁻). The lower availability of sorption sites affects sorption of other metals such as Cd, Cu, Ni, Pb, Zn and As and thus influences the mobility of these heavy metals in the natural environment.

The adsorption onto HFO plays an important role for the oxidation processes of Fe-rich Zn-(Pb) sulphide ores. The high amount of iron within the initial sulphide ore is a requirement for the formation of two different types of non-sulphide ore: the red zinc ore and the white zinc ore. The results of the calculated metal sorption (Fig. 100) onto HFO supports the explanation of several aspects and phenomena related to the formation of the red zinc ore and the white zinc ore. It is possible to envisage several scenarios of pH for the oxidation zone. The most interesting range of pH reflects acidic conditions of approximately pH 5 to 6.5 within the oxidation zone, where several effects interact. By applying the effects of HFO adsorption to the hypothetical Zn-Pb-Fe-rich solution of an oxidation zone, one can assume that HFO is able to adsorb up to 3 % of the zinc from the solution.

Fig. 100: PHREEQC precipitation and adsorption simulation of a hypothetical metal-rich, which contains 2.4 10⁻² mol Zn, 1.6 10⁻⁵ mol Pb. In simulation 1 the Zn-Pb solution is in reaction and equilibrium with hydrous ferric oxides (HFO). The adsorption curves of Zn²⁺ and Pb²⁺ show clearly the dependence of the amount of adsorption to the pH. The quantitative adsorption of lead starts at approximately pH 3, and zinc at pH 5. Simulation 2 is more realistic and shows the effect of the additional removal of Zn and Pb due to the precipitation of anglesite, cerussite, and hydrozincite. Until Point A nearly 75 % of lead have been removed from the solution due to the precipitation of anglesite. At point (A) additional adsorption effects take account and the concentration of lead reaches the adsorption isotherme at point (B). Zinc does not form insoluble sulphate minerals. Thus, zinc is removed from solution due to adsorption effects exclusively. At point (C) precipitation of hydrozincite starts and most portion of the zinc is removed from solution.
and additionally adsorb up to 18% lead from this solution. In contrast to zinc, which is exclusively bound to HFO, the biggest portion of lead is removed from the solution due to the precipitation of anglesite. Thus, the final aqueous solution, which leaves the oxide zone is still rich in zinc but shows only traces of lead.

The ability of HFO to bind particularly zinc within the oxidation front depends on the local characteristics of each oxidation front.

5.4 Formation of hemimorphite, smithsonite, and hydrozincite, occurrence and mechanisms

5.4.1 Hemimorphite

Hemimorphite occurs as the most common zinc hydrosilicate mineral in all of the Iranian non-sulphide zinc deposits examined in this study. Other secondary zinc silicates, such as sauconite or willemite are rare or absent. In most cases, hemimorphite occurs in veins and open spaces of the ‘white-’ and ‘red zinc-ore’, within fault zones and -breccias and in the matrix of fault breccias as euhedral crystals, which have grown perpendicular to the underlying surface of fractures and spaces (Fig. 102). The size of the hemimorphite crystals ranges from sub-mm up to several millimetres. In some cases, several generations of hemimorphite can be distinguished. This phenomenon of several stages of hemimorphite precipitation is common, especially at the Mountain Ore Body (MOB) of Mehdi Abad (REICHERT & BORG, 2003), but also visible at Irankuh.

Zinc carbonates are soluble under acidic conditions and start to precipitate as smithsonite/hydrozincite at approximately pH 6.5, depending on the $P_{CO_2}$ and the activity of $Zn^{2+}$ (Fig. 103 and Fig. 104). Zinc silicate minerals will form if silica is available and the partial pressure of CO$_2$ is
Data interpretation and numerical modelling of carbonate-hosted non-sulphide zinc deposits

low (Fig. 104). Hemimorphite is not commonly observed as a first stage mineral within the paragenetic sequence. Observations from Mehdi Abad and Irankuh (and reports for carbonate host rocks by TAKAHASHI, 1960 and others) have shown that hemimorphite is related to late or even last stages of non-sulphide mineralisation processes growing within fractures and open spaces of the ‘white-’ and ‘red zinc-ore’ Fig. 102 growing over long periods.

The quantitative precipitation of hemimorphite and other zinc-silicates is dependent on the availability of silica. For this reason, it is necessary to consider the geochemical behaviour of such fluids with respect to SiO$_2$ as well. The solubility of silica phases increases drastically from crystalline quartz to amorphous silica (DOVE & RIMSTIDT, 1994). H$_4$SiO$_4$ is a weak acid and dissociates appreciably about two pH units above neutrality (DOVE & RIMSTIDT, 1994). The carbonate dissolution process within a ‘closed’ system consumes enough H$^+$ to increase the solubility of SiO$_2$ significantly. The availability of dissolved silica is limited by the solubility of SiO$_2$ in water and the slow dissolution rate of SiO$_2$. Thus, silica within natural waters is not sufficient for an effective and quantitative binding of zinc. The biggest portion of zinc will precipitate as carbonates. Calculations with PHREEQC (Tab. 20) show, that SiO$_2$ concentration in carbonate-buffered solutions reaches 9.6·10$^{-4}$ mol·l$^{-1}$ for crystalline quartz and up to 2.0·10$^{-3}$ mol·l$^{-1}$ for amorphous quartz (chert). Thus, chert provides the highest concentrations of SiO$_2$ in aqueous solution. The low concentrations of dissolved silica lead to the precipitation of small amounts of Zn-silicates only, and, consequently, zinc precipitates at the oxidation stage predominantly as zinc carbonates from the supergene fluids.

Hemimorphite is less soluble than hydrozincite over a pH range from 5 up to approximately 7.6 under atmospheric pressure log P$_{CO_2}$ = -1.5 kPa (Fig. 103). Under these conditions, hemimorphite is more stable than hydrozincite and should precipitate. However, the stability fields occur close together and can be shifted easily by varying the P$_{CO_2}$ values and by the chemistry of the mineral assemblage in equilibrium with the aqueous solution (Tab. 18).

According to Tab. 18, an intimate association of dolomite/calcite with smithsonite and/or hydrozincite results in ph-values, which do not reach the stability of hemimorphite. The ‘white zinc ore’, found in numerous deposits, consists predominantly of smithsonite and/or hydrozincite. Thus, the phases, which are in equilibrium with the aqueous solution, are limited to smithsonite and/or hydrozincite. The resulting pH values for the equilibrium with aqueous solutions are lower with re-
spect to the calcite/dolomite-dominated mixtures (Tab. 18). Here, the stability of hemimorphite is reached for log$_{10}$ P$_{CO2}$ < -0.5 kPa. Higher values of P$_{CO2}$ (log$_{10}$ P$_{CO2}$ > -0.5 kPa) support the precipitation of hydrozincite or smithsonite. Thus, the precipitation of hemimorphite is limited to relatively low P$_{CO2}$ values, which occur preferentially in arid climates with low biological activities within the soil and deep groundwater tables.

Tab. 18: pH values for equilibrated mineral associations dependent on P$_{CO2}$.

<table>
<thead>
<tr>
<th>Log P$_{CO2}$ [kPa]</th>
<th>-1.5</th>
<th>-1</th>
<th>-0.5</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value for dolomite/sm/hy association</td>
<td>8.28</td>
<td>7.95</td>
<td>7.62</td>
<td>7.30</td>
<td>6.97</td>
<td>6.65</td>
</tr>
<tr>
<td>pH values for calcite/sm/hy association</td>
<td>8.18</td>
<td>7.85</td>
<td>7.53</td>
<td>7.2</td>
<td>6.88</td>
<td>6.55</td>
</tr>
<tr>
<td>pH values for sm/hy association</td>
<td>7.42</td>
<td>7.2</td>
<td>6.96</td>
<td>6.73</td>
<td>6.46</td>
<td>6.14</td>
</tr>
</tbody>
</table>

sm: smithsonite, hy: hydrozincite, equilibrium reaction calculated with PHREEQC.

The data and calculations presented by TAKAHASHI (1960), MCPHAIL ET AL. (2003) and INGWERSEN (1990) indicate that the zinc silicates hemimorphite and willemite are the least soluble and most stable Zn-minerals in a pH range less than pH 7 (at atmospheric P$_{CO2}$) compared with zinc carbonates. Thus, hemimorphite can be interpreted as a mineral, formed under acidic to slightly basic conditions and thus should precipitate as the earliest non-sulphide zinc mineral.

In general, hemimorphite was formed after the oxidation of a sulphide ore, probably as a result of dissolution and re-precipitation of precursor zinc carbonate minerals. An exception, in which hemimorphite can be assumed as a quantitatively important first stage mineral, is the Mountain Ore Body (MOB) of Mehdi Abad. Here, at the MOB, hemimorphite occurs in large quantities and at least two different stages for the formation of hemimorphite are distinguishable (REICHERT ET AL., 2003).

