The adsorption of gold(I) hydrosulphide complexes by iron sulphides

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Publication Date:
1999

Permanent Link:
https://doi.org/10.3929/ethz-a-003881069

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THE ADSORPTION OF GOLD(I) HYDROSULPHIDE COMPLEXES BY IRON SULPHIDES

A dissertation submitted to the
Swiss Federal Institute of Technology Zürich (ETHZ)

for the degree of
Doctor of Natural Sciences

presented by

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December 1999
ACKNOWLEDGEMENTS

When Terry Seward had proposed the Ph.D. topic to me it sounded like this thesis would be a “piece of cake”, as typically he would say. Well structured into blocks, all of which seemed to be manageable. Yet – as I am now allowed to say – history showed that this was wrong. Experiments tend to be challenging and, especially in experiments, the devil lies in the details. These details, nearly turned the thesis into a never ending story and led to something I would call a standing, and often repeated, expression of Terry’s: “We are just there”. Looking back, this expression has two meanings, one as being fed with hope and the other as being put off until later. Especially in the last months, when writing the thesis, my feelings of hatred for the work and being enthusiastic about it alternated at short intervals. For this enthusiasm, the guidance, and the support while writing, I would like to thank Terry Seward, as boss, teacher and friend.

As this chemical topic was challenging for me as a more classically orientated earth scientist it is my wish to thank the persons who helped me to link both fields. Hervé Cousin, Sabine Metzger and Terry Seward were never to exhausted for discussion; they never gave me the impression that a question was stupid or unnecessary.

Through the different stages of my Ph.D. work different people were involved and supported me, as this topic did not have many similarities with other studies going on in our institute many of these people were at other institutes, in particular I would like to mention:

- In construction of the high-pressure synthesis line I was supported by Urs Graber and Bruno Zürcher.
- Noldi Stahel for his patience and help with the XRD analysis of my samples.
- The quantification of the gold adsorption was not possible without ICP-MS analysis. The specialists for tickling out the last ppt of the machine were Detlef Günther and Rolf Frischknecht of the IMGR. Their effort outside of normal working hours is worth a special applause.
- With Hervé Cousin’s help I could manage to get samples dissolved without any residuals of sulphur and quantify the amount of solid by ICP-OES.
- For the analysis of the surface composition, I was supported by the members of the LSST lab. Irene Pfund-Klingenfuss aided me in the XPS analysis and discussions with Antonella Rossi-Elsener and Markus Textor were very fruitful.
- The members of the Laboratory of Crystallography for their discussions on mineral, solid state chemistry and crystallography, especially Melchior Fehlmann, Volker Gramlich and Michael Estermann.
- The SNF for the support of the research project.
- Volker Trommsdorff, Rainer Kuendig and Christoph Heinrich for their support at the later stages of my Ph.D..

Additionally a number of persons have moulded the everyday life at the institute and the ETH, to which I am obliged:

- Pulmer the anvil, with his best calibrated multianvils, as official boss for the computer work.
- Former office colleges from E 20, like Jürgen Konzett, Monika Weiss, Christoph Wahrenberger, Peter Nievergelt in memory of Friday's Weisswürstel events.
- The fellow combatants of the group on the search for the holy grail of science. Especially I would like to mention Liane Benning, Thomas Driesner, Oleg Souleimenov, Dip Banerjee, Andri Steffanson and Sasha Likholyot.
- My present office college Rolf Schmid for his hospitality, help and constant fruit supply when requested.
- Jamie Connolly for his support when dealing with letters and pamphlets in English and the "ultimately" fast delivery of bike tools.
- Former and present day members of the department for the friendship: Marcel Pfiffner, André Puschnig, Felix Mattenberger, Ralf Kägi, Roland Stalder, Andreas Meier, Trudi Semeniuk and Markus Auernhammer.
- As well as all not personally named friends, colleges and fellow employees for their collegiality and perpetual readiness to help.

An important refuge for me to recuperate from failed experiments, and tank energy to continue, was the KOSTA/Polyballkommission. The student organisation forms a kind of family with the possibility for endless discussions like the one about the meaning of life. The duties that had to be done formed for me an important counterpart to the rather lonely scientific work.

Sabine Metzger, for her affection, patience when writing and the occasional required kick.

Last thanks go to my parents, who have wherever possible, supported me on my way to the end of the thesis.
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The adsorption of gold by pyrite, pyrrhotite and mackinawite from solutions containing up to 40mg/kg (8μm) gold as hydrosulphidogold(I) complexes has been measured over the pH range from 2 to 10 at 25°C and at 0.10m ionic strength (NaCl, NaClO₄).

The pH of point of zero charge, pHₚₑₑ, has been determined for all three iron sulphides and shown to be 2.4, 2.7 and 2.9 for pyrite, pyrrhotite and mackinawite, respectively. In solutions containing hydrogen sulphide, the pHₚₑₑ is reduced to values below 2. The surface charge for each sulphide is therefore negative over the pH range studied in the adsorption experiments. Adsorption varied from 100% in acid solutions having pH < 5.5 (pyrite) and pH < 4 (mackinawite and pyrrhotite). At alkaline pH’s (e.g. pH = 9), the pyrite surface adsorbed 30% of the gold from solution whereas the pyrrhotite and mackinawite surfaces did not adsorb.

The main gold complex which is adsorbed is AuHS⁺ as may be deduced from the gold speciation in solution in combination with the surface charge. The adsorption of the negatively charged Au(HS)₂⁻ onto the negatively charged sulphide surfaces is not favoured.

The X-ray photoelectron spectroscopic (XPS) data revealed different surface reactions for pyrite and mackinawite surfaces. While no change in redox state of adsorbent and adsorbate was observed on pyrite, a chemisorption reaction has been determined on mackinawite leading to the reduction of the gold(I) solution complex to metallic gold and to the formation of surface polysulphides.

The data indicate that the adsorption of gold complexes onto iron sulphide surfaces such as that of pyrite is an important process in the "deposition" of gold from aqueous solutions over a wide range of temperature and pressure.
ZUSAMMENFASSUNG

Die Adsorption von Gold durch Pyrit, Pyrrhotin und Mackinawit aus Lösungen mit Konzentrationen bis zu 40mg/kg Gold in Form von Gold(I) Schwefelwasserstoffkomplexen wurde über den pH-Bereich von pH 2 bis pH 10 bei 25°C und einer Ionenstärke von 0.10m (NaCl, NaClO₄) bestimmt.

Der pH des „Point-Of-Zero-Charge“ der Eisensulfide konnte als 2.4, 2.7 und 2.9 für Pyrit, Pyrrhotin und Mackinawit bestimmt werden. Ist die Lösung angereichert an Schwefelwasserstoff, so sinkt der pH des „Point-Of-Zero-Charge“ auf einen Wert kleiner 2. Die Oberflächenladung der Sulfide ist folglich über den ganzen pH-Bereich der Adsorptionsexperimente negativ.


Die Adsorption von Gold ist bei tiefem pH maximal, wie auch der Anteil des neutralen AuHS⁺ Komplexes in der Lösung, deshalb lässt sich schliessen, dass dieser bevorzugt adsorbiert wird, zumal die anderen Gold (I) Lösungskomplexe (Au(HS)₂⁻ und Au₂S₄³⁻) wie die Mineraloberflächen negativ geladen sind und sich dementsprechend abgestossen.

Die Oberflächenreaktionen wurden mit der Röntgenphotoelektroenspektroskopie bestimmt. Im Falle von Pyrit konnte keine Änderung des Oxidationszustandes der Mineraloberfläche und des aus der Lösung adsorbierten Goldkomplexes festgestellt werden. Bei Mackinawit zeigte es sich, dass das Gold(I) der Lösung mit der Mineraloberfläche reagierte und bei einer Redoxreaktion metallisches Gold und Polysulfide an der Mineraloberfläche entstanden sind.

Gold occurs in pyrite in hydrothermal environments throughout the earth’s crust at conditions ranging from high grade metamorphism and near magmatic to the lower temperature regimes of epithermal ore deposition and seafloor hydrothermal systems. The precipitation of gold in hydrothermal systems is generally regarded as being determined by decreases in the equilibrium solubility due to changing gold complex stability in the response to processes such as boiling and fluid mixing and associated changes in pH and reduced sulphur activity. However, the role of surface adsorption by sulphide minerals such as pyrite is seldom considered despite the demonstrated role of sulphide mineral surfaces in scavenging gold as reported by Renders and Seward (1989b) and Schoonen et al. (1992). Several other recent experimental studies by Aretaki and Morse (1993) and Kornicker and Morse (1991) have also considered the adsorption of heavy metals such as manganese by pyrite and mackinawite as function of pH but the nature of the adsorbed manganese on the sulphide surface was not discussed. A fundamental aspect of surface adsorption is that a trace component such as gold may be coprecipitated from a hydrothermal fluid by a phase such as pyrite at concentrations below the equilibrium saturation.

There is some evidence for the role of surface adsorption in the precipitation or concentration of gold by surface effects in ore-depositing hydrothermal systems. In a recent study, Simon et al. (1999) suggested that 50% of the total gold in the Twin Creeks deposit, a Carlin-type deposit in the USA, had been extracted from solution during the ore forming process by adsorption. Gold in such samples has been observed either as small inclusions of metallic gold or as submicroscopic inclusions of gold(I), which is generally termed "invisible gold" (Sha, 1993; Simon et al., 1999a, b). Both have attributed the observation of at least the Au(I) to surface adsorption processes in analogy to the study of Renders and Seward (1989b) and Cardile et al.(1993). The similar, still active Ladolam epithermal deposit on Lihir island contains gold reserves of 600t and is still boiling at depth (Moyle et al., 1990). The main ore phases in the deposit are gold enriched pyrite and native gold. In the fore-arc basin of Lihir on top of the Conical seamount volcano at a depth of 1050m iron sulphides containing up to 43ppm Au have been discovered (Herzig and Hannington, 1995). In contrast to the known subareal systems, greigite (Fe₃S₄) and amorphous FeS have been recognised in the exhalative precipitates, in addition to pyrite and marcasite.
Hydrothermal black smoker systems are favorable places for metal adsorption due to the rapid formation of large amounts of fine grained to colloidally sized sulphides with a large specific surface area as consequence of cold seawater mixing with hydrothermal solutions at temperatures up to 400°C. The association of gold from such environments has been studied by Hannington et al. (1986), Hannington and Scott (1989), Hannington et al. (1991) and Herzig et al. (1993) but the fine grained nature of the samples has inherent analytical limitations, as gold analysis of single phases are not feasible due to the low concentrations and small grain size. The chimney precipitates can be organised in three associations, (1) the high temperature chalcopyrite - pyrrhotite - isocubanite association with low gold concentrations formed above 350°C, (2) the medium temperature association with pyrite and chalcopyrite with up to 4.9ppm Au and (3), the low temperature phases like sphalerite, galena, tennantite, Pb-Ag-sulfosalts, pyrite, bornite which can contain small inclusions of native gold (Herzig et al., 1993) and total assemblage gold concentrations of up to 30ppm. The detailed gold contents of iron sulphide precipitates are not known and many present day minerals may as well be the result of recrystallisation.

**Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemography</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite/Marcasite FeS₃⁺</td>
<td></td>
<td>Fe⁺⁺⁺</td>
</tr>
<tr>
<td>Greigite</td>
<td></td>
<td>Fe⁺⁺⁺</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td></td>
<td>Fe⁺⁺⁺</td>
</tr>
<tr>
<td>Troilite</td>
<td></td>
<td>Fe⁺⁺ │ S⁻⁻⁻</td>
</tr>
<tr>
<td>Mackinawite</td>
<td></td>
<td>Fe⁺⁺⁺</td>
</tr>
<tr>
<td>Cubic FeS</td>
<td></td>
<td>Fe⁺⁺⁺</td>
</tr>
<tr>
<td>Amorphous FeS</td>
<td></td>
<td>Fe⁺⁺⁺</td>
</tr>
</tbody>
</table>

*The existence of a Fe₃S₈ phase is not secured, yet such a phase has been observed in several studies (details see result XPS section).*

Iron sulphides with variable elemental ratios achieve this by lattice vacancies. To maintain charge balance traces of iron and sulphur change their oxidation state:

The following exchange reaction can be defined:

* A: 3 Fe²⁺ ⇌ 2 Fe³⁺ + O (Pratt and Nesbitt, 1994)
* B: Fe²⁺ + S⁻⁻⁻ ⇌ O + S²⁻⁻⁻ (Vaughan and Craig, 1978)
* C: Fe²⁺ + S⁻⁻⁻ ⇌ Fe⁺⁺ + O

**Figure 1**

Chemography of iron sulphide phases and oxidation states of iron and sulphur (main [black background] and traces [grey background]).
Laboratory experiments (Schoonen and Barnes, 1991a-d) have shown that by reacting sulphide/polysulphide solutions with iron containing solutions at temperatures up to 150°C, an amorphous to partly crystalline FeS phase is initially formed, which reacts with the residual sulphur from the solution to form iron sulphide phases (figure 1) such as greigite and then finally pyrite (figure 2). The detailed reaction path depends on the availability of zero valent sulphur and free oxygen as well as on the pH (Berner, 1964; Berner, 1967; Rickard, 1969; Sweeney and Kaplan, 1973; Rickard, 1975; Morse et al., 1987; Rickard, 1989, Luther, 1991; Schoonen and Barnes, 1991a-d; Lennie and Vaughan, 1992; Lennie and Vaughan, 1996; Rickard, 1997; Rickard and Luther, 1997). These metastable iron sulphides (e.g. FeS) are sensitive to oxidation and are often not observed (overlooked) in epithermal ore depositing environments. In contact to air and humidity they are fully oxidised within minutes.

Experimental studies on gold(I) complexes in solutions have demonstrated that hydrosulphide (HS⁻) ligands play a fundamental role in gold transport by hydrothermal fluids in the Earth's crust. They are up to 20 orders of magnitude more stable than the equivalent chloride complexes (Seward 1991). In active, ore depositing geothermal systems such as Ohaaki-Broadlands, the aqueous gold chemistry and gold precipitation reactions are entirely dominated by the stability of gold(I) hydrosulphide complexes. Seward (1973), Renders and Seward (1989a), Shenberger and Barnes (1989), Vlassopoulos and Woods (1990), Pan and Wood (1994), Wood et al. (1994), Benning and Seward (1995, 1996) and Seward and Barnes (1997) have studied and summarised the aqueous chemistry of gold in more detail.
Traditionally, only solubility controls have been invoked to predict the gold concentration in hydrothermal solutions in response to changes in temperature, pressure, hydrogen fugacity, pH and ligand concentration. The scavenging of gold by mineral sulphide surfaces, by means of adsorption, surface precipitation and surface reduction has been largely ignored. In recent years, more interest has been given to the metal adsorption on sulphides. Studies of Bancroft and Gilles (1982), Jean and Bancroft (1985), Hyland et al. (1986), Jean and Bancroft (1986), Bancroft et al. (1988), Hyland and Bancroft (1989), Bancroft and Hyland (1990), Mycroft et al. (1995b), Scaini et al. (1995), Maddox et al. (1996), Scaini et al. (1997), Maddox et al. (1998), Scaini et al. (1998), have studied the adsorption of various heavy metals onto sulphides (arsenopyrite, pyrite, pyrrhotite, marcasite, sphalerite, cinnabar, galena, molybdenite and pentlandite) using XPS, SEM, SIMS, Auger spectroscopy and Rutherford backscattering spectroscopy. Studies of gold adsorption onto pyrite by Jean and Bancroft (1985) (Au(III) chlorides), Mycroft et al. (1995b) (Au(I) and Au(III) chlorides) and Maddox et al. (1998) (Au(III) chlorides) observed (using X-ray photoelectron spectroscopy) a two step reaction forming first a metastable Au(I) surface complex, which further reacted to metallic gold. Schoonen et al. (1992) and Mirnov et al. (1981) have studied the interaction of very low gold concentrations in water and chloride solutions at variable pH with pyrite. Only the study of Scaini et al. (1998) in which Au(I) hydrosulphide complexes were present in solution showed that at least some adsorbed gold was retained on pyrite surfaces in the Au(I) state although Au(0) was also present. In general the oxidation of surface sulphur was observed. Due to the long reaction times of their experiments, contamination of atmospheric oxygen and light may have affected their results.

In addition to the above mentioned studies involving iron sulphide surfaces, the adsorption of gold(I) hydrosulphide complexes onto amorphous arsenic and antimony sulphide has been studied by Renders and Seward (1989b) and this formed the experimental foundation for this present study. They observed gold adsorption at slightly acid to acid pH on both phases. With Mössbauer spectroscopy (Cardile et al., 1995), they have demonstrated the existence of a single oxidation state in form of a linear, triatomic Au(I) surface complex.

The variation of the surface charge also plays an important role in metal adsorption by sulphide mineral surfaces. A few early electrophoresis studies (e.g. Ney et al., 1973) reported a pH
\[ \text{pH}_{\text{pre}} \]
for pyrite of \( \approx 7 \) due to oxidation of the surface being studied. More recent electrophoretic measurements by Fornasiero et al. (1992), Dekkers and Schoonen (1994) and Bebić et al. (1998) suggest a pH
\[ \text{pH}_{\text{pre}} \approx 2 \] for pyrite.
Surface reactivity and composition of iron sulphides is of much interest in several other fields; these include the early history of life (Wächtershäuser, 1988; Wächtershäuser, 1990; Drobner et al., 1990; Russell et al., 1994; Russell and Hall, 1997), mineral flotation (Ney, 1973; Healy and Moignard, 1976; Buckley and Woods, 1984; Buckley et al. 1984; Buckley and Woods, 1985a,b; Buckley and Woods, 1987; Kelebek and Smith, 1989; Buckley and Riley, 1991; Sun et al., 1991; Pratt et al., 1994; Buckley and Woods, 1995; Nesbitt et al., 1995; Buckley and Woods, 1997; Vaughan et al., 1997; Nesbitt et al., 1998; Schaufuss et al., 1998) and photovoltaic effects of pyrite (Dasbach et al., 1993; Bronold et al. 1994a,b). Their results evaluated by XPS help to understand the mineral surface composition and reactivity.

The scope of this study is the evaluation of the gold(I) hydrosulphide adsorption by the different iron sulphides involved in the pyrite formation as a function of pH. The primary aim of this research has therefore been to address the frequently encountered association of gold with pyrite from a surface chemistry point of view. This has involved a multi-pronged approach which included, (1) the synthesis of the three iron sulphides (pyrite, pyrrhotite and mackinawite), (2) the determination of their surface charge properties (i.e. pH \(_{zc}\) or pH of point of zero charge) by potentiometric titration, (3) the adsorption of gold(I) hydrosulphide complexes on these sulphide surfaces as a function of pH, and (4) the application of X-ray photoelectron spectroscopy (XPS) to gain insight into the nature of adsorbed gold on surfaces of pyrite and mackinawite.

The careful synthesis of the various iron sulphides provided crystalline material with pristine surfaces that were not contaminated by atmospheric oxygen and “undamaged” as would be the case with crushed, natural mineral grains. This material was then used in the potentiometric titrations of surface charge to determine the pH \(_{zc}\). A knowledge of the charge of iron sulphide mineral surfaces is important to the understanding of the adsorption mechanism, bearing in mind that negatively charged species are not easily adsorbed onto negatively charged surfaces. The reason for studying mackinawite adsorption was because iron monosulphide is considered to be an important precursor in pyrite formation at \( t < 200^\circ C \) (see for example, Schoonen and Barnes, 1991a-d) and the adsorption behaviour could be important in understanding the nature of the observed concentration in some natural pyrites. Finally, the gold adsorbed onto pyrite and mackinawite was studied using XPS in order to establish whether gold(I) surface complexes were present or if chemisorptive redox reactions had occurred leading to the formation of Au\(^+\).
2 EXPERIMENTAL METHODS

2.1 Mineral synthesis

The adsorption of gold(I) hydrosulphide complexes has been measured on pyrite, pyrrhotite and mackinawite surfaces using both synthetic and natural phases. For the adsorption experiments, mono-phase, crystalline samples with a pristine, unoxidised surface are required. Ideally, such samples should have a homogeneous particle size in order that adsorbent and adsorbate can be separated by filtration. The general strategy for the synthesis was to react a sulphur-containing solution with an iron-containing solution at a given temperature, pressure and pH over a range of temperatures from 25 to 240°C and pressures up to 100bar.

Sulphide mineral syntheses up to 90°C were conducted in 1litre volume glass vessels having a number of ports which permitted the continuous monitoring of pH (Ross electrode) as well as the addition and removal of reactants and products under an atmosphere of oxygen-free nitrogen. The deoxygenated nitrogen employed in these experiments was produced by passing commercially available “oxygen free nitrogen” through a 50cm long column of copper filings maintained at 420°C. The hydrothermal synthesis (figure 3) experiments were conducted in a stainless steel autoclave of 100ml volume which was mounted vertically in a simple resistance furnace, the temperature of which was controlled and monitored to ±2°C. Pressure was controlled and monitored by a back-pressure regulator and a pressure gauge which were connected to the reaction autoclave via a stainless steel separator vessel containing a mobile piston. Solution could also be added to and reacted with hot solution in the reaction vessel by injection under pressure using a spindle press.

The surface area was determined by BET nitrogen adsorption (10 point measurement) using a Micromeritics Gemini 2360 apparatus with gas quality grades of 5.0 (99.999%) for nitrogen and helium. The mineral suspension was initially filtered under nitrogen and the precipitate transferred to tubes and dried. In case of pyrite and pyrrhotite, the precipitate was dried for 2 hours at 200°C in vacuum. The mackinawite sample was not heated, but dried in vacuum for 12h to avoid recrystallisation.

The synthesis of pyrite proved to be rather troublesome, mainly because of our requirements that the synthesis product must be monomineralic and thus free of other phases. The methods described by Berner (1964), Rickard (1969, 1997) and Schoonen and Barnes (1991 a-d) produced pyrite which was usually associated with varying amounts of other iron sulphide
phases. This was unacceptable because the presence of additional phases would mean that the adsorption of gold from solution could also be affected by mineral phases other than pyrite.

In this study, pyrite was synthesised using a method similar to that described by Wei and Osseo (1995). Two solutions (0.067m NaHS and 0.034m FeCl₃) were prepared using deoxygenated water and mixed in glass reaction vessel at 80°C. The pH was adjusted to pH ~ 3.5 and the mixture allowed to react for 36 hours. As a precaution, the filtered product was then washed with 1m HCl in order to remove any iron sulphide phases other than pyrite. X-ray diffraction measurements confirmed that the resulting pyrite was well crystallised and no other phases could be detected (figure 4a). Given the sensitivity of the X-ray diffractometer, contaminant phases might have been present at a < 1-2% level. Nevertheless, fine grained amorphous FeS and other sulphide minerals would have been removed during the acid washing procedure. Natural pyrite (Huanzala, Peru) was also employed in some of the adsorption experiments and potentiometric titrations. This material was crushed and sieved and the < 125µm fraction subsequently washed in 6N HCl, deoxygenated ethanol and dried under vacuum. This material had a BET surface of 4.5m²/g.
Pyrrhotite was synthesised hydrothermally. A 0.30m NaHS solution containing 0.05m $\text{KH}_2\text{PO}_4$ and 0.01m $\text{Na}_2\text{HPO}_4$ was heated to 230°C and 100bar. A solution of 1.10m Mohr’s salt (FeSO$_4$(NH$_4$)$_2$SO$_4$ 6H$_2$O) was then injected into the autoclave using a spindle press and the system allowed to react for 10 hours. The resulting product was monomineralic, well crystalline (figure 4b) and had a BET surface area of 16.8m$^2$/g.

