Spectroelectrochemical investigation of chalcopyrite leaching

by
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Abstract

This thesis describes an experimental investigation, utilising primarily spectroelectrochemical techniques, into the mechanism of chalcopyrite leaching and the properties of the metal-deficient product layer. A systematic comparison of the leaching behaviour and products in chloride and sulfate lixiviant was undertaken, and variation of leach conditions was also considered. The product layer distribution, structure and morphology was examined, and various model systems and compounds investigated to aid in identifying the product layer composition and properties. A range of chalcopyrites, and other pertinent sulfide-minerals, were investigated.

The behaviour of chalcopyrite in both chloride and sulfate electrolytes was investigated in situ and ex situ. Electrochemical experiments demonstrated similar initial behaviour in both chloride and sulfate systems. Potentiostatic techniques combined with normal Raman interrogation of the mineral surface showed much thicker product layers formed on the chalcopyrite leached in chloride electrolytes, over the entire surface. The product layer formed on chalcopyrite leached in chloride solutions consisted of octasulfur and/or a Raman-inactive product phase that could be activated under 442 nm laser irradiation to form polymeric sulfur. The parent phase could not be positively identified but is probably an amorphous metal-deficient remnant lattice on the oxidised mineral surface, which can be restructured under specific conditions to polymeric sulfur. Model compound investigations demonstrated that the induced phase converted to elemental sulfur at ~70°C. Polymeric sulfur was present on leached surfaces even in the absence of laser-inducement but was generally overwhelmed by the octasulfur signal (but identified on samples kept under ultrahigh vacuum conditions). Similar product was rarely observed over the sulfate-leached chalcopyrite surface, as the product layer was too thin to be detectable. However, at “active” sites (cracks, fissures and grain boundaries) product with a lower v(SS) Raman shift was encountered, indicating longer sulfur bonds and probably less metal-deficiency. Polysulfides, polysulfanes, jarosite and sulfoxy anions were not detected on acid-leached samples.

Model sulfide compounds, and proposed intermediates in chalcopyrite oxidation, were investigated using spectroelectrochemical and neutron reflectometry techniques. The same laser-induced polymeric sulfur phase was identified on high-Fe sphalerite and
pyrite surfaces during acid-chloride leaching, though not on covellite surfaces. Sulfoxy anion intermediates were observed on pyrite oxidation in acid solution, confirming a different mechanism to that observed for chalcopyrite oxidation. CuS showed distinctly different spectroelectrochemical behaviour to chalcopyrite and thus is not an intermediate in chalcopyrite oxidation.

More aggressive leaching of chalcopyrite was investigated at circumneutral pH. Raman, Environmental Scanning Electron Microscopy (ESEM) and X-ray Photoelectron Spectroscopy (XPS) indicated the presence of highly soluble sulfate salts on the sample surface, though the majority of the product consisted of ferric oxyhydroxides and elemental sulfur. Optical and electron microscopy revealed that the product layer thickness and properties varied as a function of grain orientation. Dynamic Secondary Ion – Mass Spectroscopy (SIMS) and XPS were used to yield elemental composition and valence-state information of oxidation products, and how these varied with depth. Oxidation appeared to be incongruent in the early stages of oxidation, with iron more deficient on the surface than copper. The metal-deficiency extended to some depth (up to hundreds of nanometres) on both chloride and sulfate leached samples. Copper maintained a formal univalent oxidation state on the corroding chalcopyrite surface, while iron was present as ferric ion and sulfur present in oxidation states intermediate between sulfide and elemental sulfur.

Submonolayer in situ investigations of chalcopyrite oxidation in acid chloride and sulfate solutions were undertaken via development of a technique to facilitate surface-enhanced Raman scattering (SERS) from the chalcopyrite surface. Both ex situ and in situ investigations were undertaken and showed an amorphous product containing sulfur bonds but distinct from polysulfides, polythionates or elemental sulfur allotropes. The product spectrum was similar in sulfate and chloride solutions, in good agreement with electrochemical observations. Normal Raman and SERS investigations indicate that chalcopyrite oxidation proceeds via a mechanism of cation removal and concomitant oxidation of the remnant sulfide lattice. Sulfur bonding does not appear to commence immediately, and when it does occur, an amorphous structure is formed. This amorphous leached layer is stable for relatively long periods of time at room temperature and extends to some depth. In the case of the chloride, the leached layer ages to sulfur, though of a somewhat amorphous nature that does not volatilise extensively under vacuum. The greater
aging of the leached layer on chloride-leached samples is probably facilitated by the ability of copper to leave the lattice as a cuprous complex.
Declaration

