

# Chapter 4: Hydrothermal processes of ore formation

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Hydrothermal processes involve fluids (hydro) and a heat source to increase the temperature above ambient conditions to produce a thermal system. Hydrothermal processes alter the rock due to fluid-rock interaction. Hydrothermal systems are diverse in character depending on the temperature or distance from the heat source, composition of the fluid and host rock, volume of water compared to the volume of the rock, timescale and environmental conditions such as redox state. Low temperature hydrothermal systems are considered to extend up to 100°C and high temperature systems are between 250°C and 450°C (Alt, 1995).

## Goals:

After reading this chapter you should be able to:

- Describe the role of solubility on mineral precipitation.
- Describe the processes of hydrothermal alteration and how they concentrate ore minerals.
- Discuss how alteration can be used to trace hydrothermal activity and as a tool for exploration.

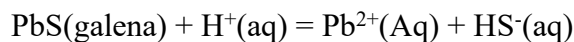
## 4.1 Hydrothermal fluids

The nature of the fluid plays an important role in the conditions of a hydrothermal system. A seawater or meteoric based fluid will begin close to neutral but during heating and reaction with the rock, the fluid becomes highly acidic and the redox changes from oxidising conditions to reducing conditions. In contrast brines are high density fluids, rich in dissolved salts, such brines cause efficient fluid-rock reactions at low temperature and oxidising conditions. The water/rock ratio, or volume of water compared to the volume of rock

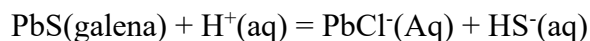
and the permeability also control how efficiently hydrothermal fluid will alter the rock.

## 4.2 Sulphide solubility in fluids

The dissolution and precipitation of sulphide from fluids is controlled by complex interdependent physiochemical processes, such as changes in pH, temperature and oxidation. Solubility of sulphides in fluids can be described by simple dissolution-precipitation reactions, such as:



where galena is precipitated from Pb bearing hydrogen sulphide fluids releasing acid. However in the aqueous environment  $\text{Cl}^-$  and  $\text{HS}^-$  can form complexes with the metals, trapping them in the fluids, e.g.  $\text{CuCl}_3^{2-}$ ,  $\text{CuH}_4\text{S}_3^-$ . The formation of such complexes is called dissociation, for instance:



where Pb is dissolved by acidic fluids signified by the reaction going from right to left, and kept in solution by the formation of  $\text{PbCl}^-$  complexes (Reed and Palandri, 2006).

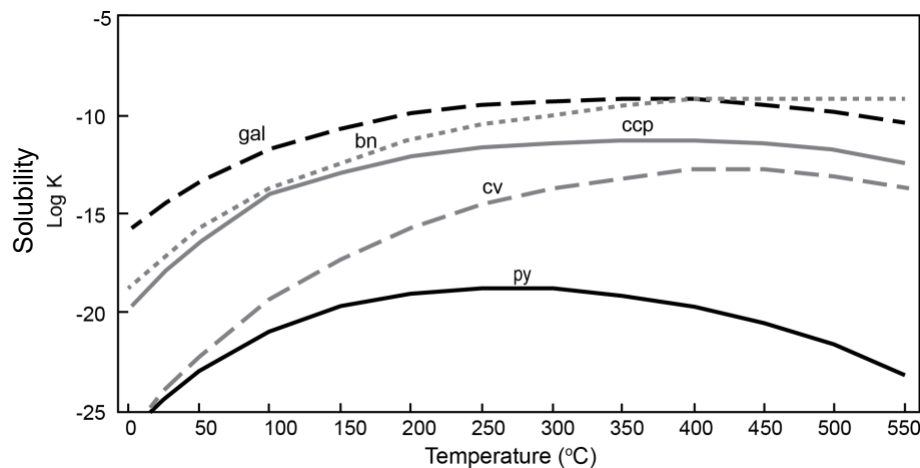


Fig 4.01 Sulphide mineral solubility. Modified from Reed and Palandri, 2006.

Thermodynamic modelling of aqueous sulphide solubility shows that decreasing temperature below 100°C, decreases the solubility facilitating sulphide precipitation (Figure 4.01; Reed and Palandri, 2006). However pyrite solubility is also low between 400 and 500°C, suggesting that in a high temperature hydrothermal system,

pyrite is likely to be a stable phase and can therefore precipitate at a wide range of temperatures.