Mackinawite was synthesised by reaction of H$_2$S / HS$^-$ solutions with Fe$^{3+}$ in a deoxygenated environment over a range of temperatures from 25 to 130°C. The preferred method involved preheating a 0.30m NaHS solution containing phosphate buffer (i.e. 0.05m $\text{KH}_2\text{PO}_4$ / 0.01m $\text{Na}_2\text{HPO}_4$) to 130°C at 100bar. A 1.10m solution of Mohr’s salt was then injected into the hot reaction vessel and allowed to react for 20 hours. This produced a crystalline mackinawite (figure 4c) with a BET surface area of 80m$^2$/g.
2.2 Potentiometric titrations

Several methods may be used to characterise a mineral surface with regard to charge distribution as a function of pH. The electrophoresis method provides information about the isoelectric point and the zeta potential as a function of pH, which are functions of innersphere and outersphere complexes. Potentiometric titration permits the determination of the pH of point of zero charge and can provide additional information about the number of the reactive surface sites. A mineral suspension is titrated against acids and bases and the pH as a function of titre is recorded. The stoichiometric point, as observed with acids and bases represents the pH of point of zero charge. From the difference of titre needed to reach a certain pH between sample suspension and blank solution and knowing the amount of solid added and its specific surface area, the density of reactive surface sites can be calculated.

The surface charges of both natural and synthetic pyrite, synthetic pyrrhotite and synthetic mackinawite were determined by potentiometric titration at 25°C. The titre solutions were prepared with deoxygenated water and stored in flasks under an oxygen-free nitrogen atmosphere. Fresh solutions were prepared after 2 days. The acid titre was standardised by titration against a solution prepared from recrystallised borax. NaOH titre was standardised against the acid titre. The experimental conditions are summarised in table 1.

For the titrations, a potentiostat/titrator (Metrohm GP736 Titrino) with an additional external plunger pump (Dosimat 685), both with 20ml volume, were used. The measured values of pH were stable to within 2mV/minute (equivalent of pH change of 0.033pH unit per minute or a minimal waiting time of 26s prior to further addition of 0.05ml of titre). pH was monitored with an Orion Ross 8102 combination electrode and recorded by the Metrohm TiNet software package for further evaluation/processing. The inlet ports of the reaction vessels (figure 5) were sealed by Viton/silicon/Teflon rings. During the experiments, the vessel was kept under a small nitrogen overpressure to avoid ingress of air. The solid was added as a suspension after the determination of its surface area. In the titrations, the suspensions were first titrated down to pH = 1.2 by addition of HCl/HClO4 and afterward by addition of NaOH until pH = 12 was reached. The titration curves for both titration directions were recorded but only the titration with acid showed a reaction with the surface.
Figure 5 Experimental setup for potentiometric titrations

Table 1 Overview of the conditions used for the potentiometric titration experiments

<table>
<thead>
<tr>
<th>mineral</th>
<th>surface area per experiment (m²)</th>
<th>initial H₂O volume (ml)</th>
<th>acid</th>
<th>base</th>
<th>inert electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrite, nat.</td>
<td>1.35</td>
<td>141</td>
<td>1m HCl</td>
<td>1m NaOH</td>
<td>NaCl</td>
</tr>
<tr>
<td>pyrite, syn.</td>
<td>4.90</td>
<td>62</td>
<td>1m HCl</td>
<td>1m NaOH</td>
<td>NaCl</td>
</tr>
<tr>
<td>pyrrhotite, syn.</td>
<td>1.35</td>
<td>141</td>
<td>1m HCl</td>
<td>1m NaOH</td>
<td>NaCl</td>
</tr>
<tr>
<td>mackinawite, syn.</td>
<td>1.35</td>
<td>282</td>
<td>2m HClO₄</td>
<td>2m NaOH</td>
<td>NaClO₄</td>
</tr>
</tbody>
</table>
2.3 Gold adsorption

The adsorption of aqueous gold(I) hydrosulphide complexes by natural and synthetic pyrite, synthetic pyrrhotite and synthetic mackinawite was studied over the pH range from 2 to 10 at 25°C and ionic strength equal 0.1 m NaCl. The concentration of gold in solution was always below equilibrium saturation and the ratio of sulphide mineral surface area to total gold in solution was maintained constant. Gold(I) hydrosulphide stock solutions were prepared by the reaction of fine grained elemental gold and a sulphide solution containing 0.15 m total reduced sulphur at pH ~ 7 at 20°C. Fine grained metallic gold was prepared the following way: gold metal was dissolved in concentrated, boiling aqua regia. The cooled solution was then reacted with a 0.10 m FeSO₄ solution in order to produce a gold precipitate which was then filtered, washed and dried.

The aqueous sulphide solutions were prepared by bubbling H₂S through a 0.075 m NaOH solution made from deoxygenated water until a pH ~ 7 was obtained. The equilibration of the near neutral sulphide solution with the fine grained gold precipitate was carried out at 20°C in a glass flask wrapped in aluminium foil which was stirred continuously and kept in the dark. After five days, a solution containing ~ 10 mg/kg of gold was obtained. The concentration was determined by ICP-MS.

The adsorption experiments were carried out in stirred, black glass reaction vessels of 0.5 and 2.0 litre volume which were immersed in a thermostated water bath at 25°C. Initially, aliquots of mineral suspension and sodium chloride or sodium perchlorate were added to a given volume of saturated (1 bar at 25°C) H₂S solution in the reaction vessel. A titrator / potentiostat (Metrohm Titrino 736) and a Ross combination pH electrode were used to monitor the pH which was adjusted by addition of HCl, HClO₄ or NaOH to the required pH. A suitable aliquot of gold(I) hydrosulphide stock solution was then added and the pH further adjusted as required.

At this point, a number of points should be further emphasised. Firstly, all aspects of the solution and sample preparation must be free from reactive oxygen (air) contamination. Not only must the mineral surfaces be uncontaminated by oxidation but the solutions as well as the acid and base titre must be deoxygenated and handled under deoxygenated nitrogen. Secondly, the preparation of gold-containing solutions as well as the adsorption experiments themselves must be free of light contamination to avoid the photo-reduction of light sensitive Au(I) species to Au°. And thirdly, care must be taken when adding the gold stock solution to the sulphide
solution in the adsorption reaction vessel that the solution remains undersaturated when the pH is adjusted to acid or alkaline conditions, in order to avoid the precipitation of $\text{Au}_2\text{S}$. This may be monitored by calculation of the solubility of $\text{Au}_2\text{S}$ (figure 6) at various pH’s and total reduced sulphur concentrations using the thermodynamic data of Renders and Seward (1989a) and Suleimenov and Seward (1997).

Experiments with high gold concentration and long reaction times up to 10h (initial gold concentration = 350µg/kg, solution volume = 1.6litre, mineral surface area per experiment ≈ 4.5m²) were performed with synthetic pyrite. Experiments with lower gold concentration (initial gold concentration = 40µg/kg, solution volume = 0.42litre, mineral surface area per experiment ≈ 2m²) were performed with natural, acid cleaned pyrite, synthetic pyrrhotite and synthetic mackinawite. The iron sulphide phases onto which gold had been adsorbed were filtered, dried and weighed. The samples were digested in aqua regia contained within a Teflon reaction vessel in a microwave oven. The total iron was then determined using an Iris ICP-OES facility with an analytical precision of ±3%.

Figure 6  Solubility of $\text{Au}_2\text{S}$ as function of pH at 25°C, 1bar, $\Sigma S=0.1m$ and NaCl=0.1m.
Gold analyses were performed using a Perkin Elmer ELAN 6000 ICP-MS. Thallium was used as internal standard and indium, cobalt and cerium were additionally measured to provide further information about sample and system stability. For the sample preparation, only “Suprapur” reagents (Merck: HCl 30%, HNO₃ 65%, H₂O₂ 30%) and doubly distilled (in quartz glass), deionised water were used. Liquid samples from the adsorption experiments were transferred to flat bottomed flasks, acidified with HCl under nitrogen stream to allow H₂S to escape and evaporated to near dryness. Four millilitres of aqua regia were added and the solution was brought up to boiling, cooled and diluted to 10ml. Then 0.2ml of a 799µg/kg Tl standard was added.

2.4 XPS measurements

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique that provides the semi-quantitative analysis of chemical composition as well as giving insight into the oxidation and binding state of the elements involved. X-rays with energy $E_{\text{X-ray}}$ are used to eject core electrons from surface atoms. By measuring their kinetic energy, $E_{\text{kin}}$, the binding energy, $E_{\text{bin}}$, of the core electrons can be determined as defined by equation (1)

\[
E_{\text{bin}} = E_{\text{X-ray}} - E_{\text{kin}}
\]

The binding energy of the core electrons depends on the oxidation state and on the binding partners of the elements. For example, the binding energy of the sulphur 2p₃/₂ electrons for sulphide (S²⁻) is approximately 162eV, whereas for elemental sulphur, the binding energy is around 164.2 and is 169.0eV for sulphate (SO₄²⁻). In general, the more oxidised an element, the higher is the core electron binding energy.

However, the detection limits for conventional XPS mean that higher gold concentrations are required on the sulphide mineral surfaces in order to obtain useful spectra. This was accomplished by decreasing the mass of solid onto which gold was adsorbed while at the same time increasing the total amount of gold available for adsorption by adding larger volume of gold-containing stock solution to the system. Gold was adsorbed onto 0.02g of pyrite and mackinawite at pH = 4 during a three hour run time to give a maximum calculated loading of 39g/kg Au in pyrite and mackinawite. The "gold-adsorbed" suspensions were then filtered under oxygen-free nitrogen and dried in a desicator over silica gel under the same atmosphere. The samples were mounted onto the XPS sample plate under a stream of nitrogen to minimise contact with atmospheric oxygen.
X-ray photoelectron spectra were obtained on a Specs Sage100 system operating at a base back pressure of less than 7x10^{-8}bar. The X-ray source was focused on a study area of 3x4mm. Overview and narrow region XPS scans were recorded at an analyser pass energy of 50 and 14eV respectively, using a hemisphere detector and Mg Kα X-rays (12kV and 25mA) as exciting radiation. With the Mg Kα radiation employed (conventional X-ray tube, no monochromator), a sample depth of about 50Å was studied. The spectrum measured for metallic gold foil gave a full width at half maximum (FWHM) of 1.05eV with 85% Lorenzian and 15% Gaussian contributions to the peak shape.

With non-metallic mineral powders, the correction of the shift originating from the charging of the sample presents a major problem. In most cases the static charge effect, which occurs with non-metals is corrected by setting the carbon 1s electron binding energy to 284.6eV (the carbon originates from oil within the apparatus). In our samples the carbon is from residual polydimethylysilicone (PDMS), a major compound of silicon vacuum grease. For PDMS, the following binding energies are tabulated (Beamson and Briggs, 1992): C 1s 284.38eV, O 1s 532.0eV and Si 2p_{3/2} 101.79eV relative to O 1s to 532.0eV. To decide upon which binding energy of C 1s to use in order to correct the spectrum for surface charge, the S 2p_{3/2} values of pyrite were employed. Setting the C 1s electron binding energy to 284.6eV, the resulting electron binding energy was within the range of binding energies determined in other studies (see results section) on pyrite and was therefore preferred.

Background subtraction was performed using the algorithm proposed by Shirley (1972). Au 4f, C 1s, O 1s, S 2p and Si 2s electron binding energy spectra were fitted after background correction with symmetric curves of mixed Gaussian and Lorentzian character, including the Mg Kα satellites. The fitting of the Fe 2p spectra were performed with the additional inclusion of asymmetry terms which account for the asymmetry caused by the many-body-effect as mentioned in the results chapter. For the iterative fitting procedure, the robust algorithm in the pro Fit software package (QuantumSoft, 1998) was applied using the equations from Briggs and Rivière (1983) for the peak shape.
3 RESULTS

3.1 Potentiometric titrations and surface charge

Potentiometric titration methods have been extensively employed in determining the pH of the point of zero charge ($\text{pH}_{\text{zc}}$) of oxides and (Parks and De Bruyn, 1962, Stumm, 1981, Sposito, 1984, Dzombak and Morel, 1990) but studies of sulphide surfaces are rare. Potentiometrically derived $\text{pH}_{\text{zc}}$ data exist for sphalerite, galena (Sun et al, 1991), arsenic and antimony sulphide (Renders and Seward, 1989b). Other studies on the charge development of sulphides have employed electrophoresis or flocculation methods in order to study the surface charge as a function of pH. Most are aimed at increasing mineral separation efficiency in flotation processes with additives like cyanide or organic ligands (i.e. xanthate). Little interest has been focused on the nature of the surface sites or the details the surface reactions.