Fig. 103: Stability of zinc carbonates in the chemical system Zn-O-H-C dependent to P$_{CO2}$ and the pH. The activity of zinc is a(Zn)= $10^{-5}$ (after MCPHAIL ET AL. (2003))

Fig. 104: Zinc mineral stabilities dependent to pH and P$_{CO2}$ for a silica and carbonate containing solution. Smithsonite becomes stable at relative high partial pressures of CO$_2$ (P$_{CO2}$> 3.16 kPa) in the chemical system Zn-O-H-C-Si (after MCPHAIL ET AL. (2003)).
5.5 Geochemical genetic model for carbonate-hosted non-sulphide deposits

5.5.1 A metallogenetic model for carbonate hosted non-sulphide zinc deposits

The model attempts to explain the genesis of carbonate-hosted non-sulphide zinc deposits sensu lato and related ore types, such as red zinc ore and the white zinc ore sensu stricto and is primarily adapted to carbonate-hosted non-sulphide zinc deposits with a distinct karst- and acid-karst breccia zone. Good examples for this type of deposit are the Mountain Ore Body (MOB) of Mehdi Abad and the Kohladarvazeh pit within the Irankuh deposit. These share similar typical geological attributes, resulting in the occurrence of the same types of non-sulphide zinc ore. At least three important factors for the genesis of this type of non-sulphide zinc deposit can be distinguished:

(i) The first important feature is a proto-sulphide ore close to surface. All of the investigated Iranian deposits are characterised by sulphide ore at or closely below the surface due to intensified exhumation rates, and which can easily be reached by supergene meteoric fluids and by oxygen. The (present) depths of the sulphide ore ranges from 10’s of meters (Irankuh) to 130 meters and more (Mehdi Abad). The near-surface and partly exposed position of the sulphides in areas of high topographic relief are important factors that support a fast and effective oxidation process.

(ii) Secondly, the presence of karst-originated breccia clasts seems to be important for the formation of large quantities of non-sulphide ore. The breccia clasts are characterised by high surface area, high porosity and good permeability that allows metal-carrying groundwater to penetrate easily. The non-sulphide zinc minerals precipitated from these fluids and now form pore-filling cements to the karst fragments.

(iii) The third important factor in the investigated deposits is the proximity of an aquiclude or aquifer, such as shales (Irankuh, Kuh-e-Surmeh (REICHERT & BORG, 2002), shaly limestone (Mehdi Abad: Mountain Ore Body) and schists (Angouran) (DALIRAN & BORG, 2004). The aquiclude acts as a nearly impermeable and insoluble barrier for meteoric water, the groundwater system, and the metal-delivering fluids. This hydraulic barrier stops descending fluids, such as meteoric recharge from the surface and leads to a mixing with the local aquifer. These mixing processes can result in an increased capability to dissolve calcite and thus causes additional karst processes. The underlying aquiclude leads to a “ponding” of fluids in front of the hydraulic barrier.

These geological features suggest a general process of oxidation and the formation of non-sulphide zinc ore that can be explained in several stages:

At a first step, the sulphide-ore-bearing carbonate sequence was uplifted and the overburden eroded. Subsequently, the carbonate sequence reached a near surface environment and was penetrated by meteoric water and groundwater. This activated karst processes in the saturated zone and the adjacent strata. Extensive karst processes, supported by numerous faults and fractures, have affected the carbonate host rock. Partitioning of the bedding planes and the related fractures might have been additionally used by meteoric water for karst-processes.

The karst system supported the influx of oxygen and thus supported the oxidation process of the sulphide ore. Bedding planes and related (karst-) fractures additionally act as conduits for the supergene Zn-(Pb-) bearing fluids and the metal-bearing supergene fluids migrated to the underlying
breccia zone. The volume of the karst breccia zone and the related high surface area of the breccia-clasts provided a highly reactive surface and excellent porosity for the precipitation of the non-sulphide ore. A high portion of the non-sulphide zinc ore occurs as a cement to breccia clasts that originated from karst-collapse and the size of the breccia clasts ranges from sub-centimetre up to several decimetres.

![Figure 105: Conceptual model for the formation of a carbonate-karst and the subsequent emplacement of non-sulphide zinc ore as a cement to the karst breccia clasts.](image)

(A) Initial stage: small amounts of water pass the limestone through fractures. Underlying shales act as an aquiclude. (B) At later stages, more water reaches the groundwater zone through karst-widened fractures. A mixing-effect of the recharge with the groundwater leads to accelerating karst processes. (C) The fractures and pathways are wide enough to provide access for a large quantity of oxygen and water to the sulphide ore. The oxidation speed increases and zinc-carbonates precipitate at deeper levels as cement to karst breccia clasts. At this time, the water table has been lowered due to a extremely arid climate.

Typical massive and disseminated sulphide ores contain iron, which is bound to pyrite, sphalerite, and Cu-Fe-sulphides. Most of the iron, released during the oxidation process precipitates as largely insoluble hydrous ferric oxides (goethite, ferrihydrite) (reaction R3 & R4). The oxidation front and the adjacent areas are characterised by low pH-values, due to the precipitation of CaSO₄ (reaction R9) and subsequent coating of the calcite/dolomite host rock. This coating inhibits the neutralisation of sulphuric acid as described above. The pH-value should be relatively stable over a broad spatial range of the oxidation front and the adjacent regions and deeper levels, which are typically affected by the acidic fluids with low pH values. The low pH-value (pH<5) within the oxidation front, in turn, is important for the sorption of metals onto these ferrihydrites and, as a consequence, the metal fractionation processes.
5.5.2 Theoretical studies on the precipitation of secondary supergene minerals

The solubility and the precipitation of secondary minerals are predominantly triggered by pressure, temperature, $P_{\text{CO}_2}$, pH, and element concentration of different species within the aqueous solution (Takahashi, 1960). The Eh (oxidation-reduction potential) is not related to the stability boundaries and the precipitation of these minerals, since there is no change in the valences of the elements during the (re-) precipitation process (Takahashi, 1960). Temperature and pressure of supergene conditions have been assumed to be constant at 25 °C and 101.3 kPa. Thus, the controlling factors involved in the formation of the most common secondary minerals (anglesite, cerussite, smithsonite, hydrozincite, hemimorphite, Fe-oxihydroxides, gypsum, calcite, dolomite) can be assumed as pH, total carbon dioxide in solution (dependent on the $P_{\text{CO}_2}$), concentration of silica, sulphur (predominantly as $\text{SO}_4^{2-}$), and the concentration of the (metal-) cations ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Zn}^{2+}$, $\text{Pb}^{2+}$, $\text{Fe}^{3+}$).

The occurrence of minerals is determined by their solubility, which can be calculated for equilibrium conditions. A mineral starts to precipitate under equilibrium conditions if its solubility limit is reached and the saturation index $\text{SI}_{[\text{mineral}]}$ equals 0. These individual conditions for various minerals will be described below.

Smithsonite and hydrozincite

Fig. 103 shows the stability field for zinc carbonates at different $P_{\text{CO}_2}$ values, which depend on the mineral stability, on the pH value and the influence of the $P_{\text{CO}_2}$. Generally, an increase of $P_{\text{CO}_2}$ leads to an increased stability of Zn- and Pb-carbonates within the relevant pH interval for a carbonate environment/host rocks. This effect is due to the raised activity of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ ions within the aqueous solution.

The most common zinc carbonate hydroxide mineral at Irankuh and the MOB of Mehdi Abad is hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$). Smithsonite ($\text{ZnCO}_3$) is detectable in most of the non-sulphide mineralised samples, but occurs only in subordinated amounts compared to hydrozincite. The reason for this disproportion between hydrozincite and smithsonite is the influence of the partial pressure of CO₂. The precipitation of smithsonite is restricted to relatively high $P_{\text{CO}_2}$ values ($\log P_{\text{CO}_2} = 0.2$ kPa) Takahashi (1960). Thus, regarding the atmospheric $P_{\text{CO}_2}$ value (Tab. 19), it is not possible to precipitate smithsonite from an aqueous solution, which is in equilibrium with the atmosphere. The atmospheric $P_{\text{CO}_2}$ is much lower (Sigg & Stumm, 1989) as the minimum conditions required for the precipitation of smithsonite ($\log P(\text{CO}_2)_{\text{atm}} << \log P(\text{CO}_2)_{\text{soil}} << \log P(\text{CO}_2)_{\text{smithsonite}}$)(Tab. 19).
Fig. 106: BSE image of partly oxidised sulphide ore. The most common non-sulphide zinc minerals are smithonite and hydrozincite. Relics of galena (Ga) are surrounded by cerussite (Ce). Massive and anhedral smithsonite (Sm) is overgrown (or was altered to) hydrozincite (Hy). The formation of smithsonite indicates the presence of high CO$_2$ partial pressures most likely at a precursor stage. However, the overgrown and smithsonite replacing hydrozincite at later/last stages indicate that hydrozincite became more stable. The process of alteration of smithsonite to hydrozincite is believed to be still active today and caused by open fractures and thus by equilibrium processes with the atmospheric P$_{CO_2}$. (Irankuh, Sample IK02145)

Tab. 19: Typical values of P$_{CO_2}$ within the atmosphere, soils and partial pressure for smithsonite precipitation.