Metal complexing with Cl or HS species creates ligands that increase the solubility of metals in the fluid and prevent mineral precipitation. The solubility in aqueous systems during dissociation increases with decreasing temperature, suggesting that Cl complexes are most stable at low temperatures (Figure 4.02). Hence at high temperatures Cl complexes do not inhibit sulphide precipitation but dissociation does control metal availability at lower temperatures (Figure 4.02; Reed and Palandri, 2006). Copper behaviour is complex, with peak solubility at around 200°C due to the Cl complexes. Furthermore at temperatures lower than 300°C HS complexes also occur with decreasing solubility as the temperature decreases. Whereas Pb forms complexes with HS, where peak solubility occurs at around 200°C, preceding the peak solubility associated with Cl complexes and potentially influencing early galena precipitation.

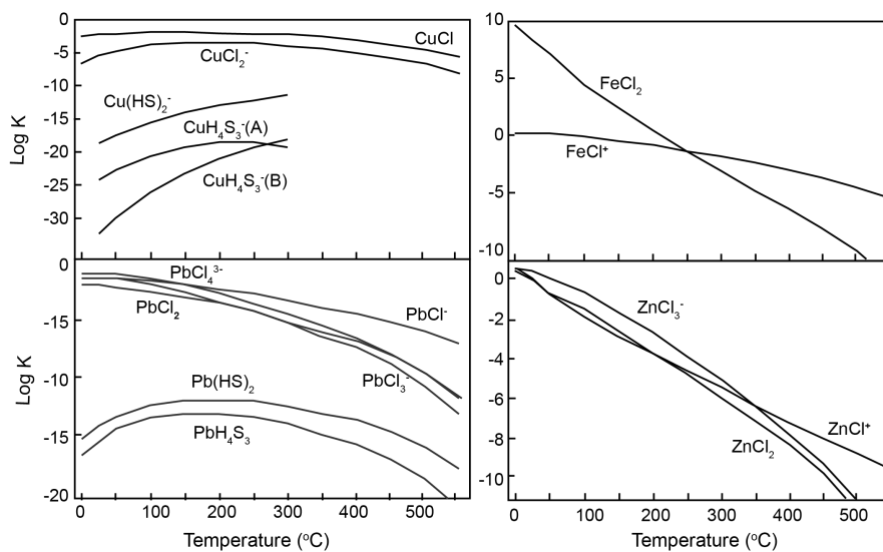


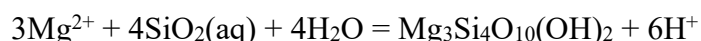
Fig. 4.02 Stability of chloride and hydrogen sulphide complexes with Cu, Pb, Fe and Zn. Modified from Reed and Palandri, 2006.

### 4.3 Experimental mechanisms for hydrothermal processes

Experimental designs react fluid and rock at a range of water/rock ratios, temperatures, pressures, fluid and rock compositions. They are typically multicomponent systems, reflecting full rock compositions and are therefore silica buffered assemblages. The resulting fluids and altered rock can be analysed to investigate both

the sulphide and silicate systems. Such experiments can also be used to explore the kinetics or rates at which hydrothermal processes act.

Heating seawater to 150-350°C in contact with basalt at low water/rock ratios leads to saturation of the fluid in Mg. The Mg then reacts with the basalt (SiO<sub>2</sub>), to produce Mg-rich minerals such as talc and at higher temperatures Mg-chlorite, additionally lowering the pH:



Under these low pH, acidic conditions base metals are dissolved or leached from the basalt (Figure 4.03). The dissolution of base metals increases the pH and thus this mechanism only continues as long as Mg is available. The dissolution of base metals is also accompanied by sulphur dissolution releasing H<sub>2</sub>S into solution. Fe and Mn mobility are simply functions of pH, which is also dependent on fluid chemistry, temperature and pressure. Zn and Cu are more complicated and depend upon the concentration of H<sub>2</sub>S in the fluid and iron in the rock as well as temperature and pressure (Seyfried, 1987). High iron concentration limits Cu and Zn mobility by stabilising Cu-Fe and Fe-Zn phases.