The sensitivity of sulphide surfaces to oxidation is well illustrated by the various electrophoresis studies of sphalerite and pyrite. For sphalerite, isoelectric points (iep), the equivalent to $\text{pH}_{\text{zc}}$ (potentiometric titration) of below pH of 2 and up to 8 have been measured (Bebié et al., 1998; Healy and Moignard, 1976; Ney, 1973; Williams and Labib, 1985). For pyrite, the interval varies from 1.2 to 7 (Bebié et al. 1998; Fornasiero, 1992; Healy and Moignard, 1976; Ney, 1973). The low pH values are interpreted to represent the fresh, unoxidised surfaces and the high pH determinations represent oxidised surfaces.

In the standard method, a suspension of iron sulphide in aqueous solution with a given ionic strength (0.001 to 1m) is titrated with acid or base of the same ionic strength over the pH range to be studied. Blank titrations are also performed without the solid phase and these curves are then subtracted from the titrations containing solid. In an ideal perfect plot, all these lines intersect at one point, which represents the pH of the point of zero charge, as shown in figure 7. This technique has been developed and extensively used in the study of oxides. Potentiometric titration of oxide surfaces may generally be performed in systems open to air and hence, are quite straightforward. For other systems involving solid carbonates, a closed apparatus may have to be used in order to control the CO$_2$ concentration.
However, the titration of metal sulphide surfaces is very much more difficult as will be detailed below. The solid surface must be completely uncontaminated by reaction with atmospheric oxygen and in addition, the aqueous suspension must be free of atmospheric oxygen as must all reagents employed. Fresh, unoxidised sulphide surfaces have a pH$_{pzc}$ at low pH, generally between 1 and 4. In order to be able to reach such low pH's without adding large volumes of titre, relatively concentrated acids have to be used. If, for example, 0.1m acid is used then the ionic strength is fixed at inconveniently high value and order of magnitude variations in the ionic strength are also not feasible.

Some sulphides, such as pyrrhotite and mackinawite are known to possess an increased solubility at low pH as indicated by the solubility product for the three sulphides studied in this research (table 2). The high solubility and often, rapid dissolution rates for a phase such as mackinawite make an accurate determination of the pH$_{pzc}$ almost impossible.
Table 2  Solubility products of iron sulphides determined by Davidson (1991)

<table>
<thead>
<tr>
<th>mineral</th>
<th>log $k_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrite</td>
<td>-16.4</td>
</tr>
<tr>
<td>pyrrhotite</td>
<td>-5.1</td>
</tr>
<tr>
<td>mackinawite</td>
<td>-3.6</td>
</tr>
</tbody>
</table>

Note: The solubility products, $k_{sp}$, are defined as $k_{sp} = [Fe^{2+}][HS] \gamma Fe^{2+} \gamma HS^{-1}$ for monosulphide phases and $k_{sp} = [Fe^{2+}][HS] \gamma Fe^{2+} \gamma HS^{-1} [H^{+}]$ for pyrite.

Finally, it should be mentioned that all standard electrolyte salts such as NaCl, NaClO₄ and NaNO₃ and their equivalent acids are potentially problematic in the titrations of sulphide surfaces. For example, the formation of Fe²⁺ chloride complexes (Heinrich and Seward, 1990) may enhance iron sulphide mineral dissolution due to iron(II) chloride complexing. In addition, perchlorate or nitrates may act as oxidising agents in higher concentrations.

Given the limitations and difficulties above, the approach taken in evaluating the pH$_{pzc}$ was as follows. The uncorrected (for blank) titration data for various ionic strengths together with blank data (without solids and salts) were plotted against pH. The set for pyrrhotite is shown in figure 8. Only the curve with no added salt shows a change in the shape of the curve. Figure 9 shows this behaviour in detail for pyrrhotite in comparison to the blank. An inflection is observed, which offsets the low pH part of the titration curve to higher values between pH = 2.3 and 2.9 as the surface becomes protonated. The pH of the point of zero charge is defined as the pH where there are as many positively charged as well as negatively charged surface groups, such that the total charge is zero. If only one inflection is observed, which represents the reaction with only one kind of active surface site, then the pH$_{pzc}$ is at the half height of the inflection, where half of the sites are occupied. The position of the half height of the inflection is marked with a vertical line in the graphs (figures 9 to 12). For pyrrhotite, this is at about pH = 2.7. Similar data are shown for mackinawite in figure 10 where the pH$_{pzc}$ was estimated to be 2.9.

The pH$_{pzc}$ is defined as the pH where the net charge on the surface is zero. In the case of synthetic pyrite, different explanations for the two inflections (figure 11) are possible. One includes a site specific sensitivity where the two sites are protonated at different pH's. The other case includes the further protonation of a surface site that was already partially protonated in an earlier step. The lower pH inflection is considered to represent the pH$_{pzc}$ where all negative charges have been neutralised.
The different behaviour of synthetic (figure 11) and natural (figure 12) pyrite cleaned with diluted HCl is to be expected because in the process of fracturing pyrite crystals, Fe\(^{2+}\)-S\(^2-\) and S\(^2-\)-S\(^0\) bonds are broken. Surface sites therefore exist (i.e. =Fe\(^{2+}\), =S\(^-\) and =S-S\(^2-\)) with different charge depending on bond saturation due to different structural positions (i.e. in a plane, on the corner or at the edge). Spectroscopic studies from Schaufuss et al. (1998) and Nesbitt et al. (1998) using synchrotron and conventional XPS have observed this effect. Their studies showed the high reactivity of the singly charged S\(^-\) atom which reacts with surface Fe\(^{2+}\) sites to form Fe\(^{3+}\) and S\(^2-\). The synthetic pyrite has been formed without this fracturing and therefore not all the same surface sites exist.

![Figure 8](image)

**Figure 8** Potentiometric titration results for pyrrhotite suspensions at various initial salt concentrations and for blank sample without any salt added. Temperature 25°C, initial starting volume = 141ml.

<table>
<thead>
<tr>
<th>mineral</th>
<th>point of zero charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrite (synthetic)</td>
<td>2.0</td>
</tr>
<tr>
<td>pyrite (natural)</td>
<td>2.4</td>
</tr>
<tr>
<td>pyrrhotite (synthetic)</td>
<td>2.7</td>
</tr>
<tr>
<td>mackinawite (synthetic)</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Figure 9  Potentiometric titration results for pyrrhotite suspension (solid line) and blank sample (dotted line) without any salt added. Temperature 25°C, initial starting volume = 141ml. Vertical line marks position of pH of point of zero charge.

Figure 10  Potentiometric titration results for mackinawite suspension (solid line) and blank sample (dotted line) without any salt added. Temperature 25°C, initial starting volume = 282ml. Vertical line marks position of pH of point of zero charge.

Figure 11  Potentiometric titration results for synthetic pyrite suspension without any salt added. Temperature 25°C, initial starting volume = 32ml. Vertical lines mark positions half height of the inflections.

Figure 12  Potentiometric titration results for natural pyrite suspension (solid line) with 0.01m initial NaCl concentration and blank sample (dotted line) without any salt added. Temperature 25°C, initial starting volume = 141ml. Vertical line marks position of pH of point of zero charge.
All potentiometric titrations of iron sulphide suspensions exhibited a response from the surface only at low ionic strength. For pyrrhotite and mackinawite, the titrated suspensions were free of background electrolyte. For natural pyrite, it was possible to observe an inflection at a background electrolyte concentration of 0.01 m. All suspensions saturated with hydrogen sulphide showed no surface response. Similar observations have been made by Bebié et al. (1998) who showed that pyrite acquired a negative surface charge over the entire measured pH range down to pH = 2 in solutions containing appreciable concentrations of H$_2$S or HS$. Thus, H$_2$S and HS$^-$ are apparently potential determining species for the iron sulphide surfaces. The potentiometrically determined pH$_{zpc}$ data for pyrite, pyrrhotite and mackinawite obtained in this study are summarised in table 3 and are in good agreement with the values determined by electrophoresis (table 4).

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Summary of electrophoresis studies of unoxidised iron sulphides and sulphur in literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>mineral</td>
<td>isoelectric point</td>
</tr>
<tr>
<td>pyrite (nat.)</td>
<td>2</td>
</tr>
<tr>
<td>pyrite (nat.)</td>
<td>1.2 (±0.4)</td>
</tr>
<tr>
<td>pyrite (nat.)</td>
<td>1.x - 2.3</td>
</tr>
<tr>
<td>greigite (syn.)</td>
<td>3.0 - 3.5</td>
</tr>
<tr>
<td>pyrrhotite (nat.)</td>
<td>2</td>
</tr>
<tr>
<td>pyrrhotite (syn.)</td>
<td>2.0 - 2.5</td>
</tr>
<tr>
<td>pyrrhotite (nat.)</td>
<td>2.3 - 3.5</td>
</tr>
<tr>
<td>sulphur (syn.)</td>
<td>&lt;2.6 - 3.1*</td>
</tr>
<tr>
<td>sulphur (syn.)</td>
<td>&lt;3</td>
</tr>
<tr>
<td>sulphur (syn.)</td>
<td>2.2</td>
</tr>
</tbody>
</table>

* Estimated from flocculation rates
3.2 Adsorption experiments

The adsorption of gold(I) hydrosulphide complexes onto iron sulphide mineral surfaces has been measured at 25°C over the pH range from 2 to 10 and 0.1 M ionic strength. The time taken to obtain equilibrium adsorption by the different sulphide surfaces was normally about one hour (Figure 14) at intermediate pH and in the low pH experiments, equilibrium is achieved within 20 minutes. Experiments with high gold concentrations using synthetic pyrite phases did not reach equilibrium after 6 h which may possibly be attributed to contamination by reactive oxygen (air) and/or the influence of light (photo-reduction of gold (I)). Therefore for the more sensitive monosulphides, the maximum reaction time was never more than 45 minutes. At low pH, only a few minutes were necessary to reach equilibrium.

All results of the experiments are displayed in terms of percent gold adsorbed and remaining in solution, versus time plots for each pH and mineral in figures 13 to 16. To summarise the adsorption experiments, plots of percent adsorption as a function pH for each mineral have been prepared (figures 17-19).

![Graphs showing adsorption of gold(I) hydrosulphide complexes by synthetic pyrite at 25°C.](image-url)

*Figure 13* Adsorption of gold(I) hydrosulphide complexes by synthetic pyrite at 25°C. Percentage of total gold in solution (open circles) and adsorbed (filled circles) on pyrite as a function of time for various pH's; initial gold concentration 350 μg/kg, solution volume = 1.6 l and total surface area ~ 4.5 m².
Figure 14  Adsorption of gold(I) hydrosulphide complexes by natural pyrite at 25°C. Percentage of total gold in solution (open circles) and adsorbed (filled circles) on pyrite as a function of time for various pH. Initial gold concentration 40μg/kg, solution volume = 0.42l and total mineral surface area ~ 2m². Gold concentration and mineral surface area are proportionally reduced at pH = 2 and pH = 3 to avoid gold supersaturation in solution.
Chapter 3

Results

Figure 15 Adsorption of gold(I) hydrosulphide complexes by synthetic pyrrhotite at 25°C. Percentage of total gold in solution (open circles) and adsorbed (filled circles) on pyrrhotite as a function of time for various pH; initial gold concentration 40μg/kg, solution volume = 0.42l and total mineral surface area ~ 2m². Gold concentration and mineral surface area are proportionally reduced at pH = 2 and pH = 3 to avoid gold supersaturation in solution.
Figure 16  Adsorption of gold(I) hydrosulphide complexes by synthetic mackinawite at 25°C. Percentage of total gold in solution (open circles) and adsorbed (filled circles) on mackinawite as a function of time for various pH; initial gold concentration 40 µg/kg, solution volume = 0.42 l and total mineral surface area ~2 m². Gold concentration and mineral surface area are proportionally reduced at pH = 2.5 and pH = 3 to avoid gold supersaturation in solution.
For both, the natural and synthetic pyrite, maximum adsorption was observed at pH ≤ 5 (figure 17). At higher pH, the percent gold adsorbed from solution decreases but did not fall below ~30% at pH’s up to 10 (figures 13 and 14). Thus, adsorption extends to higher pH than with either of the two monosulphides. The comparison of both natural and synthetic pyrite with different gold concentrations shows equivalent behaviour within the experimental error. A maximum surface loading of 0.057 and 0.26 atoms/nm² for natural and synthetic pyrite respectively, which results in concentrations of 91mg/kg for natural and 340mg/kg for synthetic pyrite.