The work contained in this thesis has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

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Gretel Kristen Parker
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This thesis is dedicated to the memory of Ronald Edward Heber.
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<tr>
<td>A</td>
<td>Ampere/s</td>
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<tr>
<td>Å</td>
<td>Angstrom/s</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope/microscopy</td>
</tr>
<tr>
<td>at.%</td>
<td>atomic percent</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>BSE</td>
<td>backscattered electron</td>
</tr>
<tr>
<td>C</td>
<td>Coulomb/s</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
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<td>ccp</td>
<td>cubic close-packed</td>
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<td>CPE</td>
<td>carbon paste electrode</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammogram</td>
</tr>
<tr>
<td>δ</td>
<td>bending vibration (vibrational spectroscopy)</td>
</tr>
<tr>
<td>DDI</td>
<td>doubly-deionised</td>
</tr>
<tr>
<td>E</td>
<td>potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;a&lt;/sub&gt;</td>
<td>activation energy</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray</td>
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<tr>
<td>EME</td>
<td>electromagnetic effect</td>
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<tr>
<td>ESEM</td>
<td>environmental scanning electron microscope/microscopy/micrograph</td>
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<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier-transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>full-width half-maximum</td>
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<tr>
<td>hcp</td>
<td>hexagonal close-packed</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<tr>
<td>HPLC-MS</td>
<td>high performance liquid chromatography - mass spectrometry</td>
</tr>
<tr>
<td>I</td>
<td>current</td>
</tr>
<tr>
<td>ICPMS/AES</td>
<td>inductively coupled plasma - mass spectrometry/atomic emission spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>kV</td>
<td>kilovolt</td>
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<td>LEED</td>
<td>low-energy electron diffraction</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>$S_{\Psi}$</td>
<td>plastic sulfur</td>
</tr>
<tr>
<td>ToF</td>
<td>time-of-flight</td>
</tr>
<tr>
<td>UHV</td>
<td>ultrahigh vacuum</td>
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<tr>
<td>ULWD</td>
<td>ultralong working distance</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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<tr>
<td>V</td>
<td>volts/voltage</td>
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<tr>
<td>Vis</td>
<td>visible</td>
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<tr>
<td>VP</td>
<td>vapour pressure</td>
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<td>vs</td>
<td>versus</td>
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<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
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<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
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<tr>
<td>XES</td>
<td>X-ray emission spectroscopy</td>
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<tr>
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<td>X-ray photoelectron spectroscopy</td>
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Spectroelectrochemical investigation of chalcopyrite leaching

by

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Abstract

This thesis describes an experimental investigation, utilising primarily spectroelectrochemical techniques, into the mechanism of chalcopyrite leaching and the properties of the metal-deficient product layer. A systematic comparison of the leaching behaviour and products in chloride and sulfate lixiviants was undertaken, and variation of leach conditions was also considered. The product layer distribution, structure and morphology was examined, and various model systems and compounds investigated to aid in identifying the product layer composition and properties. A range of chalcopyrites, and other pertinent sulfide-minerals, were investigated.

The behaviour of chalcopyrite in both chloride and sulfate electrolytes was investigated in situ and ex situ. Electrochemical experiments demonstrated similar initial behaviour in both chloride and sulfate systems. Potentiostatic techniques combined with normal Raman interrogation of the mineral surfaces showed much thicker product layers formed on the chalcopyrite leached in chloride electrolytes, over the entire surface. The product layer formed on chalcopyrite leached in chloride solutions consisted of octasulfur and/or a Raman-inactive product phase that could be activated under 442 nm laser irradiation to form polymeric sulfur. The parent phase could not be positively identified but is probably an amorphous metal-deficient remnant lattice on the oxidised mineral surface, which can be restructured under specific conditions to polymeric sulfur. Model compound investigations demonstrated that the induced phase converted to elemental sulfur at ~70°C. Polymeric sulfur was present on leached surfaces even in the absence of laser-inducement but was generally overwhelmed by the octasulfur signal (but identified on samples kept under ultrahigh vacuum conditions). Similar product was rarely observed over the sulfate-leached chalcopyrite surface, as the product layer was too thin to be detectable. However, at “active” sites (cracks, fissures and grain boundaries) product with a lower v(SS) Raman shift was encountered, indicating longer sulfur bonds and probably less metal-deficiency. Polysulfides, polysulfanes, jarosite and sulfoxy anions were not detected on acid-leached samples.