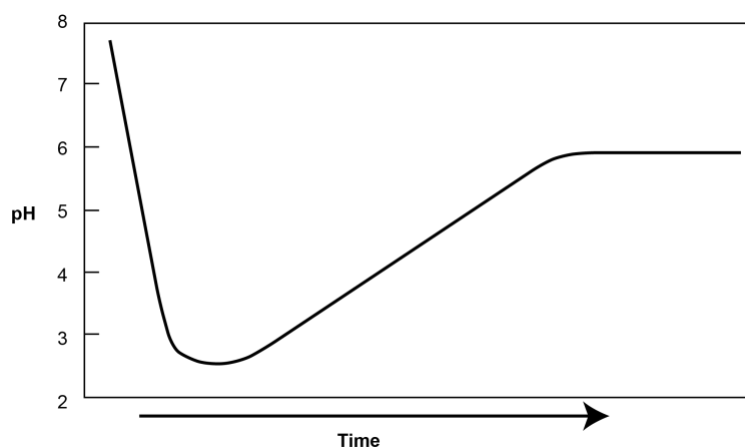


Fig. 4.03 Evolution of pH with time as seawater is hydrothermally heated. Modified from Staudigel, 2003.

Experimentally formed hydrothermal fluids have low pH (ca. 3.5) at high temperature (400°C), associated with high SiO<sub>2</sub> content and high dissolved H<sub>2</sub>S, Fe, Zn and Cu concentrations (Figure 4.04; Seewald & Seyfried, 1990). When the temperature decreases, the corresponding fluid pH increases, and the H<sub>2</sub>S and metal concentrations decrease, implying sulphide precipitation would result. The concentration of Zn and Fe in the fluid decreases

stepwise whereas Cu is quickly depleted from the fluid, explaining potential sulphide mineral zonation. The fluid Cu concentrations increase at lower temperature, due to dissociation in HS<sup>-</sup> complexes (Seewald and Seyfried, 1990).

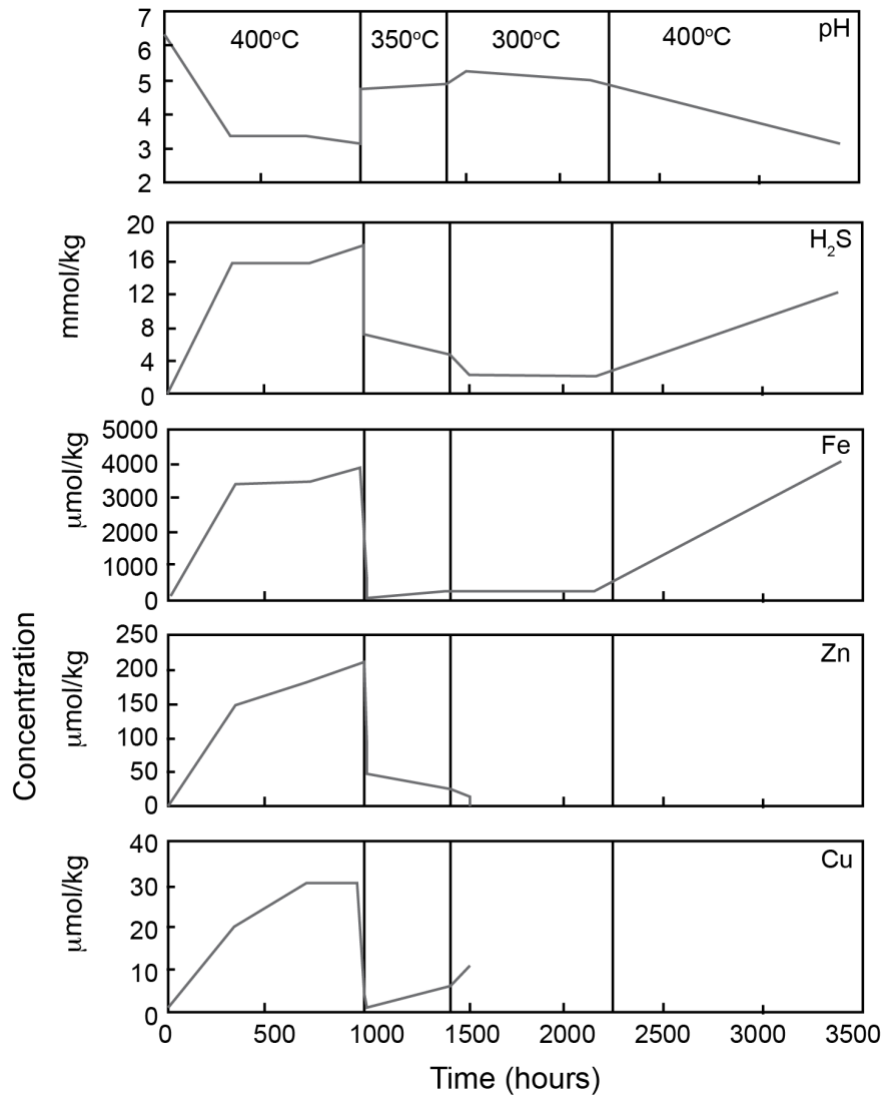


Figure 4.04 Variations in fluid chemistry during hydrothermal experiments of seawater and basalt. Modified from Seewald and Seyfried, 1990.