![Figure 17](image)

Figure 17 Adsorption of gold(I) hydrosulphide complexes by pyrite (squares: synthetic, circles: natural origin) at 25°C. Percentage of total gold in solution (open symbols) and adsorbed (filled symbols) on pyrite as a function pH. Details see experimental section.

Pyrrhotite and mackinawite show similar adsorption behaviour (figure 15 and 18). The adsorption is complete at pH = 2 and decreases until pH ≥ 6 where the adsorption is zero within the limits of analytical error. For pyrrhotite, a maximum surface loading of 0.086 atoms of gold per nm² equivalent to 470mg/kg is measured.
In the case of mackinawite, the attainment of equilibrium gold adsorption takes place within 25 min (figure 16). A maximum adsorption of 80% is observed at pH = 3 (figure 19). At pH = 2.5, lower adsorption (25%) is measured which is regarded as the effect of mineral dissolution caused by increased solubility. At pH > 3, the adsorption rapidly decreases. Based on the known specific surface area, a surface loading of 0.018 atoms of gold per nm$^2$ equivalent to 480 mg/kg in the solid was determined.
Figure 20 summarises the gold adsorption data for all three iron sulphide phases. The experiments with natural and synthetic pyrite at different gold concentrations show agreement within the experimental uncertainty. All iron sulphides show an adsorption of 90% or more at pH = 2. While the relative adsorption of mackinawite and pyrrhotite decreases quickly at higher pH and is zero at neutral pH, pyrite still adsorbs 90% of the gold from solution at pH = 5 and 30% at pH = 10. From the pH_{pzc} determination, no major differences in the surface charge of the three minerals, especially in solutions saturated with H_2S, can be expected although the experiments show an enhanced sensitivity to AuHS\(^-\) concentration for the iron monosulphide surfaces in comparison to that of the pyrite.

![Graph showing gold adsorption data for different iron sulphide phases](image)

Figure 20 Summary graph: Percentage of total gold in system adsorbed on natural pyrite (circles), synthetic pyrite (rhombus), pyrrhotite (squares) and mackinawite (triangles) at 25°C as a function of pH ( compilation of separate experiments).
3.3 XPS measurements

The potentiometric titrations provided some information about the charge on the surfaces as a function of pH. The adsorption experiments gave insight into the nature of removal of gold from aqueous solutions by the negatively charged surfaces as a function of pH. The question then arises as to the nature of the adsorbed gold on the sulphide mineral surfaces. Is the gold (in solution as hydrosulphide complexes) adsorbed and bonded to the different iron sulphide surfaces as surface complexes or do chemisorption redox reactions occur leading to the reduction of Au⁺ to Au° on the surface. In order to further elucidate the molecular basis for the adsorption of the gold complexes by these surfaces, we have therefore carried out X-ray photoelectron spectroscopic (XPS) measurements.

The X-ray photoelectron spectroscopy uses X-rays to eject core electrons from the surface atoms and measures the kinetic energy of the ejected atoms, thus permitting the determination of the electron binding energies. The p, d and f levels become split upon ionisation, leading to vacancies in the $p_{3/2}, p_{1/2}, d_{3/2}, d_{5/2}, f_{5/2}$ and $f_{7/2}$ orbitals. Spin orbit splitting results in characteristic energy shifts and area ratios, which are orbital dependent (e.g. $p_{3/2}$ and $p_{1/2}$ have an area ratio of 2:1). In addition, the energy shifts are element sensitive (e.g. S 2p = 1.18eV and Fe 2p = 13.1eV). Fe 2p$_{3/2}$, S 2p$_{3/2}$ and Au 4f$_{7/2}$ are referred simply as Fe 2p, S 2p and Au 4f in further discussion.

XPS techniques have been widely used in the surface study of sulphide minerals. The main focus of the studies are mineral formation (Lennie et al., 1995), flotation (Buckley and Woods, 1984; Buckley et al. 1984; Buckley and Woods, 1985a,b; Buckley and Woods, 1987; Nesbitt and Muir, 1994; Pratt et al., 1994; Buckley and Woods, 1995; Mycroft and Jean, 1995; Nesbitt et al., 1995; Vaughan et al., 1997, Nesbitt et al., 1998; Schauffuss et al., 1998) and adsorption (Bancroft and Gilles, 1982; Jean and Bancroft, 1985; Hyland et al., 1986; Jean and Bancroft, 1986; Bancroft et al., 1988; Hyland and Bancroft, 1989; Bancroft and Hyland, 1990; Mycroft et al., 1995b; Scaini et al., 1995; Maddox et al., 1996; Scaini et al., 1997; Maddox et al., 1998; Scaini et al., 1998). Other often used techniques to determine the chemical state of metal adsorbates at low to moderate concentration are Mössbauer spectroscopy and XAS (XANES and EXAFS) whereas methods like SIMS, STM, AFM, SEM, Auger spectroscopy tend to have a rather image oriented focus.

XPS was used because it provides information on both the mineral surface itself and the adsorbate, as well as permitting the possibility to discriminate several surface species of one element. The use of a synchrotron light source or monochromatic radiation would have been preferable because of increased energy resolution. Futhermore, a synchrotron source would also give rise to enhanced surface sensitivity.
We have used the technique to study the nature of the adsorbed gold complexes and the oxidation state of iron and sulphur on the iron sulphide surfaces. Surfaces of natural pyrite and synthetic mackinawite enriched in adsorbed gold at pH = 4 have been studied. In the broad scan spectra of both pyrite and mackinawite, peaks of carbon, gold, iron, sodium, oxygen, silicon, sodium and sulphur can be observed (figures 21 and 22). Trace polydimethylsiloxane (PDMS), a major component of silicon vacuum grease, was used to correct for shifting due to charging (for details see experimental methods chapter).

Before proceeding further in our discussion of the XPS spectra which were obtained for pyrite and mackinawite as well as for gold adsorbed onto their surfaces, some aspects need to be introduced to facilitate interpretation of the spectra.

![Figure 21](image1.png) The XPS spectrum of pyrite.

![Figure 22](image2.png) The XPS spectrum of mackinawite.
**Multiplet splitting**

Multiplet splitting (also termed exchange or electrostatic splitting) (Briggs and Rivière, 1983) of core-level peaks can occur when the system has unpaired electrons in the valence levels. For Fe$^{2+}$ in the ground state, six 3d electrons form one filled and four single occupied orbitals (denoted $^4S$). After the ejection of a 2s electron during the measurement, a further unpaired electron is present. If the spin of this electron is parallel to that of the 3d electrons (final state $^6S$), then exchange interaction can occur, resulting in a lower energy than for the case of antiparallel spin (final state $^4S$). Thus, the core level will be a doublet and the separation of the peak is the exchange interaction (Carlson, 1975; Briggs and Rivière, 1983; Hüfner, 1996). Multiplet splitting of non-s levels is more complex because of the additional involvement of orbital-angular momentum coupling. Multiplet spitting is strongest when both levels involved are in the same shell (as with 3s, 3p-3d), but the effects are still apparent in transition metal systems for 2p-3d interaction.

For a given transition metal ion the multiplet splitting in a chemical compound is determined by three major factors (Carlson, 1975):

- the extent of decoupling in the d orbital due to strong field ligand bonding
- the extent that the d electrons are delocalised due to the nature of the chemical bond
- correlation effects.

A correlation between the core electron splitting for various compounds and the hyperfine fields determined by Mössbauer spectroscopy has been determined (Hüfner and Wertheim, 1973).

**Many-body screening effect**

The many-body phenomenon is also called Mahan-Nozières-De-Dominicis effect. In metals, it arises from the excitation of the electrons at the Fermi surface and takes the form of a logarithmic divergence in the number of electron-hole pairs as the excitation energy approaches zero. The physical basis for this was originally put forward by Mahan (1967). Doniach and Sunjic (1970) proposed a one-parameter shape function to describe the influence on the peak shape. In contrast to insulators, valence electrons are mobile (delocalised) in metals due to the intersection of the conductivity and valence bands leading to filled orbitals up to the Fermi level. The ejection of one electron in a metal by X-rays does not lead to a vacancy in a localisable molecular orbital between two atoms as with covalent bonded insulators. In the case of metals, the Fermi level is reduced by a minute amount. The same process is considered to cause the core electron line shape asymmetry in semimetals and semiconductors as proposed by Wertheim and Buchanan (1977).
Chapter 3 35 Results

Magnetic properties and conductivity of the iron sulphides
Many of the iron sulphide compounds have been studied by Mössbauer spectroscopy and spin state of the iron as well as the magnetic properties are summarised in table 5. The observation of hyperfine splitting determined by Mössbauer spectroscopy can be positively correlated to high spin state of the studied atom (Wertheim and Hüfner, 1975), which causes the multiplet splitting.

A new approach has been introduced by Nesbitt et al. (1998) based on their study of pyrite using synchrotron radiation. They tuned the synchrotron radiation for maximal surface sensitivity (Sean and Dench, 1979) and explained their spectrum using a multiplet splitting model. They claimed that multiplet splitting of low spin compounds could occur due to unsaturated bonds on the mineral surface which cause iron to be in a high spin state. This effect can play an important role when using synchrotron radiation tuned to maximal surface sensitivity, but is minor in studies using conventional Mg Kα radiation as a source.

Both pyrite and marcasite (table 5, group I) contain both low spin iron and their conductivity is based on their semiconductor properties. Therefore multiplet splitting can be excluded and peak broadening is caused by the many-body phenomenon.

Table 5  Some physical properties of iron sulphides

<table>
<thead>
<tr>
<th></th>
<th>marcasite</th>
<th>pyrite</th>
<th>mackinawite</th>
<th>pentlandite</th>
<th>pyrrhotite</th>
<th>greigite</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical formula</td>
<td>FeS₂</td>
<td>FeS₂</td>
<td>Fe₆₋₇S₆</td>
<td>(Ni,Fe)S₆</td>
<td>Fe₆₋₇S₆</td>
<td>Fe₆₋₇S₆</td>
</tr>
<tr>
<td>hyperfine splitting</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>existing</td>
</tr>
<tr>
<td>Fe - spin</td>
<td>low spin</td>
<td>low spin</td>
<td>low spin</td>
<td>low spin</td>
<td>low spin</td>
<td>high spin</td>
</tr>
<tr>
<td>conductivity</td>
<td>semiconductor</td>
<td>semiconductor</td>
<td>metallic conductor</td>
<td>metallic conductor</td>
<td>metallic conductor</td>
<td>metallic conductor</td>
</tr>
<tr>
<td>magnetism</td>
<td>diamagnetic</td>
<td>diamagnetic</td>
<td>Pauli paramagnetic</td>
<td>Pauli paramagnetic</td>
<td>antiferromagnetic</td>
<td>ferrimagnetic</td>
</tr>
<tr>
<td>group</td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>multiplet splitting</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>many-body effect</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>comment</td>
<td>high energy tail due to metallic conductivity</td>
<td>high energy tail due to metallic conductivity</td>
<td>intermediate between II and IV: weak multiplet splitting and high energy tail</td>
<td>both effects are expected, high spin causes multiplet splitting and metallic conductivity forms high energy tail</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data from Vaughan and Craig (1979) unless otherwise specified;

* A number of studies using Mössbauer spectroscopy on mackinawite have been reported. Morice & al. (1969) observed hyperfine splitting, Vaughan & Ridout (1971) found weak intensity hyperfine splitting with and without the magnetic field. They attribute the lines to impurities of greigite and iron in the studied material. A third study by Bertaut & al. (1965) showed the absence of an ordered magnetic moment.

** Rajamani & Prewitt (1973) favor high spin due to the inter-atomic distances, although no hyperfine splitting could be observed.
Mackinawite belongs to the group II of layered sulphides (i.e. sulphur-iron-sulphur layers) in which iron is tetrahedrally co-ordinated by sulphur (figure 23). With respect to hyperfine splitting, the Mössbauer data are somewhat contradictory. Rather strong hyperfine splitting was observed by Morice et al. (1969) but Vaughan and Ridout (1971) detected only a weak effect and attributed it to impurities of iron and greigite. Bertaut et al. (1965) showed the absence of an ordered magnetic moment and measured no hyperfine splitting. In combination with the Pauli paramagnetism which is found only in metallic materials (in which the outermost electrons are extensively delocalised), we therefore conclude that the iron is in a low spin state in mackinawite. Pauli paramagnetism arises from a partly filled band in which the application of an external field causes an imbalance between spin-up and spin-down electrons and hence a net magnetic moment. The Pauli paramagnetism confirms the delocalised electrons in the iron plane. Therefore, the peak broadening can be attributed to the many-body effect.