<table>
<thead>
<tr>
<th>atmospheric log P$_{CO_2}$</th>
<th>soil log P$_{CO_2}$</th>
<th>minimum log P$_{CO_2}$ – smithsonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>0…-2 kPa (actual log P(CO$_2$)=-1.5kPa)</td>
<td>0.5…5 kPa</td>
<td>0.24 kPa (15 °C) 1.4 kPa (40 °C)</td>
</tr>
</tbody>
</table>

After SIGG & STUMM, 1989; thereafter S CHEFFER & SCHACHTSCHABEL, 2002; GRYSHKO & HORLACHER, 1997; A TAKAHASHI, 1960;

A logP$_{CO_2} = 0.2$ kPa (at 15 °C) is valid for the formation of smithsonite according to the equation (after TAKAHASHI, 1960):

$$5ZnCO_3 + 3H_2O \leftrightarrow 2Zn_2(CO_3)_2(OH)_6 + 3CO_2$$

The reaction would be driven to the right in case of logP$_{CO_2} < 0.2$ kPa and hydrozincite would precipitate. These conditions are common for aqueous solutions, which are in equilibrium with the atmosphere, such as surface near solutions in unsaturated zones.

In contrast to these equilibrium conditions, aqueous solutions at deeper levels or water-saturated zones are in disequilibrium with the atmospheric CO$_2$ and reach values, which are favourable for the precipitation of smithsonite. Increasing carbonate concentrations as well as a high P$_{CO_2}$ tend to stabilise smithsonite and other carbonate-bearing minerals (McPHAIL ET AL., 2003). Thus, the dominance of hydrozincite in the non-sulphide deposits of Iran-Kuh, and Mehdi Abad, Kuh-e-Surmeh (REICHERT & BORG, 2002), support the thesis of (near-) equilibrium conditions with the atmosphere.

All these examined non-sulphide zinc deposits are near-surface examples or are situated on the flanks of high topographic relief mountain ranges, associated with faults and intensively brecciated host-rocks. However, the occurrence of corroded traces of smithsonite, mostly replaced by hydrozincite within these three observed deposits suggests periods of raised P$_{CO_2}$ during which this early smithsonite was formed.
5.5.3 Possible reasons for high CO₂ partial pressures for the formation of smithsonite

Several sources of CO₂ are possible to explain the elevated P_{CO₂} and thus the disequilibrium with the atmosphere. The authors consider that the biggest portion of smithsonite as having been produced during the early stages of formation of the non-sulphide zinc deposits - contemporaneous with the oxidation of the sulphide ore body. The smithsonite in samples of Mehdi-Abad and Irankuh shows textures of corrosion and alteration to hydroyazincite, which is the most common zinc carbonate mineral at the investigated non-sulphide deposits. The present atmospheric and climatic related P_{CO₂} conditions in Iran favour the formation of hydroyazincite only. As seen above, the precipitation and stability of smithsonite is limited to sufficiently high P_{CO₂}. Since the formation of smithsonite is limited to high partial pressures of carbon dioxide, one has to consider additional sources of CO₂ that was available during its formation.

One well-known source of carbon dioxide are biological processes. These processes consume O₂ and oxidise mainly organic carbon to CO₂. The partial pressure of the biological induced CO₂ is able to increase up to values that reach the stability field of smithsonite. However, thick organic soil coverage in a humid climate on top of the oxidising sulphide ore consumes oxygen and thus hinders/inhibits the oxidation process of the sulphides.

Another important additional source of CO₂ is probably from the generation during the neutralisation of the acidic aqueous solution, derived from the oxidation process of the sulphide ore. This acidic solution reacts with the carbonates of the host rock (PALMER & PALMER, 2000; RITCHIE, 1994; LAPAKKO, 2002). The results of his reaction are gypsum (and other salts), water and carbon dioxide. The highest portion of the CO₂ generated through this neutralisation reaction dissolves in the aqueous solution as H₂CO₃. The dissolved H₂CO₃ can degas CO₂ to achieve equilibrium with the pore gasses. This process has been measured at carbonate-bearing sulphide mine tailings. Here, carbon dioxide increases from 0.15 vol. % at surface near tailing regions to concentrations as high as 24 vol. % within the tailings (GERMAIN ET AL. 1994) that is equivalent to a partial pressure of log-P_{CO₂}=1.38 kPa.

\[
\begin{align*}
\text{CaCO}_3 + 2H^+ + SO_4^{2-} &\rightarrow H_2CO_3 + CaSO_4(s) \cdot 2H_2O & \text{pH}>6.4 \\
\text{CaCO}_3 + 2H^+ + SO_4^{2-} &\rightarrow HCO_3^- + H^+ + CaSO_4(s) \cdot 2H_2O & \text{pH}<6.4
\end{align*}
\]

R19  
R20

Thus, one can consider that H₂CO₃ dissociation to H₂O and CO₂ increases the partial pressure of CO₂ not only locally at the oxidation zone of the sulphide ore, but also adjacent to the oxidation zone due to four principal processes. These processes can be postulated as:

1. Immediate degassing of CO₂ as a result of the equilibration with the pore gas
2. Transport of CO₂ mainly dissolved as H₂CO₃ into adjacent areas of the host rock and thus the time-delayed degassing of CO₂
3. Diffusion of CO₂ through the open pores of the host rock and/or karst spaces. The time-delayed degassing of CO₂ is due to a slow equilibrium reaction
The neutralisation processes is favoured here as the main source of carbon dioxide, which caused the high partial pressures of CO₂ and thus precipitation of the first-stage smithsonite. This CO₂-source is independent of the climate and is available even at low temperatures (which additionally support the formation of smithsonite). The high partial pressure of carbon dioxide is active as long as the oxidation process is in progress. Thus, it is possible to generate high P_{CO2} in an arid climate without or with low biological activities only. Additionally, a vegetation- and soil-free surface would support an effective penetration of oxygen to the sulphide and the effective formation of a non-sulphide ore body.

5.5.4 Anglesite and cerussite

The solubility of anglesite in pure water is relatively high and results in calculated activities of Pb^{2+} and SO_{4}^{2-} of approximately log\_a = -3.5 mol/l\(^1\) (Fig. 107). However, the solubility is dependent on the activity of SO_{4}^{2-}. Thus, additional SO_{4}^{2-} ions will decrease the solubility of anglesite and therefore decreases the activity of lead within the aqueous solution to a_{Pb}=10^{-5} mol/l\(^1\) (Fig. 108). Additional sources of SO_{4}^{2-} ions are the generation sulphuric acid during the oxidation process and/or the presence of gypsum and other SO_{4}^{2-} bearing minerals.

Calculations with PHREEQC indicate, that the presence of gypsum (and of course other sulphate sources) is able to force anglesite to precipitate at even lower concentrations of Pb^{2+} compared to anglesite’s precipitation in pure water. The equitation R21 is shifted to the right side and the resulting concentrations of Pb^{2+} decrease in order to fulfil the formula F 4.
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\[ \text{Pb}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4 \downarrow \quad \text{R21} \]

\[ K_{sp} = \frac{a_{\text{Pb}^{2+}} a_{\text{SO}_4^{2-}}}{a_{\text{PbSO}_4}} \approx \left[ \text{Pb}^{2+} \right] \left[ \text{SO}_4^{2-} \right] = 1.58 \times 10^{-8} \quad \text{(FAURE, 1998)} \]

After the oxidation of the sulphide ore, the pH value tends to change to basic conditions and cerussite becomes more stable than anglesite, according to figure Fig. 104. Thus, anglesite will be replaced by cerussite according to the following equitation R22 (after SANGAMESHWAR & BARNES, 1983):

\[ \text{PbSO}_4 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{PbCO}_3 + \text{SO}_4^{2-} + 2\text{H}^+ \quad \text{R22} \]

Reaction R22 shows the dependence of the activities of pH, H\textsubscript{2}CO\textsubscript{3} and SO\textsubscript{4}\textsuperscript{2-}. Active oxidation processes are associated with high activities of both SO\textsubscript{4}\textsuperscript{2-} and H\textsuperscript{+}, which shifts the reaction to the left. After the oxidation process, the concentration of SO\textsubscript{4}\textsuperscript{2-} decreases an pH will increase, which supports the formation of cerussite.

The armoring process and reaction inhibition of galena due to coating with anglesite/cerussite results in a decreased reactivity of galena (Fig. 98). Thus, the de facto reactivity of galena is much lower than the proposed theoretical rate, which would suggest that galena should be supposedly 5-times more reactive compared to sphalerite (ZEMAN, 1985). It is known, that the behaviour of sulphide oxidation, especially the oxidation of galena and sphalerite is highly dependent on the geochemical environment (pH, host rock geochemistry, hydrology) and is often different from the proposed theoretical values (JAMBOR, 1994).