#### 4.4 Thermodynamic insights into hydrothermal processes

Mineral precipitation occurs below 300°C causing pyrite, sphalerite, galena and chalcopyrite to precipitate due to the breakdown of chloride complexes. At temperatures of less than 200°C, chalcopyrite redissolves to form CuH<sub>x</sub>S<sub>y</sub> complexes (Reed and Palandri, 2006).

The acidity is reflected in the chemical equilibria represented in the reactions outlined above (section 4.2), with acid released by the precipitation of metal sulphides. Metals may redissolve to form  $\text{Cl}^-$ ,  $\text{HS}^-$  or  $\text{OH}^-$  complexes and chalcopyrite is partly replaced by bornite, then chalcocite with increasing pH. Mineral zonation can reflect pH conditions precipitating in the order covellite, chalcocite, bornite, chalcopyrite, galena and sphalerite with increasing pH, where pyrite occurs throughout. Gradients in pH are often associated with increased wall-rock interaction, such as the envelopes of alteration associated with porphyry deposits (Figure 4.05). An example is the Butte Main Stage Horsetail porphyry deposits that records zonation associated with increasing pH, sulphur addition and changing oxidation state (Meyer, 1968). Minerals are zoned from covellite-pyrite with an inner argillic alteration, chalcocite-pyrite, then bornite-pyrite and finally chalcopyrite-pyrite.

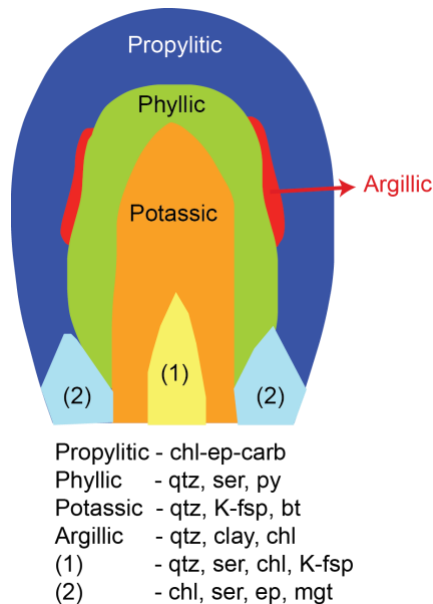


Fig. 4.05 Zonation of alteration in porphyry deposits. After Lowell and Guilbert, 1970.

Chl - chlorite  
Ep - epidote  
Carb - carbonate  
Qtz - quartz  
Ser - sericite  
Py - pyrite  
K-fsp - K-feldspar  
Bt - biotite  
Mgt - magnetite

*Mineral zonation in Nansatsu porphyry deposit, Japan*

- Potassic core of K, Na alteration
- Phyllic zone of clay minerals, kaolinite, illite, smectite
- Propylitic outer zone (Hedenquist et al., 1994)

*Porphyry deposit alteration zones:*

Potassic  
Phyllic  
Propylitic  
Argillic

Addition of NaCl, replicating the production of brines or mixing of seawater, increases the solubility of metal chloride complexes. Hence brines or seawater percolating through ocean crust will promote dissolution of sulphides.

Mixing of fluids with different NaCl compositions in the presence of silicate wall-rock to buffer the system can lower the solubility leading to the precipitation of base metals. Fractures and veins in wall-rock adjacent to hydrothermal systems and propylitic alteration associated with porphyry deposits are examples of such mixing scenarios.

*Propylitic alteration at porphyry deposits trace the salinity gradient as fluids from different sources mix.*

Addition of cool fluids, such as the mixing of hydrothermal fluids with seawater where they discharge at black smokers, causes the hydrothermal fluids to rapidly cool and precipitate sulphides. The cooling is associated with a change in pH and chloride complexes become unstable.