The mineralogical data for pentlandite (group III) are still ambiguous and therefore pentlandite cannot be assigned to group II or IV and a special group had to be created (table 5). Rajamani and Prewitt (1973) proposed that in addition to low spin iron, the high spin state also exists and therefore multiplet splitting is possible. The metallic conductivity also gives rise to the many-body effect as well as to Pauli paramagnetism.

The magnetic, high spin iron minerals greigite and pyrrhotite (group IV) both exhibit metallic conductivity. Here multiplet splitting and the many-body-effect will contribute to the wide, high-energy tail.
3.3.1 Pyrite
The low intensity and therefore poor resolution observed for the iron spectra (figure 24) nevertheless permits the determination of an electron binding energy of 707.05 eV for the Fe 2p\textsubscript{3/2}. This binding energy is within the range given by Buckley and Woods (1985) at 707 eV and by Lennie et al. (1996) at 707.2 eV (table 6). Comparison of the iron peaks for pyrite and mackinawite suggests that the pyrite surface is depleted in iron, probably as the consequence of the cleaning of the mineral surface with 6N HCl acid prior to the adsorption experiment. However, the reactivity of natural, cleaned pyrite with respect to metal adsorption and surface charge is not modified in significant way. By comparison, the sulphur 2p and iron 2p electron binding energies for vacuum fractured pyrite are unmodified, but a few other minor contributions to the spectra such as surface moieties of mono- and polysulphides observed in other studies (Nesbitt and Muir, 1994; Nesbitt et al., 1998; Schaffuss et al., 1998) could not be observed in the spectrum.

The S 2p\textsubscript{3/2} electron binding energy can be fitted best with one peak (figure 25). This peak is at 162.30 eV within the range of other studies on pyrite which are summarised in table 6. No additional peaks are found that would include the occurrence of surface polysulphides.

![Figure 24 XPS spectrum of the pyrite sample after reaction with gold(I) hydrosulphide solution at 25°C at pH 4: Fe 2p spectrum, which shows the separated Fe 2p\textsubscript{3/2} (around 720 eV) and Fe 2p\textsubscript{1/2} (around 707 eV) orbitals.](image)
Table 6. *S 2p and Fe 2p binding energies (eV) for iron sulphide compounds*

<table>
<thead>
<tr>
<th>Mineral</th>
<th>S 2p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>Fe 2p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>Charge correction</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>162.3</td>
<td>707</td>
<td></td>
<td>Buckley and Woods, 1985</td>
</tr>
<tr>
<td>Pyrite</td>
<td>162.4</td>
<td>-</td>
<td></td>
<td>Bancroft and Hyland, 1989</td>
</tr>
<tr>
<td>Pyrite</td>
<td>162.4</td>
<td>-</td>
<td></td>
<td>Nesbitt and Muir, 1994</td>
</tr>
<tr>
<td>Pyrite</td>
<td>162.3</td>
<td>-</td>
<td></td>
<td>Knipe et al., 1995</td>
</tr>
<tr>
<td>Pyrite</td>
<td>162.5</td>
<td>707.2</td>
<td>C 1s = 284.6</td>
<td>Lennie and Vaughan, 1996</td>
</tr>
<tr>
<td>(50%G/50%L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Greigite</td>
<td>-</td>
<td>709.15 (16.5%)</td>
<td>C 1s = 285.0</td>
<td>Herbert et al., 1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>710.35 (8.8%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>711.39 (5%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>712.67 (1.7%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrrhotite Fe&lt;sub&gt;0.98&lt;/sub&gt;S</td>
<td>161.1</td>
<td>708</td>
<td></td>
<td>Buckey and Woods, 1985</td>
</tr>
<tr>
<td>Pyrrhotite Fe&lt;sub&gt;7&lt;/sub&gt;S&lt;sub&gt;8&lt;/sub&gt;</td>
<td>161.25</td>
<td>707.5</td>
<td></td>
<td>Pratt et al., 1994</td>
</tr>
<tr>
<td>Mackinawite</td>
<td>161.82</td>
<td>707.25</td>
<td>C 1s = 284.6</td>
<td>Lennie and Vaughan, 1996</td>
</tr>
<tr>
<td>(80%G/20%L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mackinawite*</td>
<td>160.95</td>
<td>706.4 (14%)</td>
<td>C 1s = 285.0</td>
<td>Herbert et al., 1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>707.3 (38.9%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>708.2 (13.2%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>713.3 (1.9%)**</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Herbert et al. (1998) used a triplet for mackinawite to fit the Fe 2p<sub>3/2</sub> peak, area proportion in brackets
** Satellite.
The main interest is focused on the chemical state of the Au (4f½) electron binding energy and is based on a one peak fit at 84.8eV (figure 26a,b). This value is in accordance with the study by Scaini et al. (1998). In their study of gold adsorption onto pyrite, they found (variable reaction time from 1 day to one week at 25 and 90°C) gold compounds with binding energies of 84.7 to 85.1eV and 84.0eV (table 7). The low energy peak (84.0eV) was attributed to elemental gold (i.e. Au°) which was present in all but one of their experiments. The higher energy compound was determined by comparison with binding energies given by van de Vondel (1977) as a gold(I) surface complex. They studied gold(I) complexes with linear S-Au-S arrangement and found binding energies of 85.0 to 85.2eV. Another possibility might have been the presence of Au clusters which have been studied by Di Cenzo et al. (1988) but they have binding energies in the interval of 84.0 to 84.7eV and cannot account for the higher values reported here and by Scaini et al. (1998). Our data are also consistent with the formation of Au(I) surface complexes, which have been identified on amorphous arsenic and antimony sulphides by Mössbauer spectroscopy (Cardile et al., 1993).
Figure 26  XPS spectrum of the pyrite sample after reaction with gold(I) hydrosulphide solution at 25°C at pH 4:

(a):  Au 4f spectrum, which shows the separated Au 4f₇/₂ (around 84 eV) and Au 4f₅/₂ (around 87 eV) orbitals.

(b):  Detailed Au 4f₇/₂ spectrum with one symmetric peak fit. The upper solid line shows the upper total fit with added background, the lower the background fitted with the Shirley function.

Table 7  Au 4f₇/₂ binding energies in eV for gold compounds

<table>
<thead>
<tr>
<th>compound</th>
<th>Au 4f₇/₂</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (metallic)</td>
<td>83.9 - 84.0</td>
<td>Moulder et al., 1992</td>
</tr>
<tr>
<td>Au clusters (5-7 Atoms)</td>
<td>84.0 - 84.7</td>
<td>DiCenzo et al., 1988</td>
</tr>
<tr>
<td>compounds with linear S-Au-S arrangement*</td>
<td>85.0 / 85.2</td>
<td>Van de Vondel, 1977</td>
</tr>
<tr>
<td>Au(l) S surface complex</td>
<td>84.7 - 85.1</td>
<td>Scaini et al., 1998</td>
</tr>
<tr>
<td>AuCl</td>
<td>85.2</td>
<td>Kishi and Ikeda, 1974</td>
</tr>
<tr>
<td>Au₂O₃</td>
<td>89.5</td>
<td>Aita and Tran, 1991</td>
</tr>
<tr>
<td>Au(OH)₃</td>
<td>91.3</td>
<td>Aita and Tran, 1991</td>
</tr>
</tbody>
</table>

* Charge correction with C 1s 285eV
3.3.2 Mackinawite

Figure 27a shows the iron 2p electron binding energy spectrum of the synthetic mackinawite. The figure 27b shows the detail spectrum between 716.5 and 705.5 eV and the observed peak can be attributed to the Fe 2p\textsubscript{3/2} electron binding energy and shows an asymmetric broadening on the high-energy side. Several explanations can account for this. Herbert et al. (1998) studied poorly crystalline iron sulphides precipitated by sulphate reducing bacteria. By analogy to the spectroscopic studies of Pratt et al. (1994) on pyrrhotite, they used four symmetric peaks for mackinawite and three peaks for greigite to fit the spectrum and account for the peak shape. Three of the mackinawite peaks are attributed to multiplet splitting and one to a satellite. Gupta and Sen (1974, 1975) calculated the multiplet splitting of core 3p vacancy levels in transition metals compounds using a Hartree-Fock free ion approach. Their calculations give rise to a fit of one satellite and three peaks for the Fe\textsubscript{2p} for Fe\textsuperscript{2+} and Fe\textsuperscript{3+} each.

![Figure 27](image.png)

**Figure 27**  XPS spectrum of the mackinawite sample after reaction with gold(I) hydrosulphide solution at 25°C at pH 4:

(a): Fe 2p spectrum, which shows the separated Fe 2p\textsubscript{3/2} (around 720 eV) and Fe 2p\textsubscript{1/2} (around 707 eV) orbitals.

(b): Detailed Fe 2p\textsubscript{3/2} spectrum with one, asymmetric peak fit. The upper solid line shows the upper total fit with added background, the lower the background fitted with the Shirley function. Dashed lines represent contributions to total fit: Upper: primary fit, lower: satellite of primary line as correction for non-monochromatic source (Mg K\alpha\textsubscript{3,4} contribution).
However, in their study of freshly synthesised mackinawite, Lennie et al. (1995) employed one peak with a wide tail to fit the spectrum. Their approach was based on Wertheim and Buchanan's (1977) study of semi-metals and semiconductors which showed that the formation of asymmetric peaks is a common feature due to excitation of the electrons at the Fermi surface for these substances. This phenomenon had been previously only described for metals and alloys. From the results of their earlier Mössbauer spectroscopic study of mackinawite, Kjekshus et al. (1972) had also proposed the delocalisation of electrons in the iron-containing layers (figure 23). The distance between the iron atoms is 2.60 Å, which is just little more than in the body-centred cubic form of iron with a distance of 2.59 Å (table 8).

As mentioned above, mackinawite belongs to the group II (table 5), where the peak shape is accounted for by the delocalisation of the electrons in the iron layer. Therefore, the peak shape is approximated with one peak with a tail, which fits the data points quite accurately. The measured value of 707.3 eV coincides with the energy of the main peak determined by Herbert et al. (1998) in their three peak multiplet model. The value is also consistent with the study by Lennie et al. (1995) who proposed the tail model to fit the data.

For the S 2p$_{3/2}$ peak, fitting was performed with 50:50 Gaussian/Lorenzian relation (figure 28) with the best fitting being achieved with two peak set. This leads to peaks with full width at half maximum (FWHM) comparable to that found in other sulphide surface studies. The lower S 2p$_{3/2}$ binding energy of 161.3 eV is intermediate between the value reported in the study of Herbert et al. (1998) (160.95 eV) and the higher value (161.82 eV) reported by Lennie et al. (1995). The reason for the discrepancy between all three values may arise from the differences in the degree of crystallinity, which is indicated by the X-ray diffraction patterns and is a consequence of the method of synthesis. Studies on the synthesis of mackinawite have shown that the mixing of a sodium sulphide solution with a ferrous salt such as Fe(SO$_4$)$_2$·6H$_2$O leads to a poorly crystalline precipitate (Berner, 1964, 1967). Mackinawite synthesised in this way is thus different from that formed by the reaction of sodium sulphide solution with iron wool at a known, buffered pH as employed by Lennie et al. (1995). Differences in crystallinity can lead to changes in the stacking system of the (S-Fe-S) package layers as shown in figure 23.