5.5.5 Hydrocerussite

The investigations of the non-sulphide zinc deposits Mehdi Abad and Iran-Kuh, and Kuh-e-Surmeh (REICHERT & BORG, 2002) show either trace amounts or no hydrocerussite (Pb\textsubscript{3}(OH)\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}). Hydrocerussite also lacks on the Angouran non-sulphide zinc deposit (Iran), which was shown by studies by DALIRAN & BORG (2004). Non-sulphide zinc deposits of the United States from HEYL & BOZION (1963), and HEYL (1963 AND 1964), from Sardinia from BONI ET AL (2003) and investigations of KÄRNER (2003) and BOLAND ET AL. (2003) at Shaimerden/Kazakstan, of REYNOLDS ET AL (2003) at Mae Sod, and MULLER (1972) at Beltana are other examples of similar rare occurrence of hydrocerussite.

The scarcity of hydrocerussite can be explained by its stability parameters and the formation of hydrocerussite can be described as an equilibrium reaction as shown in reaction R23:

\[ 3\text{PbCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Pb}_3(\text{OH})_2(\text{CO}_3)_2 + \text{CO}_2 \quad \text{R23} \]

(MERCY ET AL., 1998)

The formula and thermodynamic/geochemical analysis indicate that the formation of hydrocerussite is highly dependent on the partial pressure P\textsubscript{CO\textsubscript{2}} and the temperature. ESSINGTON ET AL (2004)
show, that the formation of hydrocerussite is favoured at $P_{\text{CO}_2}$ equal or less than the atmospheric $P_{\text{CO}_2}$ at 25 °C. Partial pressures of CO$_2$ above the atmospheric level of approximately $10^{-1.5}$ kPa lead to the precipitation of cerussite instead of hydrocerussite.

The lack of hydrocerussite in all examined carbonate hosted non-sulphide zinc deposits might be due to the relatively high $P_{\text{CO}_2}$, which is equal or higher than the atmospheric $P_{\text{CO}_2}$ and the relatively low temperatures of the groundwater and in the host rock. Thus, the conditions, which are necessary for the formation of hydrocerussite, have not - or only very locally been reached.

5.5.6 Climatic effects

Acidic waters in carbonate host rocks, as a result of oxygen path oxidation with water-dissolved oxygen, are uncommon. In most cases, the concentration of dissolved oxygen in groundwater is insufficient to produce acidity greater than the alkalinity of the groundwater (DREVER, 1997). Thus, for an effective and fast oxidation, additional O$_2$ has to be introduced into the system, e.g. via faults and the drainage effects of karstification. Beside the geochemical parameters of the host rock such as limestone and dolomite, climatic and morphologic effects are other important factors for an effective oxidation process and the formation of supergene non-sulphide zinc deposits. These factors will be discussed for several scenarios below.

Climatic influence to geochemical systems and oxidation processes

The oxidation of sulphide ore bodies occurs usually in a ‘near surface’ environment. Water is readily available, as well as oxygen, nitrogen, carbon dioxide, and biological activities can also occur within this zone.

At a first stage, the meteoric water with no significant concentrations of metal ions is in equilibrium with the atmosphere. The gasses O$_2$ and CO$_2$ dissolve, depending on the temperature and on their related partial pressure $P_{\text{O}_2}$ and $P_{\text{CO}_2}$. Although other gasses are available in the atmosphere and in equilibrium with the meteoric water, gasses other than O$_2$ and CO$_2$ are not important for the geochemical behaviour of water during the oxidation of sulphides and the precipitation of non-sulphide minerals and are thus not included in the present geochemical models.

Biological activity is a possible source for disequilibrium of soil and host rock pores with the atmosphere. An example might be the relatively high partial pressure of CO$_2$ within soil horizons of humid climates (SCHEFFER & SCHACHTSCHABEL, 2002). The $P_{\text{CO}_2}$ within soils is variable, significantly elevated and not in equilibrium with the atmospheric CO$_2$ partial pressure. Thus, the $P_{\text{CO}_2}$ of deeper levels of the host rock is often significantly elevated compared to the atmosphere and has to be included in geochemical models.

Above the groundwater table, the downward percolating rainwater interacts with the atmosphere as well as with soil and regolith before the meteoric water reaches and oxidises the sulphide ore. The chemistry of the water changes dramatically during this interaction and this modification plays an important role for further oxidation, dissolution, and transport processes. There are at least two different systems, in which water can be in equilibrium: i) equilibrium with atmospheric CO$_2$ and
carbonates and ii) equilibrium with atmospheric CO\textsubscript{2} and elevated P\textsubscript{CO2} of soils and carbonates of the host rock. These hydraulic systems can be described either as ‘closed’ or ‘open’ systems.

Within an ‘open’ system, water is able to equilibrate continuously with the atmosphere. Highly porous rocks and under-saturated conditions provide these ‘open’ conditions to seepage water and descending fluids.

A predominantly ‘closed’ system is characterised by minute fissures and pores, filled with capillary water. The exchange of gasses is inhibited and, consequently, the system is not atmosphere-equilibrated. The P\textsubscript{CO2} within the water is able to drop down to zero and pH increase rapidly or P\textsubscript{CO2} may increase due to regional e.g. microbiological induced disequilibria.

These ‘open’ and ‘closed’ systems can be modelled by PHREEQC. Especially two drastically different scenarios are interesting to look at and these are either humid or arid climates.

- A humid climate is characterised by thick soil cover of the bedrock with biological activity supported by high annual precipitations of >500 mm. Thus, the soils show a highly increased P\textsubscript{CO2} due to (micro-) biological activities. The seepage rates are high and the groundwater level is generally higher than in arid influenced regions.
- An (hyper-) arid climate shows generally low biological activities and is characterised by a low mean annual precipitation between 0-50 mm (hyper arid) or 50-200 mm (arid) (LLOYD, 1986). Therefore, the biological activity within the soil is rather limited compared to humid conditions. As a result of these limited biological processes, the P\textsubscript{CO2} of such soils is nearly equal to that of the atmosphere.

**Humid climate, ‘open’ system:**

In a region with soil covered limestone and carbonate rocks, water that infiltrates through the soil approaches saturation with dissolved carbonates while still in contact with abundant CO\textsubscript{2}. This reaction consumes CO\textsubscript{2} especially during contact with and dissolution of calcite from carbonate host rocks. The consumed gasses will be rapidly replenished by CO\textsubscript{2} from the overlying soil and/or atmosphere (PALMER & PALMER, 1995). This process stabilises the pH and leads to slightly increased pH-values. The pore water is characterised by relatively high CO\textsubscript{2} and low O\textsubscript{2} concentrations.

**Humid climate, ‘closed’ system:**

The first equilibrium reactions of the meteoric water within the closed system are similar to the open system. The water is in equilibrium with the atmosphere and the raised partial pressure of CO\textsubscript{2} of the soil. However, in contrast to the open system, here the dissolution of calcite/dolomite consumes most of the dissolved CO\textsubscript{2}. Due to the lack of atmospheric CO\textsubscript{2} within the small fissures and the water-filled pores, the pH value increases drastically. The pore water is characterised by low CO\textsubscript{2} and O\textsubscript{2} concentrations (APPELO & POSTMA, 2005).
Arid climate, ‘open’ system:

An arid climate is characterised by low rates of precipitation (rainfall) and only subordinate biological activities within soils and associated with $P_{CO_2}$ and $P_{O_2}$ values similar to those of the atmosphere. The meteoric fluids are in equilibrium with the atmosphere. The pH is slightly increased and the fluids are relatively rich in dissolved $O_2$.

Arid climate, ‘closed’ system:

Similar to a “closed” system in a humid environment, the pH increases due to the dissolution process of calcite. However, in contrast to the humid climate, the concentrations of $O_2$ in water are higher, due to the lack of $O_2$-consuming organisms within the soil.