Seawater is oxidised and hosts sulphate (SO<sub>4</sub>), during hydrothermal circulation, the temperature of the downwelling seawater increases, and iron in the ocean crust is oxidised as the fluids become reduced. The base metals are correspondingly leached or dissolved from the ocean crust by the acidic reducing fluids (Barker et al., 2010; Galley, 2007; Reed and Palandri, 2006). Chloride and hydrogen sulphide complexes likely occur in the hydrothermal fluids. The hydrothermal circulation continues and upwelling fluids discharge at black smoker vents, where large scale mixing with seawater decreases the temperature and leads to sulphide precipitation. In some scenarios hydrothermal mounds are formed, trapping the fluids, which then cool and precipitate sulphides to be later zone refined to concentrate them and also produce zonation.

#### 4.5 Connection with silicate alteration

Hydrothermal sulphide mineralisation is found in volcanic massive sulphide (VMS) deposits, porphyry deposits as well as sedimentary exhalative (SEDEX) and Mississippi valley type (MVT) deposits. All of these settings have important (silicate) alteration assemblages, which are complementary to the sulphide mineralisation and are hence important exploration indicators.

VMS deposits are often hosted by basaltic ocean crust, but more felsic assemblages occur in e.g. back arc basins. The low temperature alteration assemblages in mafic ocean crust are characterised by smectite, talc, carbonate and zeolites. The increasing temperature gradient is gradual and thus the change to higher grade alteration, essentially greenschist, is also gradual. The greenschist alteration is characterised by Mg-chlorites and tremolite (Mg-amphibole). The highest temperatures found deeper and closer to the heat source, result in actinolite and epidote, deemed amphibolite facies alteration. Low temperature alteration leads to elevated K, Rb and Li concentrations that along with Fe<sup>3+</sup>/Fe<sup>total</sup> decrease downwards (Alt et al., 1996). The corresponding zones of chlorite alteration are enriched Mg and Na and depleted Si and Ca, whereas the

#### *Alteration vectors*

Vector 1- sericite  
Vector 2- sericite-chlorite-pyrite  
Vector 3- chlorite, pyrite  
Vector 4- chlorite-carbonate  
Vector 5- sericite-carbonate  
Vector 6- K feldspar-sericite

CCPI – chlorite-carbonate-pyrite index  
AI- (K+Mg)/(K+Mg+Na+Ca) –  
Ishikawa Alteration Index(AI)

amphibolite alteration is less depleted in Si and Ca (Heft et al., 2008).

Surrounding the upwelling hydrothermal fluids and underlying the hydrothermal mound, an alteration pipe forms. Where water/rock ratios are highest, quartz will precipitate, plus chlorite, sericite and phengite (Galley, 2007).

Porphyry deposits typically have zoned alteration aureoles, with the centre characterised by potassic alteration and phyllic and propylitic alteration zones form sequentially outwards, away from the heat source (Figure 4.05). The wall-rock protolith is often felsic volcanics surrounding the porphyry granite intrusion. Potassic alteration is associated with K-feldspar, biotite,  $\pm$ amphibole  $\pm$ magnetite. Phyllic alteration is defined by quartz, sericite and pyrite alteration. Additional quartz, clay minerals, pyrite and calcite can be associated with argillic alteration occurring in irregular association with the phyllic alteration. Propylitic alteration is associated with quartz, chlorite, epidote, calcite and localised albite-pyrite.

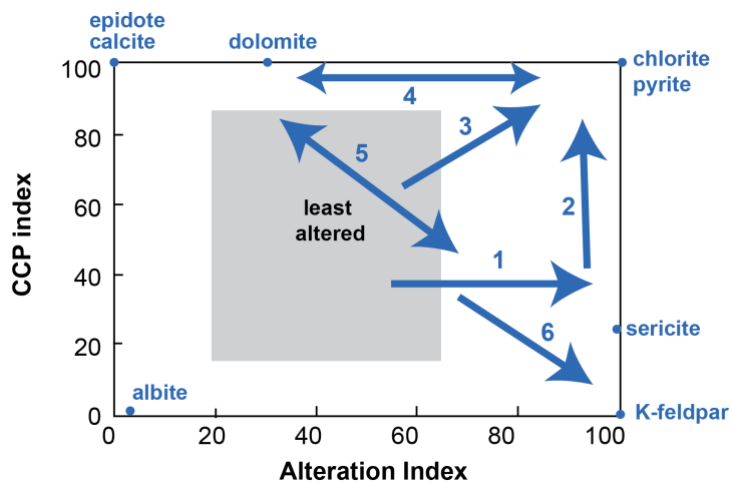


Fig 4.06. Alteration vectors. Modified from Large et al., 2001

Alteration is a regional feature, extending well beyond the mineralisation, and therefore can be a useful indicator for exploration. Geochemical surveys aim to trace alteration zones towards the mineralisation and are often represented as vectors (Figure 4.6).