In a first step, single layers can be formed in which each sulphur may contain two additional protons. To enable the stacking, these protons have to be removed. Thus, the atomic environment around the sulphur is modified, which would cause a minor change in the binding energies. It should be noted that the value (161.3 eV) is more or less equivalent to the binding energies measured of pyrrhotite (161.1 eV: Jones et al., 1992; 161.25 eV: Pratt et al., 1994; 161.4 eV: Thomas et al., 1998).
Table 8  Summary of structural data of mackinawite, pyrite and pyrrhotite

<table>
<thead>
<tr>
<th></th>
<th>pyrite</th>
<th>pyrrhotite</th>
<th>mackinawite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>chemistry:</strong></td>
<td>FeS₂</td>
<td>Fe₁₋ₓS</td>
<td>Fe₉S₈</td>
</tr>
<tr>
<td><strong>crystallography:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>crystal system</td>
<td>cubic</td>
<td>hexagonal</td>
<td>tetragonal</td>
</tr>
<tr>
<td>symmetry group</td>
<td>Pa₃</td>
<td>P63/mmc</td>
<td>P4/nmm</td>
</tr>
<tr>
<td>unit cell size: a, b [Å]</td>
<td>5.41</td>
<td>3.44</td>
<td>3.68</td>
</tr>
<tr>
<td>unit cell size: c [Å]</td>
<td>5.41</td>
<td>5.69</td>
<td>5.03</td>
</tr>
<tr>
<td>unit cell: angles if different to 90°</td>
<td>α 120°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of formula units per unit cell</td>
<td>4.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>volume of unit cell [Å³]</td>
<td>158.05</td>
<td>58.31</td>
<td>68.12</td>
</tr>
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<td><strong>structure description:</strong></td>
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<td></td>
</tr>
<tr>
<td>Fe-S co-ordination</td>
<td>6</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>bond distance</td>
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<td>2.88</td>
<td>2.88</td>
</tr>
<tr>
<td>iron-sulphur co-ordination</td>
<td>octahedrons</td>
<td>octahedrons</td>
<td>tetrahedrons</td>
</tr>
<tr>
<td>linked among themselves</td>
<td>corner shared</td>
<td>face shared</td>
<td>edge shared</td>
</tr>
<tr>
<td>comments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of atoms on (100) plane/unit cell:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iron</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>sulphur</td>
<td>4.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>number of atoms on (100) plane/nm²:</td>
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<td></td>
</tr>
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<td>iron</td>
<td>7</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>sulphur</td>
<td>14</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>iron and sulphur</td>
<td>21</td>
<td>20</td>
<td>22</td>
</tr>
</tbody>
</table>
Figure 28 S 2p / Si 2s XPS spectrum of the mackinawite sample after reaction with gold(I) hydrosulphide solution at 25°C and pH 4: Upper solid line shows result of best fit, the lower being the background curve. For details see figure caption of figure 25.

Table 9 Selected S 2p$_{3/2}$ binding energies (eV) for sulphur surface compounds

<table>
<thead>
<tr>
<th>surface compound</th>
<th>substrate</th>
<th>S 2p</th>
<th>charge correction</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S</td>
<td>Au</td>
<td>163</td>
<td>C 1s = 285</td>
<td>Leavitt and Bebbe, 1991</td>
</tr>
<tr>
<td>HS$^-$</td>
<td>Au</td>
<td>162.4</td>
<td>C 1s = 285</td>
<td>Leavitt and Bebbe, 1991</td>
</tr>
<tr>
<td>monosulphide</td>
<td>pyrite*</td>
<td>161.65</td>
<td>S 2p disulphide</td>
<td>Nesbitt and Muir, 1994</td>
</tr>
<tr>
<td>disulphide</td>
<td>mackinawite/greigite</td>
<td>162.2</td>
<td>C 1s = 285.0</td>
<td>Herbert et al., 1998</td>
</tr>
<tr>
<td>polysulphide</td>
<td>mackinawite*/greigite*</td>
<td>163.15</td>
<td>C 1s = 285.0</td>
<td>Herbert et al., 1998</td>
</tr>
<tr>
<td>polysulphide</td>
<td>various</td>
<td>163.01-163.6</td>
<td>S 2p disulphide</td>
<td>details see table 10</td>
</tr>
<tr>
<td>sulphur</td>
<td>pyrrhotite*</td>
<td>164.35</td>
<td>C 1s = 285.0</td>
<td>Pratt et al., 1994</td>
</tr>
<tr>
<td>S$_8$</td>
<td>S$_8$</td>
<td>164.2</td>
<td>C 1s = 285.0</td>
<td>Lindberg et al., 1970</td>
</tr>
<tr>
<td>sulphite</td>
<td>pyrrhotite*</td>
<td>164.35</td>
<td>C 1s = 285.0</td>
<td>Pratt et al., 1994</td>
</tr>
<tr>
<td>thio sulphate</td>
<td>pyrite*</td>
<td>166.45</td>
<td>S 2p disulphide</td>
<td>Nesbitt and Muir, 1994</td>
</tr>
<tr>
<td>sulphate</td>
<td>pyrite*</td>
<td>168.25</td>
<td>S 2p disulphide</td>
<td>Nesbitt and Muir, 1994</td>
</tr>
</tbody>
</table>

* Formed by surface oxidation
Section 3.4 Results

The second peak with an S 2p 3p electron binding energy of 162.90eV is higher than values determined for pyrite (162.3 to 162.5eV). Higher oxidised compounds such as thiosulphates or sulphates have binding energies that are several electron volts higher (table 9). Surface H₂S on gold metal has been measured with a binding energy of 163eV (Leavitt and Bebbe, 1994), but after drying in nitrogen atmosphere over silica blue gel as in these experiments, surface adsorbed H₂S is not expected. In addition, Jones et al. (1992) have proposed the formation of a surface Fe₃S₄ moiety with such a binding energy. They have studied the interaction of pyrrhotite with air, water and perchloric acid and found a compound at a binding energy of 162.9eV. This value, which cannot be attributed to either disulphide (S₂²⁻) (162.2 to 162.5eV) or to elemental sulphur (around 164.2 to 164.35eV), was interpreted as being due to an Fe₃S₄-like compound in an iron depleted layer at the mineral surface. Such layers have been described as the result of selective removal of iron(III) hydroxides formed by the surface oxidation of iron sulphides (e.g. Sasaki et al., 1995) in combination with the formation of oxidised sulphur compounds. However, the reported X-ray data for the supposed Fe₃S₄ phase are in poor agreement (Schrader and Pietzsch, 1969; Yamaguchi and Wada, 1973a,b; Stiller et al., 1978; Sugiura, 1981; Sasaki et al., 1995). There is no reliable consensus as to its properties or whether such a phase has actually been synthesised.

Various studies (table 10) have proposed S 2p 3p binding energies for a variety of polysulphide compounds using the same apparatus with monochromatic Al radiation. These energies range from 163.0 to 163.6eV binding energy, with extremes from 162 to 165.9eV (table 10) and the full widths at half maximum varying from 0.95 to 2.2eV. The variation is greater than could be attributed to the variation of instrumental parameters and charging only.

In considering the presence of polysulphide moieties on iron sulphide surfaces, the following points need to be taken into account:

- Polysulphides can show more than one single characteristic binding energy (Themes et al., 1987; Buckley et al., 1988).
- The variations in the binding energies permits the identification of at least "polysulphides" and "disulphides", if not even "monosulphides" when comparing to literature data (table 9).
- The longer the chain, the smaller the individual charges and the smaller the differences in distance of the central atom to its neighbour and hence an increasing similarity to the measured binding energies of S₄ rings or elemental sulphur.
- Instrumental resolution, even when using monochromatic radiation, might fail in resolving the individual peaks, at least in low concentrations.
- Fitting should include the area ratios based on the number of occurrences of an equivalent site within the chain.
Table 10: $S\,2p_{3/2}$ binding energies (eV) with full width at half maximum (FWHM) of the peaks. The measured binding energies have been interpreted as polysulphide surface groups.

<table>
<thead>
<tr>
<th>Author</th>
<th>Substrate</th>
<th>$S,2p_{3/2}$</th>
<th>FWHM</th>
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<tr>
<td>Hyland (1989)*</td>
<td>pyrite</td>
<td>163.2</td>
<td>1</td>
</tr>
<tr>
<td>Mycroft (1990)*</td>
<td>pyrite</td>
<td>163.3,163.7</td>
<td></td>
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<tr>
<td>De Donato et al. (1993)***</td>
<td>pyrite ($S_n$)</td>
<td>165.3 - 165.9</td>
<td>1.6 - 1.8</td>
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<tr>
<td>Nesbitt and Muir (1994)*</td>
<td>pyrite</td>
<td>163.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Scaini (1995)*</td>
<td>pyrite</td>
<td>163.5</td>
<td></td>
</tr>
<tr>
<td>Chaturvedi et al. (1996)**</td>
<td>pyrite</td>
<td>164.1</td>
<td></td>
</tr>
<tr>
<td>Rinker et al. (1997)*</td>
<td>marcasite</td>
<td>163.5 - 163.62</td>
<td>2.0</td>
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<tr>
<td>Nesbitt et al. (1995)*</td>
<td>arsenopyrite</td>
<td>163.25</td>
<td>1.6</td>
</tr>
<tr>
<td>Pratt et al. (1994)*</td>
<td>pyrrhotite</td>
<td>163.01</td>
<td>0.95 - 1.2</td>
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<td>Pratt et al. (1994)*</td>
<td>pyrrhotite</td>
<td>163.25</td>
<td>0.95 - 1.2</td>
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<tr>
<td>Thomas et al. (1998)**</td>
<td>pyrrhotite</td>
<td>163.4</td>
<td>2.2</td>
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<tr>
<td>Herbert et al. (1998)*</td>
<td>mackinawite/greigite</td>
<td>163.15</td>
<td>1.3</td>
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<tr>
<td>Legrand et al. (1998)*</td>
<td>millerite</td>
<td>162 - 164</td>
<td>1.6</td>
</tr>
</tbody>
</table>

* All these samples have been measured with the same equipment, using monochromatic Al X-ray radiation at the University of Western Ontario.

** Non monochromatic Mg Kα

*** Non monochromatic Al Kα

Therefore, special care has to be taken in the fitting and interpretation of XPS spectra of sulphide surfaces containing compounds with binding energies of 163 to 164 eV.

Recent studies on pyrite using synchrotron XPS with a source energy of 200 eV (Bronold et al., 1994b; Schaufuss et al., 1998; Nesbitt et al., 1998) have observed variable binding energies due to surface groups and these have been interpreted as the result of restructured surfaces and fractured bonds. This must also be taken in account when interpreting such spectra, especially when using methods with enhanced surface sensitivity (low angle, kinetic energy of ejected electrons of around 40 eV).
Preference is given to a polysulphide with one higher binding energy as displayed in figure 28. An attempt to fit the measured mackinawite S 2p spectrum with sets of predefined intensity ratios and a triplet with intensity of 1:2:2 corresponding to an $H_2S_3$ moiety led only to a minor improvement which was not statistically meaningful. Thus, a polysulphide species of short chain length with two to four sulphurs where the low energy peak would be indistinguishable from the monosulphide peak was preferred. The short chain length is proposed because the high energy peak binding energy is still low in comparison to the other described polysulphides.

Although the concentration of the gold at the mineral surface is low, a good spatial energy resolution was achieved. The measured binding energy of 84.1eV confirms the formation of metallic gold (83.9 - 84.0eV, figure 29) on the mackinawite surface. Other compounds such as gold (III) chloride, sulphide, oxide and hydroxide show distinctly higher binding energies (table 11). The value of 84.1eV has an inherent analytical uncertainty of 0.2eV arising from the spectrometer calibration, but confirms the formation of metallic gold or gold clusters of larger size (Di Cenzo et al., 1988).

Figure 29 XPS spectrum of the mackinawite sample after reaction with gold(I) hydrosulphide solution at 25°C at pH 4:
(a): Au 4f spectrum, which shows the separated Au 4f$^{7/2}$ (around 84 eV) and Au 4f$^{5/2}$ (around 87eV) orbitals.
(b): Detailed Au 4f$^{7/2}$ spectrum with one symmetric peak fit. The upper solid line shows the upper total fit with added background, the lower is the background fitted with the Shirley function.
3.3.3 Summary of observations from the XPS measurements

On the mackinawite and pyrite surfaces which were studied after gold adsorption, there was no evidence of formation of iron (III) oxide / hydroxide or sulphate which might have resulted from atmospheric oxygen contamination. The pyrite shows electron binding energies for iron and sulphur which are typical of a freshly fractured, unoxidised surface. However, the XPS data for the mackinawite surface indicate a contribution from zerovalent sulphur, very probably in the form of a short chain polysulphide having two to four sulphurs. Such polysulphide surface moieties may provide the initial precursor mechanism for the transform of reactive, metastable mackinawite to pyrite. Others (Berner et al., 1964, 1967; Schoonen and Barnes, 1991a,b; Rickard and Luther, 1997) have discussed the precursor role of mackinawite in the formation of pyrite.