It is important to note, that the climate as well as the local geology (fragmentation, karstification) of the carbonate host rocks influence the $O_2$ and $CO_2$ concentrations of the descendent fluids, and thus, influence the pH and the ability of the fluid to dissolve the carbonate host rock. Calculations with PHREEQC have shown that arid environments provide best conditions for the oxygen-driven oxidation of sulphide ores (Tab. 20). The oxidation by Fe(III) is not included here, since Fe(III) itself is provided by oxygen and affects the oxidation process only on a regional scale. In arid environments, the dissolved $O_2$ reaches its maximum concentration, compared to other climates, and will not be consumed by biological activities within soils. The moderate to low rates of meteoric precipitation results in slow velocities of the seepage water and optimal conditions for equilibration with both the atmosphere and the host rocks. The groundwater table of arid climates is commonly low. This will lead to an opening of the water-filled pores and joints after an individual rainfall event and will thus provide an inward flow of gasses ($O_2$, $CO_2$) to any available sulphide ore body. This system will commonly change to a highly permeable system due to (karstic) dissolution processes of the carbonate host rock. Such a drained system allows continuous $O_2$ diffusion from the surface into the ore-bearing zones within the (water-) unsaturated zone. In this case, the oxidation rate of the sulphides is less limited by the $O_2$ concentration within the water but rather by the thickness of the overlying unsaturated zone. The possible depth of oxidation tends to deeper regions compared with oxidation processes, which are influenced by a humid climate. This is in agreement with observations of HEYL & BOZION (1962). The resulting sulphate and metal concentration within the fluids would be highly increased (APELHO & POSTMA, 2005) and pH decreases according to the generation of sulphuric acid.
Due to the limited availability of water in arid and hyper-arid climates, the fluids, which have been generated during the oxidation process, would be highly enriched in zinc and other metals. These high metal concentrations support an effective precipitation of non-sulphide base metal minerals. The low velocity seepage rates would generate aqueous solutions with high metal concentrations, the residence time of the fluid is relatively long and the oxidation process is more complete due to the mixed sources of oxygen: water-dissolved oxygen and oxygen, which has been provided by diffusion processes within the joints and pores of the host rock. These high element concentrations support an effective precipitation process within the carbonate host rock. Thus, an arid or semi-arid climate provides best conditions for the (slow, but effective) oxidation of a sulphide ore and also provides the best conditions for the preservation of a non-sulphide ore-body.
Climate change influenced Iran through the times and thus was one of the driving forces for changing mineral stabilities (Tab. 21). Especially the stability of hemimorphite is dependent on the $P_{CO_2}$ (e.g. as a result of biological processes) and thus indirectly influenced by temperatures and rainfall.

Tab. 20: Result of geochemical simulations with PHREEQC code. Seepage water has been modelled for different climates to simulate the capability to dissolve CO$_2$/O$_2$ and the ability of those waters to dissolve carbonates and SiO$_2$. Due to their different solubility, SiO$_2$ is divided into crystalline quartz and amorphous SiO$_2$. Simulations have shown that arid conditions provide the best environment for an effective oxidation of sulphide ores by dissolved O$_2$ and provide additional SiO$_2$ for the formation of zinc-silicates. Especially amorphous SiO$_2$ achieves high concentrations in aqueous solutions.

<table>
<thead>
<tr>
<th></th>
<th>Arid climate with amorphous SiO$_2$</th>
<th>Arid climate with quartz-SiO$_2$</th>
<th>Humid climate with, soil coverage, amorphous SiO$_2$</th>
<th>Humid climate with, soil coverage, quartz-SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log P_{CO_2 \text{ atm}}$</td>
<td>closed open</td>
<td>closed open</td>
<td>closed open</td>
<td>closed open</td>
</tr>
<tr>
<td>$\log P_{CO_2 \text{ soil}}$</td>
<td>-1.5 -1.5</td>
<td>-1.5 -1.5</td>
<td>-1.5 -1.5</td>
<td>-1.5 -1.5</td>
</tr>
<tr>
<td>$\log P_{O_2 \text{ atm}}$</td>
<td>1.7 1.7</td>
<td>1.7 1.7</td>
<td>1 1</td>
<td>1 1</td>
</tr>
<tr>
<td>pH</td>
<td>9.03 8.2</td>
<td>9.66 8.3</td>
<td>7.6 6.9</td>
<td>7.6 7</td>
</tr>
<tr>
<td>$\text{PE}$</td>
<td>11.5 12.3</td>
<td>10.9 12.3</td>
<td>12.8 13.5</td>
<td>12.9 13.6</td>
</tr>
<tr>
<td>$[\text{SiO}_2]$</td>
<td>$2.0 \cdot 10^{-3}$ $1.8 \cdot 10^{-3}$</td>
<td>$1.4 \cdot 10^{-4}$ $9.6 \cdot 10^{-5}$</td>
<td>$1.8 \cdot 10^{-3}$ $1.8 \cdot 10^{-3}$</td>
<td>$9.4 \cdot 10^{-5}$ $9.4 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>$[\text{Ca}^{2+}]$</td>
<td>$1.4 \cdot 10^{-4}$ $4.9 \cdot 10^{-1}$</td>
<td>$1.4 \cdot 10^{-4}$ $4.8 \cdot 10^{-4}$</td>
<td>$1.0 \cdot 10^{-3}$ $2.4 \cdot 10^{-3}$</td>
<td>$1.0 \cdot 10^{-3}$ $2.4 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$[O_2]$</td>
<td>$2.7 \cdot 10^{-4}$ $2.6 \cdot 10^{-4}$</td>
<td>$2.5 \cdot 10^{-4}$ $2.5 \cdot 10^{-4}$</td>
<td>$1.3 \cdot 10^{-4}$ $1.3 \cdot 10^{-4}$</td>
<td>$1.3 \cdot 10^{-4}$ $1.3 \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

Climate change influenced Iran through the times and thus was one of the driving forces for changing mineral stabilities (Tab. 21). Especially the stability of hemimorphite is dependent on the $P_{CO_2}$ (e.g. as a result of biological processes) and thus indirectly influenced by temperatures and rainfall.

Tab. 21: A provisional chronology of Quaternary climate in the southwestern part of the Arabian region. (after SADIQ & NASIR (2002))

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Date in years</th>
<th>Climate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holocene</td>
<td>0-700</td>
<td>Hyperarid</td>
</tr>
<tr>
<td></td>
<td>700-5,500</td>
<td>Slightly moist</td>
</tr>
<tr>
<td></td>
<td>5,500-6,000</td>
<td>Hyperarid</td>
</tr>
<tr>
<td></td>
<td>6,000-10,000</td>
<td>Wet (pluvial)</td>
</tr>
<tr>
<td>Late Pleistocene</td>
<td>10,000-17,000</td>
<td>Hyperarid</td>
</tr>
<tr>
<td></td>
<td>17,000-36,000</td>
<td>Wet (pluvial)</td>
</tr>
<tr>
<td></td>
<td>36,000-70,000</td>
<td>Arid</td>
</tr>
<tr>
<td></td>
<td>70,000-270,000</td>
<td>Moist</td>
</tr>
<tr>
<td></td>
<td>270,000-325,000</td>
<td>Arid</td>
</tr>
<tr>
<td>Middle Pleistocene</td>
<td>325,000-560,000</td>
<td>Wet</td>
</tr>
<tr>
<td></td>
<td>560,000-700,000</td>
<td>Arid</td>
</tr>
<tr>
<td>Early Pleistocene</td>
<td>700,000-2,500,000</td>
<td>Wet humid (pluvial)</td>
</tr>
</tbody>
</table>
5.5.7 Numerical simulation of precipitation processes within a carbonate host rock

The aqueous solution, on which the computer model is based upon, represents a hypothetical acidic fluid, which was formed during the oxidation process of a primary pyrite-galena-sphalerite-bearing sulphide ore (see Methods section). The resulting theoretical initial solution has been allowed to equilibrate under different geochemical conditions with respect to $P_{CO2}$ and host rock composition (dolomite-calcite).

**Scenario A: Low $P_{CO2}$ and limestone host rock (limestone or marble)**

The scenario A simulates the reaction of a near-surface aqueous solution, which is in equilibrium with the atmospheric $P_{CO2}$ ($log P_{CO2} = -1.5$ kPa), and which migrates from the oxidation zone through reactive limestone. The following assumptions have been made for this simulation: An initial solution (as described in Tab. 4) reacts with limestone (99% CaCO$_3$ and 1% CaMg(CO$_3$)$_2$). This geochemical system continuously equilibrates with the atmospheric $P_{CO2}$.

The first and most important reaction within the highly acidic environment is the precipitation of anglesite (Fig. 110). All simulations (scenario A and scenario B) show a rapid and immediate precipitation of anglesite. Thus, after the first equilibrium reaction, the activity of Pb$^{2+}$ within the aqueous solution never reaches the initial value of $2.8 \times 10^{-2}$ mol·l$^{-1}$ ($loga_{Pb^{2+}} = -1.5$ mol·l$^{-1}$) but decreases to approximately $loga_{Pb^{2+}} = -5.5$ mol·l$^{-1}$. This effect is due to the precipitation of anglesite, which is nearly insoluble under the influence of the high activity of sulphate ions (Fig. 110). The immediate precipitation of anglesite and the associated process of lead-immobilisation have been discussed in detail above. Zinc, in contrast, remains dissolved under these acidic conditions with its initial activity of $a_{Zn^{2+}} = 3.8 \times 10^{-1}$ mol·l$^{-1}$ ($loga_{Zn^{2+}} = -0.42$ mol·l$^{-1}$). These results prove and support the assumptions of a highly different mobility of zinc and lead. Lead remains immobile within the oxidation zone, whereas zinc becomes mobile due to the oxidation of the sulphide minerals and migrates to levels that are more distal. The continuous neutralisation reaction leads to the precipitation of gypsum, which decreases the activity of sulphate ions (Fig. 110).