## 4.5 Oxidised hydrothermal systems

Iron-oxide (Cu, REE, Au, Ag, U) ore deposits have controversial origins, one proposal is hydrothermal circulation and deposition of metals from a range of fluid sources including magmatic to non-magmatic. Here we will review the nature of hydrothermal fluids that promote the formation of iron oxide mineralisation.

The key to metal mobility is the Cl content of the fluid, forming chloride complexes. The higher the Cl content of the fluid the higher the solubility of alkalis and metals (Figure 4.2). Furthermore the presence of higher order Cl complexes increases solubility exponentially. Therefore the higher the salinity of the fluids the more effective the transport of metals. Sedimentary brines or evaporitic brines that are high in Cl and low in S are potentially significant non-magmatic fluid sources. Both magmatic waters and seawater contain reasonable contents of sulphur and therefore promote sulphide precipitation, whereas sedimentary fluids are sulphur poor and alkaline (high pH) and limit the precipitation of metal sulphides, consequently iron oxide precipitation is promoted (Barton & Johnson, 2000).

Magmatic fluids lead to magnetite-sulphide assemblages precipitated at high temperatures with alkali (K-rich) alteration. The magnetite grades are thought to be >5 wt% (Barton & Johnson, 2000). A clear spatial link with the magmatic system is expected and the mineralisation is often associated with Cu porphyry deposits.

In contrast, non-magmatic brines are expected to lead to magnetite dominated deposits with perhaps minor hematite. The expected grades are on the order of 50 wt% magnetite. The associated alteration is sodic±potassic with a large zone of metal depletion, from leaching of country rock by large volume brines.

In the case of magmatic fluids, cooling away from the heat source and mixing with meteoric fluids will facilitate ore precipitation, similarly to porphyry settings. In contrast, metal precipitation from non-magmatic fluids requires a trap, such as a structural or stratigraphic feature, change of composition of the country rock or mixing with a compositionally different fluid.

An example of a non-magmatic hydrothermal brine system is the present day Salton Sea, southern California. The brines are metal-

rich and sulphur-poor and the accompanying mineralisation is iron oxide-Cu-Au-REE. Veins contain hematite and minor chalcopyrite, pyrite, quartz and REE bearing epidote. The accompanying “Scales” are rich in magnetite and contain gold, uranium, cobalt and copper. Alteration is layered with shallow carbonate, illite, chlorite, K-feldspar underlain by salite, actinolite, plagioclase feldspar and biotite. The fluids remain rich in Pb and Zn due to the absence of sulphur with which to precipitate galena and sphalerite (Barton & Johnson, 2000).

#### **4.6 Iron oxide mineralisation and alteration haloes**

Alteration style is associated with fluid source and origin, hence differs with fluid type as well as country rock composition. A magmatic fluid will dominantly show zonation of alteration following the thermal gradient from the high temperature core of the system towards the distal cooler margin of the system. The proximal alteration will likely be potassic and silicic, with distal argillic, sericite, chlorite alteration (Barton & Johnson, 2000). Minimal low temperature alteration affects the zone of meteoric water recharge. External non-magmatic fluids leach metals in their path, producing a metal poor, sodic±calcic, K-feldspar and hematite inflow zone. Any thermal activity leads to a zone of cooling, recorded by sodic or potassic alteration accompanying mafic or felsic host rock respectively. Further away from the mineralisation sericite, chlorite, (pyro)phyllite alteration occurs (Barton & Johnson, 2000).

#### **Study Questions**

- 1) Describe the processes of solubility and dissociation and the way they control mineral dissolution and precipitation.
- 2) Describe the conditions that drive hydrothermal systems.
- 3) Discuss the connection between alteration of host rocks and mineralisation.
- 4) Discuss the formation of iron oxide deposits by hydrothermal activity and evaluate the conditions required.

## Sources and Further reading

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