The adsorption of hydrosulphidogold(I) complexes onto pyrite and mackinawite occurs quite differently for the two different surfaces. On pyrite, the measured Au 4f₇/₂ binding energy, 84.8eV, is slightly lower than the range reported by Van de Vondel (1977) (85.0 to 85.2eV) but within the range determined by Scaini et al. (1998) (84.7 – 85.1eV). The presence of Au⁺ on the surface indicates that a surface complex has formed. Renders and Seward (1989b) also studied the adsorption of hydrosulphide complexes of Au⁺ onto amorphous arsenic and antimony sulphide surfaces and confirmed presence of linear, triatomic surface complexes using ¹⁹⁷Au Mössbauer spectroscopy (Cardile et al., 1993). These complexes form by adsorption of the neutral AuHS⁻ complex onto the negatively charged pyrite surface to give (=Sₚ𝐲𝐫𝐢𝐭𝐞ṣuiface – [Au-SH]adsorbed). Ab initio calculations by Tossell (1996) have further confirmed the formation of such species on sulphide surfaces. We note also that Scaini et al. (1998) reported the presence of Au⁺ together with Au⁺ on pyrite surfaces similar to those studied in our experiments, however, we mention again that our experiments were conducted for ≤ 3 hours with exclusion of both atmospheric oxygen and light. The presence of Au⁺ on the pyrite surfaces studied by Scaini et al. (1998) suggests the photoreduction of Au⁺ to Au⁺ due to light contamination. Their adsorption experiments were conducted for times of up to one week and despite the precautions taken to exclude light, their results strongly suggest the partial reduction of surface complexed gold(I) to elemental gold.

However, on the mackinawite surface, the XPS spectra indicate that all the gold is present as Au⁺. The mackinawite surface is delicately poised in a redox sense and immediately undergoes oxidation by a strong oxidising agent such as Au⁺. Hence, no gold(I) hydrosulphide surface complexes are preserved.
Chapter 4  Summary and Discussion

In this study, we have shown that the pH of point of zero charge ($\text{pH}_{\text{pzc}}$) in solutions of variable ionic strength for pyrite, mackinawite and pyrrhotite is at pH < 3. This is in agreement with studies of by Bebié et al. (1998) and Fornasiero et al. (1992) who studied pyrite and pyrrhotite surfaces using electrophoresis. Additionally, it could be shown that the pH of point of zero charge is further reduced to values of pH < 2 and not measurable using potentiometric titration, if the solution is $\text{H}_2\text{S}$ saturated. This is consistent with the observation of Bebié et al. (1998) and further emphasises that $\text{H}_2\text{S}$ and $\text{HS}^-$ are potential determining species when considering sulphide mineral surfaces. Therefore, we have demonstrated that for our experiments over the whole pH interval from 2 to 10, the mineral surface is negatively charged. The adsorption experiments at 25°C (figure 20) using gold(I) hydrosulphide complexes and fresh, uncontaminated (by oxidation) mineral surfaces show that mackinawite and pyrrhotite have maximum adsorption at pH ≤ 3 and that their adsorption capacity rapidly decreases at higher pH's. However, the adsorption range for pyrite of both natural and synthetic origin extends to higher pH. Greater than 90% of total gold is adsorbed pH ≤ 5. With increasing pH above 5 the adsorption of gold decreases to 30% at pH = 10. On pyrite, both the adsorbed solution species as well as the mineral surface itself show no change is the redox state. The gold 4f$_{7/2}$ electron binding energy was determined to be 84.8 eV, which is consistent with previously reported values of Au(I) of Scaini et al. (1998), Maddox et al. (1998) and Mycroft et al. (1995b) who studied the reaction of gold(I) hydrosulphide and chloride complexes as well as gold(III) chloride with pyrite. Their studies also report the presence of Au$^+$ on pyrite as a result of reaction (adsorption) with gold (I) and gold (III) chloride and hydrosulphide species which suggests possible light contamination and hence photoreduction of Au$^+$ to Au$^0$.

In our experiments, only Au$^+$ was observed on the pyrite surfaces. The Au$^+$ is considered to be present as a surface complex, FeSS$_{\text{pyrite}}$–Au–SH, formed by the adsorption of the uncharged AuHS$^-$. Such a conclusion would be compatible with the findings of Renders and Seward (1989b) and Cardile et al. (1993) who demonstrated using $^{197}$Au Mössbauer spectroscopy that the adsorption of AuHS$^-$ onto amorphous arsenic and antimony sulphide gave rise to the formation of a linear, triatomic surface complex. The pH region of highest adsorption of gold from aqueous sulphide solution onto both pyrite and mackinawite is also the low pH region (i.e. pH ≤ 3) in which the AuHS$^-$ is most stable and predominates (Renders and Seward, 1989b). The Au(HS)$_2^-$ complex becomes more stable in the near neutral and alkaline pH region but is not considered to play a significant role in the adsorption of gold onto sulphide surfaces at pH > pH$_{\text{pzc}}$ because of columbic repulsion. The XPS data indicate that the adsorption of AuHS$^-$
onto mackinawite results in the formation of Au⁺ with no evidence of any remaining Au°. Au⁺ is an oxidising agent that is easily reduced on the reactive mackinawite surface with the associated oxidation of sulphide sulphur to zerovalent sulphur.

The geochemical implications arising from these experiments is that pyrite may act as a scavenger by removing gold from aqueous solution by surface adsorption mechanisms. If gold is transported in a hydrothermal ore fluid as hydrosulphidogold(I) complexes, then any process which decreases the activity of reduced sulphur such as boiling or changes in the redox potential of the fluid (i.e. oxidation) which accompanying changes in pH as well as sulphide mineral deposition may cause the deposition of gold. We have demonstrated that surface adsorption of gold(I) complexes by pyrite is also an important mechanism which has hitherto received little attention. In fact, the coupled process of pyrite precipitation which removes reduced sulphur from solution causing gold deposition, combined with adsorption onto freshly forming pyrite surfaces, comprises an extremely effective gold concentrating mechanism.

Surface adsorption effects will be important in hydrothermal systems but there is currently no information on the variation of surface charge (i.e. pHₚₑₑₑ) of sulphide minerals in aqueous solutions at elevated temperatures and pressures. In addition, no experimentally based surface adsorption studies have been carried out under hydrothermal conditions. The adsorption of AuHS⁻ by pyrite will extend to higher temperatures because this complex becomes more stable in near neutral to alkaline conditions as pKₐ for H₂S (Suleimenov and Seward, 1997) increases to higher values.

There is evidence for the possible role of surface adsorption effects in determining the enrichment of gold in some gold-containing, natural, hydrothermal pyrite and arsenopyrite. Recent studies of natural, hydrothermal pyrite samples by Marion et al. (1991), Arehart et al. (1993), Cataineau et al. (1989) and Genkin et al. (1998) on arsenopyrite, have shown the existence of both submicroscopic, chemically bound, Au⁺ and elemental gold (i.e. Au°) using Mössbauer spectroscopy. Sha (1993) interpreted his XPS and SIMS on gold-containing arsenian pyrite in terms of AuHS⁻ adsorption. In addition, Simon et al. (1999) have studied pyrite from the Twin Creeks Carlin-type gold deposit and estimated that as much as about 50% of the total gold at the deposit may have been removed from solutions unsaturated with respect to gold by adsorption processes. In their XANES and EXAFS study, they were able to discriminate between elemental and chemically bound Au⁺ and to assign these to different mineralisation stages. It has been assumed that adsorbed Au(I) (e.g. Starling et al., 1989, Knipe et al., 1991, 1992) would react with time to form elemental gold (i.e. Au°), however in this deposit and others, the gold(I) oxidation state has been preserved and in fact, the gold(I)-
containing pyrite is older than the pyrite with native gold. In an early stage of the formation of the above mentioned deposit, subhedral to euhecdral grains with arsenic concentrations of 0.33 to 0.85wt% and a gold content up to 60mg/kg were formed at a temperature of about 250°C (fluid inclusions). These samples showed an Au⁰/Au¹ ratio determined by XANES up to 0.052, which means that Au⁺ or chemically bound gold dominates by far over Au⁰. In these samples, no individual gold grains have been observed in TEM studies and the SIMS maps showed a homogeneous distribution. As the morphology of the pyrite suggests that crystallisation was slow and therefore, a sufficiently equilibrated surface of pyrite with the solution can be assumed. Other pyrite grains from a different, later depositional stage have gold concentrations in the range of 595-1465mg/kg. The XANES analysis gave an Au⁰/Au¹ ratio of 1.17 to 1.78 indicating that about 60% of the gold exists in the zerovalent state, the residual 40% is Au(I). Such grains apparently precipitated rapidly at 120-200°C.

The formation of pyrite in this lower temperature regime may also have some implications for gold scavenging from solutions. If the initial precursors in pyrite nucleation was an iron monosulphide phase as has been suggested by Schoonen and Barnes (1991c), then gold(I) complexes would be adsorbed and then reduced to Au⁰ as we have shown for mackinawite with the formation of surface polysulphide. This surface polysulphide could then act as a pyrite nucleation site. Further growth of pyrite would occur on the original seed material and gold could then be adsorbed as AuHS⁻ to form an Au(I) surface complex.

The entire field of surface chemistry, complex adsorption and reaction by sulphide surfaces is poorly known at ambient temperature and essentially unknown under hydrothermal conditions. Further chemical insight into these important processes will come primarily from experimental studies. There is a desperate need for such data in order to better understand elemental scavenging in sulphide-containing systems over a wide range of ore forming conditions.


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2131.

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APPENDIX: LABORATORY PROCEDURES

In the following paragraphs and tables generally used laboratory procedures and the origin and grade of the chemicals are described.

Glassware
For all experiments, closed glass vessels with inlets for inert gas were used, as shown in figure A1a,b. For solutions containing Au(I) hydrosulphide complexes, the glassware was painted black with acrylic paint and covered with aluminium foil to avoid any photo-reduction of gold(I) to metallic gold.

Nitrogen gas
All the experiments were performed, if not otherwise stated, under a nitrogen atmosphere. As a starting gas, commercially available nitrogen (99.995%) was used. To remove residual oxygen the gas is led through a quartz glass tube filled with metallic copper turnings in a furnace at 420°C. Residual oxygen reacts with the copper and forms an copper oxide resulting in changing the turnings color to violet and finally to black. Before all the copper becomes oxidised, it was replaced. Copper turnings from the Fluka company were used. These filings were initially coated with cutting oil, which was removed by washing several times in 1,1,1-trichloroethane.

Deoxygenation and purification of water
In all synthesis and adsorption experiments, the water used was purified by ion exchange. To remove dissolved free oxygen, the water was boiled under deoxygenated nitrogen in special flasks (figure A.1) for 15 minutes and then cooled with flowing deoxygenated nitrogen. For the ICP-MS sample preparation, doubly distilled (in quartz glass) deionised water was used for dilution.

Grease
Glass ware and stopcocks were greased with apiezone L or silicone (Dow Chemicals) grease. The same grease was also used mixed with the iron sulfide slurry for the XRD measurements, reducing the oxidation of the sample, while working in air.
Powder diffraction X-ray studies
This technique was used to identify the mineralogical composition of the synthesis products. All the phases are sensitive to oxidation and hydrolysis (of Fe$^{3+}$) in contact with air. To minimise oxidation, the more stable, well crystalline phases (pyrrhotite or pyrite) were mixed after filtration with grease (Apiezone L or Dow Silicon grease). The extremely sensitive phases like mackinawite and amorphous FeS were held in an inert gas chamber, filled with oxygen free nitrogen or helium, for the time of the X-ray diffraction measurement. As XRD equipment a Scintag DMS 2000 with a Cu K$_{α}$ tube and a Peltier detector with a goniometer of theta-theta geometry was used, such that the sample is always in horizontal orientation.

Chemicals
The used chemicals are listed with their analar grade, usage and supplier in table A1.
### Table A-1  Chemicals used in the experiments

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CURRICULUM VITAE

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