The pH of the initial solution increases up to pH= 6.4. At this pH willemite becomes stable and precipitates up to pH= 7.71 at which point the final equilibrium of the aqueous solution with the limestone is reached. The amount of willemite, which primarily precipitates at this stage of the non-sulphide ore formation, is very low due to the low solubility and thus low availability of silica in water. Thus, the precipitation of willemite shows no visible effect on the activity of Zn$^{2+}$.

Hydrozincite becomes stable at pH= 6.4 according to the saturation index of this mineral and precipitates within the pH-range from pH= 6.4 to pH= 7.7. This precipitation consumes most of the dissolved zinc. Within this pH-range, the activity of zinc decreases from initial $loga_{Zn^{2+}} = -1.6$ mol·l$^{-1}$ down to $loga_{Zn^{2+}} = -5.9$ mol·l$^{-1}$. The saturation index of smithsonite never reaches the necessary saturation ($Si_{smithsonite} = 0$) to precipitate this zinc carbonate. Thus, smithsonite is not stable and does not form under these conditions. As described above, smithsonite is associated
with high values of approximately log$_{10}$P$_{CO_2}$ = 0.5 kPa, which is not given here. Cerussite becomes stable at pH 7.2 and its formation decreases the activity of Pb$^{2+}$ ions down to log$_{10}$Pb$^{2+}$ = -6.6 mol·l$^{-1}$ at the end of the neutralisation. The final composition of the aqueous solution is given in the following table (Tab. 22):

Tab. 22: Hypothetic composition of an initial- and final solution according to geochemical modelling of scenario A.

<table>
<thead>
<tr>
<th></th>
<th>initial</th>
<th>final</th>
<th></th>
<th>initial</th>
<th>final</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1</td>
<td>6.7</td>
<td>Fe</td>
<td>1.7 · 10$^{-3}$ mol·l$^{-1}$</td>
<td>1.2 · 10$^{-12}$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>pe</td>
<td>4</td>
<td>12.9</td>
<td>Zn</td>
<td>2.4 · 10$^{-2}$ mol·l$^{-1}$</td>
<td>1.1 · 10$^{-6}$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
<td>25</td>
<td>Pb</td>
<td>1.6 · 10$^{-6}$ mol·l$^{-1}$</td>
<td>2.7 · 10$^{-7}$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>Log P$_{CO_2}$</td>
<td>-1.5 kPa</td>
<td>-1.5 kPa</td>
<td>SO$_4^{2-}$</td>
<td>0.14 mol·l$^{-1}$</td>
<td>1.2 · 10$^{-2}$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.0 mol·l$^{-1}$</td>
<td>1.6 · 10$^{-2}$ mol·l$^{-1}$</td>
<td>Mg$^{2+}$</td>
<td>0.0 mol·l$^{-1}$</td>
<td>1.2 · 10$^{-3}$ mol·l$^{-1}$</td>
</tr>
</tbody>
</table>

Fig. 110: Activities and saturation indices of a continuous pH dependent fluid evolution, produced by application of the PHREEAC program. The solution is in equilibrium with atmospheric CO$_2$ (log$_{10}$P$_{CO_2}$ = -1.5 kPa).
Scenario B: High $P_{CO2}$ and limestone host rock (limestone or marble)

The initial conditions for the aqueous solution and the mineralogy of the host rock of the second model are identical to those from ‘Scenario A’. However, in contrast to ‘Scenario A’, the $P_{CO2}$ is assumed to be relatively high at log $P_{CO2} = 0.5$ kPa, which can be reached e.g. due to biological activity or caused by the neutralisation reaction of acidic solutions with the carbonate host rock or easily due to CO2 degassing due to neutralisation processes.

The modelling of the neutralisation process (Fig. 111 and Tab. 23) and the behaviour of anglesite precipitation are similar to ‘Scenario A’. Most of the lead precipitates as anglesite because of the first equilibrium reaction. Concentration of sulphate ions is relatively low, due to the precipitation of anglesite and gypsum. Zinc is soluble and remains within the aqueous solution. Smithsonite reaches the saturation index $Si_{smithsonite} = 0$ at pH 6 and precipitates. Hydrozincite gets close to saturation, but does not reach this point and does not precipitate. The precipitation of smithsonite occurs within the pH range of pH= 6 up to pH= 6.7, but most quantity of smithsonite precipitated between pH 6 and 6.4. After precipitation of smithsonite, the final concentration of dissolved zinc has been decreased from initial $loga_{Zn} = -1.6$ mol·l$^{-1}$ to final $loga_{Zn} = -3.95$ mol·l$^{-1}$. Cerussite is stable, according to the raised $P_{CO2}$ and thus precipitation of cerussite starts at pH=6.2. The stability of cerussite and its precipitation leads to a final activity of lead of $loga_{Pb} = -6.7$ mol·l$^{-1}$.

Tab. 23: Hypothetical composition of an initial- and a final solution, according to geochemical modelling of scenario B.

<table>
<thead>
<tr>
<th></th>
<th>initial</th>
<th>final</th>
<th>initial</th>
<th>final</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1</td>
<td>6.7</td>
<td>Fe</td>
<td>$1.7 \cdot 10^3$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>pe</td>
<td>4</td>
<td>13.9</td>
<td>Zn</td>
<td>$2.4 \cdot 10^2$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
<td>25</td>
<td>Pb</td>
<td>$1.6 \cdot 10^6$ mol·l$^{-1}$</td>
</tr>
<tr>
<td>$Log P_{CO2}$</td>
<td>0.5 kPa</td>
<td>0.5 kPa</td>
<td>SO$_4^{2-}$</td>
<td>0.14 mol·l$^{-1}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.0 mol·l$^{-1}$</td>
<td>1.65·10$^{-2}$ mol·l$^{-1}$</td>
<td>Mg$^{2+}$</td>
<td>0.0 mol·l$^{-1}$</td>
</tr>
</tbody>
</table>

Most of the zinc (85%) precipitated as smithsonite within the pH interval pH 6.0 to 6.3 and only traces of willemite precipitated due to the low concentration of SiO$_2$ within the solution.

The result of this model is close to the observations from different non-sulphide zinc deposits. Smithsonite is proposed to be the main first-stage zinc-mineral during the oxidation stage (associated with $logP_{CO2}>0.5$ kPa) and only subordinate amounts of zinc silicates are expected at this stage. Cerussite occurs, but only in traces due to its immobile behaviour within the oxidation zone and the low concentration within the initial solution. Anglesite should not precipitate outside the oxidation zone, since cerussite is more stable under the higher pH-$P_{CO2}$ conditions.
The case scenario of an arid climate with limited soil coverage and low quantities of meteoric water should be discussed here in detail. These conditions suit the examined Iranian non-sulphide zinc deposits and should be applicable to similar deposits. The most important processes for the sulphide oxidation, metal separation, and mineral precipitation can be summarised as followed.

**Stage-I: oxidation stage**

The oxidation of pyrite occurs in a surface near position. Carbon dioxide as well as oxygen penetrate and migrate through the soil and the host rock pores and spaces (Fig. 112) to the sulphide ore. Oxygen is partly consumed by organisms. The organic metabolism reduces the $P_{O_2}$ and increases the $P_{CO_2}$. The oxygen reaches the sulphide ore and reacts with the pyrite and other sulphides. The products of this oxidation influence the geochemical behaviour of the oxidation system in several important ways: The gypsum- and hydrous ferric oxide armoured carbonates of the host rock are inhibited from a fast neutralisation reaction with the acidic solution and this establishes and stabilises an acidic low pH within the oxidation zone and the adjacent strata in spite of the carbonate host rock, which usually provides high capabilities to neutralise acidic solutions.

The hydrous ferric oxides are characterised by a high surface area, which is capable to adsorb metal ions ($Ca^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Mg^{2+}$, and other ions). This sorption process is highly pH-dependent. The pH values within the oxidation zone trigger the ability of HFO to adsorb zinc from the aqueous
solution. However, the zinc concentration of the aqueous solution is still high in contrast to lead, which has been removed from solution due to both processes the precipitation of anglesite and the adsorption to HFO. It can be assumed that up to 40% of the initial dissolved zinc is adsorbed onto HFO and 60% leaves the oxidation zone and migrates into adjacent/deeper areas. Lead in contrast remains within the oxidation zone and only 1% is able to escape from the oxidation zone. The neutralisation of the sulphuric acid with the carbonates of the host rock lead to the formation/liberation/degassing of CO₂, which equilibrates with the open pores, that increases the local P_CO₂. Part of the CO₂ remains dissolved within the aqueous solution and is transported into adjacent areas. Subsequent degassing forms a CO₂-rich ‘halo’, which surrounds the oxidation zone and furthermore the local adjacent area. These high P_CO₂ levels indicate the lacking equilibrium with atmospheric CO₂ and should only be stable as long the oxidation (and neutralisation) process is active.

Smithsonite and/or hydrozincite start to precipitate at deeper levels, due to a progressing neutralisation and increasing pH-values of the migrating aqueous solution. Since the oxidation-stage is associated with a highly elevated P_CO₂ the formation of the high-P_CO₂ zinc carbonate smithsonite predominates over the precipitation of the low-P_CO₂ zinc carbonate hydrozincite. The ‘stage-I smithsonite’ precipitates as massive botryoidal layers (e.g. at Angouran; GILG ET AL. 2003; BORG ET AL., IN PREP.) or as a fine crystalline matrix of carbonate (karst-) breccia clasts of the limestone/dolomite host rock. Minor amounts of zinc precipitate as ‘stage-I zinc-silicates’, such as hemimorphite or willemite. The amount of zinc-silicate precipitation is limited by the low SiO₂ concentration within the aqueous solution. Lead precipitates in small quantities as anglesite and/or cerussite according to its low concentration.

In an exclusively carbonate-dominated environment, zinc precipitates as smithsonite or as hydrozincite. The stability and the occurrence of these zinc carbonates are dependent on the partial pressure of CO₂. Hydrozincite precipitates at relatively low P_CO₂, which indicates in most cases equilibrium of the aqueous solutions and the pore space with the atmosphere and the atmospheric P_CO₂ - typical for the unsaturated zones as a near-surface precipitation.

Stage-II: post oxidation stage

The post-oxidation stage starts with a change of the entire geochemical system (Fig. 113). At this stage, the sulphide ore has been completely oxidised and/or occurs as a small remnant. The generation of acidic fluids stops and the neutralisation process ends at this stage. The consequence of these changes is a successive lowering of the sulphuric acid-derived sulphate ion concentration. The solubility of sulphates, such as gypsum and anglesite increases with these lowering concentrations due to Le Chatelier’s Principle (MORTIMER, 1987). Gypsum starts to dissolve and is removed over time and anglesite starts to dissolve as well. The increasing pH value favours the precipitation of cerussite instead of anglesite, thus anglesite becomes unstable and dissolves or is replaced with cerussite. The liberation of Pb leads to the formation of late-stage cerussite crystals within fractures and open spaces, which were form during this post oxidation stage and are common at MOB of Mehdi Abad and Irankuh - Kolahdarvazeh Mine.

Zinc carbonate minerals become stable within the former oxidation zone since the pH value has
risen to neutral and alkaline conditions. Under these conditions zinc is immobile and will remain at this Fe-rich zone and here forms secondary zinc minerals such as hydrozincite, smithsonite and zinc-silicates.

Now the P\textsubscript{CO2} is changed now back to ‘normal’ conditions, which are equilibrium-near with the atmosphere. The low P\textsubscript{CO2} changes the stability of the zinc carbonate minerals. Thus, smithsonite becomes unstable, whereas hydrozincite reaches its stability. At this point, the stage-I hydrozincite starts to replace the stage-I smithsonite. Additionally, hydrozincite starts to precipitate within the former oxidation zone.

In most cases, the formation of large quantities of zinc silicates (hemimorphite/willemite) is not associated with the oxidation stage of sulphide ores. As long as the oxidation process is still active, only subordinate amounts of zinc silicates (willemite, hemimorphite) will precipitate. In most cases, the formation of zinc silicates becomes an important process at the post-oxidation stage. Zinc silicates, such as hemimorphite or willemite precipitate in open spaces and pores and are commonly intimately associated with the red- or white zinc ore (smithsonite/hydrozincite). Hemimorphite is common in systems, which are able to provide sufficient concentrations of silica. The successive contact with SiO\textsubscript{2}-bearing descending fluids leads to the formation of zinc silicates over the time. The amount of hemimorphite within the examined deposits seems to correlate with the availability of SiO\textsubscript{2}. Thus, the MOB, which contains chert-rich limestone, shows high amounts of late-stage hemimorphite, whereas hemimorphite is less common at Irankuh, since the SiO\textsubscript{2} content within host rock and the overlying strata is much lower.

The stage I and stage II processes should result in a non-sulphide zinc deposit with an ideal zoning pattern of two spatially separated and geochemically different types of zinc ore: the ‘red zinc ore’ (within the former oxidation zone) and the ‘white zinc ore’.
Fig. 112: Stage-I: Oxidation. (A): Descendent fluids (rain fall) partly penetrate an organic cover/soil. This process is associated with the partial loss of dissolved oxygen (HERBERT, 1999) and the increase of the CO₂ partial pressure P_{CO₂}. This water reaches the sulphide ore. (B): The sulphide ore is in contact with atmospheric O₂ and CO₂ due to diffusion of these gasses. The sulphide ore is oxidised and this process is associated with acidic pH values, the release of sulphuric acid, and the precipitation of hydrous ferric oxides. The pH is low (<4). (C): The reaction of sulphuric acid with the adjacent carbonate host rock forms a CaSO₄- and Fe-oxihydroxide-barrier, which inhibits the carbonate from further neutralisation reactions. This process stabilises the low pH of the oxidation zone. Lead precipitates as anglesite and is partly adsorbed from aqueous solution onto ferric hydrous oxides, whereas Zn²⁺ ions remain mobile and migrate into deeper levels. The pH is still acidic and increases moderately due to the CaSO₄ coating of the carbonates. (D): The pH increases, zinc silicates, such as hemimorphite will precipitate. However, due to low SiO₂ concentrations, the amount of zinc silicates is very low. Smithsonite, and/or hydrozincite start to precipitate at higher pH values as a cement of the carbonate breccia fragments. Only minor amounts of cerussite and other Pb-minerals precipitate, due to low Pb concentrations of the aqueous solution.
Fig. 113: Stage-II: (A): Descendent fluids (rain fall) partly penetrate an organic cover. This water reaches the former oxidation zone. (B): Most part of the sulphide ore is oxidised by now. $P_{CO_2}$ is relatively low, compared with stage-1 and is in equilibrium with the atmosphere. The pH within the former oxidation zone has changed to neutral or alkaline conditions. No or only minor amounts of galena are present, rimmed by an anglesite coating. Anglesite is replaced by cerussite due to changed $P_{CO_2}$. Zinc precipitates as hydrozincite. Smithsonite will precipitate only if the $P_{CO_2}$ is high enough, probably due to microbiological metabolism. (C): The gypsum armoring of stage-I dissolves and is washed out of the system. The higher pH-values support the solubility of SiO2 and zinc-silicates start to precipitate successively. The mobility of Fe, Zn and Pb is low, which limits their quantitative transport. (D): Due to the lack of CO2 generating reactions the PCO2 decreases and smithsonite becomes unstable and is replaced by hydrozincite.
5.6 Interpretation of the Mehdi Abad deposit

Mountain Ore Body of Mehdi Abad

No clear indications for the sulphide protor of the MOB have been identified, which might be due to the thorough oxidation, folding, and faulting of the strata and solution collapse. The non-sulphide mineralising and ore-modifying processes at the MOB of Mehdi Abad appear to be relatively young or have continued until relatively recently. Mineralised breccias of tectonic and solution collapse origin document the earlier stages of the non-sulphide mineralisation. Locally, the open, partly mineralised pore-, fracture-, and breccia-spaces contain extremely delicate dissolution textures and euhedral supergene non-sulphide zinc minerals without any deformation by folding or gravitational compaction. The processes of ore formation, partial dissolution, and re-precipitation have only been terminated and ‘mummified’ by the current arid to hyper-arid climate.

The ore occurs in a carbonatic host-rock, which consist of limestone or dolomitc limestone. Most of the fault-breccias show a high content of zinc and lead within the matrix of the breccia, whereas the wallrock shows relatively low concentration of base metals. All examined and sampled adits show a high content of hemimorphite. This appears rather surprising, because of the carbonate dominated environment and the carbonatic host-rock. However, the high content of hemimorphite implies a source for the silicate, which is productive enough to deliver this quantity. Two sources of SiO₂ are capable to deliver these quantities. One possible source for the silicate may be the chert-bearing members of the Abkou Formation (K₁₄, K₂₄), which hosts the non-sulphide ore of the MOB. Another source is probably the strata of the Sangestan Fm., which are (a) underlying the Abkouh and Taft Formation and (b) are lateral located to the southwest of the Black-Hill Fault. The Sangestan Formation consists, among others, of fine-grained quartzitic-feldspatic sandstones, and sandy shales. The origin of the silica from the Sangestan Formation might imply ascendant or lateral fluid systems. This fluid-transport is possible by using the faults as pathways for the ascending fluids. However, the chert-bearing member of the Abkou Formation is the favoured and more probable source of the silica. As shown above, the chert is able to interact easily with the descending meteoric fluids. It is presumed that the precipitation of hemimorphite is a long lasting process, due to low SiO₂ concentrations within aqueous solutions. Thus, the formation of hemimorphite is supposed to occur successively after the oxidation stage of the sulphide ore, as a result of dissolution and corrosion processes of hydrozincite and smithsonite and the re-precipitation as hemimorphite.

The following stages are suggested, to be important for the formation of the non-sulphide zinc ore of the MOB:

At the first stage (oxidation stage), Fe-oxihydroxides, zinc- (hydro-) carbonates (hydrozincite, smithsonite) and minor amounts of hemimorphite precipitated and two distinct and spatial separated ore types have been formed due to metal mobilisation- and separation processes : the red zinc ore and the white zinc ore. The P_CO₂ at this stage was relatively high, due to the oxidation of pyrite and the subsequent neutralisation reaction with the carbonate host rock. Thus, the non-sulphide zinc ore was smithsonite dominated. The red zinc ore was formed, which mainly consisted of smithsonite, goethite (and other Fe-oxihydroxides), hemimorphite and Pb-bearing minerals. The
white zinc ore has been formed distal to the red zinc ore trapped in karst collapse breccias and within pores and open spaces of the host rock. At this stage, the white zinc ore was also smithsonite dominated, due to a proposed halo effect of a high $P_{CO_2}$.

At a **second stage (post oxidation stage)**, the generation of $CO_2$ has stopped and smithsonite became unstable and was replaced by hydrozincite due to lower $P_{CO_2}$. The lowered $P_{CO_2}$ initiated also the alteration of the hemimorphite. Early-stage related hemimorphite became unstable at this point and was partly replaced by hydrozincite.

The **third stage** has led to the cessation of the hemimorphite dissolution/alteration. The stability-field changed again in favour of hemimorphite. The climate changed to the present arid to hyper-arid climate, and hemimorphite became more stable again and euhedral hemimorphite-II precipitated within fractures and open spaces, locally overgrowing the earlier mineral phases. This process is apparently still active.

The reasons for the changing mineral stabilities are presumably a change of pH and $P_{CO_2}$ as an immediate result of the ending of the oxidation and acid/$CO_2$ generating process. $P_{CO_2}$ and pH changes are additionally a result of a changed climate, which might have been led to a rise in $P_{CO_2}$, possibly due to microbial $CO_2$ production within the soil profile and groundwater of the palaeo-weathering surface under a more humid climate (Reichert & Borg, 2004).

**Valley Ore Body of Mehdi Abad**

The geochemical evolution of the VOB is completely different from the MOB. At least three different stages of (tectonic or collapse) displacement and mineralisation can be interpreted.

The **first stage**, which has influenced the strata of Taft Formation, is characterised by paleo-karst and partly collapse of the limestone of the Taft Formation.

A **second phase** is associated with the dolomitisation of the carbonate rock. This dolomitisation is probably genetically linked with the emplacement of the sulphide ore and barite. The sulphide ore occurs as a filling of fractures and as cement of the carbonate/dolomite breccia. However, the sulphide ore itself occurs regionally limited as breccia fragments, cemented by sulphide ore. The syn-mineralising brecciation is possibly due to the dolomitisation of the carbonate host rock. A dolomitisation of a limestone is commonly associated with a decrease of volume (Weyl, 1960) (approximately 13 vol. %). This volume reduction has led to regional collapse processes and an increased permeability. This collapse has involved both: dolomite as well as the sulphide ore. The results are angular sulphide clasts at the VOB sulphide ore. The sulphide mineralisation was associated with the dolomitisation process, resulted in a subsequent (partial) collapse of dolomite and sulphide ore and cementation with new sulphides. The occurrences of deformed and broken barite crystals support the thesis of dolomite collapse and are most likely due to one single event, which has affected the entire region of Mehdi Abad. This hypothesis is based on a constant Ba-Sr ratio in all analysed samples of VOB and MOB, whereas different barite mineralising events should be distinguishable by different Ba-Sr ratios. Barite occurs as mm- to cm-sized crystals within the breccia as well as massive barite (Black Hill). This barite is common within the (sulphide and non-sulphide) ore-bearing strata of the VOB as well as in strata of the non-sulphide ore-bearing MOB. This barite
mineralisation is

The third Phase started with the oxidation of the sulphide protore. In contrast to the MOB the oxidation process of the VOB is still active and is actually limited to the upper sulphide zone of the VOB. The most portion of the non-sulphide zone overlies the sulphides of the VOB.

The metallogenetic source for both sulphides the (thoroughly oxidised) sulphide protore of the MOB and the sulphides of the VOB is not solved. One can assume a separate sulphide mineralising phase that has probably delivered Zn- and Pb-rich (hydrothermal) fluids for the protore of the MOB or has overprinted the geochemically parameters (such as As, Cd, Ti content) of the MOB. This would explain the geochemically different behaviour of the MOB with regard to the VOB. Another possible mechanism to achieve these geochemical differences is a possible lateral-separated position during the emplacement of the sulphide protore. Thus, the different REE pattern and the Element fingerprint were generated as a function of the proximity to the vent. A subsequent thrusting and stacking after the sulphide ore emplacement has finally resulted in the present vicinity of the MOB and VOB.

5.7 The interpretation of the Kolahdarvazeh mine data

Non-sulphide zinc-(lead-) mineralisation of the Kolahdarvazeh mine occurs predominantly as cement of a dolomite breccia. This feature is similar to the Mehdi Abad deposit. However, the geochemical evolution is completely different compared to the MOB and the VOB of Mehdi Abad and represents a special case in non-sulphide ore formation. The main difference between the Kolahdarvazeh mine and Mehdi Abad is the low amount of Fe sulphides within the sulphide protor of the Koladahrvazeh mine. This fact results in a completely different geochemical behaviour of the oxidising sulphide ore. The potential of such a low-Fe sulphide ore to generate sulphuric acid is highly limited. Only small quantities of sulphuric acid were generated during the oxidation stage. This low acidity would have led to a nearly immediate neutralisation with a limited armouring effect due to the low quantity of precipitated gypsum. Furthermore, the low amount of Fe-oxihydroxides should also not have played a significant role for the metal separation process. Thus, the main portion of the non-sulphide ore is assumed to be formed as an in situ direct replacement of the sulphide ore. The geochemical analyses of the Kolahdarvazeh mine support this theory. Especially the REE pattern as well as the composition of the sulphide ore compared to the non-sulphide ore shows no signs of separation processes of mobile zinc from immobile Fe (Pb). The non-sulphide ore in fact shows nearly the same element composition compared to the sulphide protor. The lack of acidity and the lacking liberation of CO$_3^{2-}$ ions from neutralisation reactions has been balanced by the incorporation of supergene (meteoric) delivered carbonate ions. This is reflected by relatively low $\delta^{13}$C values compared to Mehdi Abad. The low $\delta^{13}$C values of the non-sulphide zinc ore of the Kolahdarvazeh mine suggest an important role of organic and meteoric CO$_2$.

The formation of non-sulphide mineralised dolomite breccias in the proximity of the Kolahdarvazeh fault is the result of a long lasting and successive dissolution process of the primary non-sulphide ore and reprecipitation nearby the Kolahdarvazeh fault. The karstification and the zinc-enrichment of the dolomite host rock have been accompanied by numerous faults and fractures. Additionally
the bedding of the dolomite and limestone dips towards the Kolahdarvazeh Fault. The partition of the bedding plains and the related fractures could have been additionally used for karst processes and as conduits by the Zn-(Pb-) bearing fluids. Black shales limit the deposit to the south at the contact of the Kolahdarvazeh fault and also underly the ore bearing dolomite strata. The shales might have acted as an impermeable and insoluble barrier for the ore-delivering fluids and the ground water system. This hydraulic barrier stopped the fluid flow and led to the ‘ponding’ of the fluids in front of the hydraulic barrier (Fig. 114).

The oxidation process of the sulphide protor is supposed to be relatively short, due to the highly fractured dolomite and the exposed location at a flank of a mountain ridge. The oxygen reaches the sulphides easily, and is not adsorbed by a deep soil horizon or hindered by a thick overlying (alluvial) cover. Thus, the following steps are proposed for the formation of the non-sulphide orebody of the Kolahdarvazeh mine:

At a **first stage** the sulphide protor has been oxidised in a fast and effective way. The non-sulphide ore has been formed as a result of a direct sulphide replacement. Only a small amount of zinc was mobilised and precipitated distal from the sulphides as cement of collapse breccias.

The **second stage** is characterised by successive dissolution of the primary non-sulphide zinc minerals according to their solubility. The mobilised zinc was transported with supergene, meteoric driven fluids towards the Kolahdarvazeh fault. Here, a concentration process and the high surface of a karst collapse breccia led to the reprecipitation of non-sulphide zinc minerals. However, a white zinc ore is the dominating type at the Irankuh mining district.

**Fig. 114: Schematic model of the fluid-flow processes, during the genesis of the Kolahdarvazeh deposit.** The impermeable and insoluble shales might have been acted as a barrier for supergene fluids, which interacted with the sulphide-ore of the dolomite/limestone. The ore has been oxidised, zinc became mobile and has been transported along fractures and faults towards the Kolahdarvazeh fault. This led to the ponding of the fluids in front of the hydraulic barrier. The result was a highly effective karst- and non-sulphide mineralising process.