Model sulfide compounds, and proposed intermediates in chalcopyrite oxidation, were investigated using spectroelectrochemical and neutron reflectometry techniques. The same laser-induced polymeric sulfur phase was identified on high-Fe sphalerite and
pyrite surfaces during acid-chloride leaching, though not on covellite surfaces. Sulfoxy anion intermediates were observed on pyrite oxidation in acid solution, confirming a different mechanism to that observed for chalcopyrite oxidation. CuS showed distinctly different spectroelectrochemical behaviour to chalcopyrite and thus is not an intermediate in chalcopyrite oxidation.

More aggressive leaching of chalcopyrite was investigated at circumneutral pH. Raman, Environmental Scanning Electron Microscopy (ESEM) and X-ray Photoelectron Spectroscopy (XPS) indicated the presence of highly soluble sulfate salts on the sample surface, though the majority of the product consisted of ferric oxyhydroxides and elemental sulfur. Optical and electron microscopy revealed that the product layer thickness and properties varied as a function of grain orientation. Dynamic Secondary Ion – Mass Spectroscopy (SIMS) and XPS were used to yield elemental composition and valence-state information of oxidation products, and how these varied with depth. Oxidation appeared to be incongruent in the early stages of oxidation, with iron more deficient on the surface than copper. The metal-deficiency extended to some depth (up to hundreds of nanometres) on both chloride and sulfate leached samples. Copper maintained a formal univalent oxidation state on the corroding chalcopyrite surface, while iron was present as ferric ion and sulfur present in oxidation states intermediate between sulfide and elemental sulfur.

Submonolayer *in situ* investigations of chalcopyrite oxidation in acid chloride and sulfate solutions were undertaken via development of a technique to facilitate surface-enhanced Raman scattering (SERS) from the chalcopyrite surface. Both *ex situ* and *in situ* investigations were undertaken and showed an amorphous product containing sulfur bonds but distinct from polysulfides, polythionates or elemental sulfur allotropes. The product spectrum was similar in sulfate and chloride solutions, in good agreement with electrochemical observations.

Normal Raman and SERS investigations indicate that chalcopyrite oxidation proceeds via a mechanism of cation removal and concomitant oxidation of the remnant sulfide lattice. Sulfur bonding does not appear to commence immediately, and when it does occur, an amorphous structure is formed. This amorphous leached layer is stable for relatively long periods of time at room temperature and extends to some depth. In the case of the chloride, the leached layer ages to sulfur, though of a somewhat amorphous nature that does not volatilise extensively under vacuum. The greater
aging of the leached layer on chloride-leached samples is probably facilitated by the ability of copper to leave the lattice as a cuprous complex.
Declaration

The work contained in this thesis has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

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Gretel Kristen Parker
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This thesis is dedicated to the memory of Ronald Edward Heber.
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<tr>
<td>A</td>
<td>Ampere/s</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom/s</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope/microscopy</td>
</tr>
<tr>
<td>at.%</td>
<td>atomic percent</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>BSE</td>
<td>backscattered electron</td>
</tr>
<tr>
<td>C</td>
<td>Coulomb/s</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>ccp</td>
<td>cubic close-packed</td>
</tr>
<tr>
<td>CPE</td>
<td>carbon paste electrode</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammogram</td>
</tr>
<tr>
<td>δ</td>
<td>bending vibration (vibrational spectroscopy)</td>
</tr>
<tr>
<td>DDI</td>
<td>doubly-deionised</td>
</tr>
<tr>
<td>E</td>
<td>potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;a&lt;/sub&gt;</td>
<td>activation energy</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray</td>
</tr>
<tr>
<td>EME</td>
<td>electromagnetic effect</td>
</tr>
<tr>
<td>ESEM</td>
<td>environmental scanning electron microscope/microscopy/micrograph</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier-transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>full-width half-maximum</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close-packed</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPLC-MS</td>
<td>high performance liquid chromatography - mass spectrometry</td>
</tr>
<tr>
<td>I</td>
<td>current</td>
</tr>
<tr>
<td>ICPMS/AES</td>
<td>inductively coupled plasma - mass spectrometry/atomic emission spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>kV</td>
<td>kilovolt</td>
</tr>
<tr>
<td>LEED</td>
<td>low-energy electron diffraction</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>LFD</td>
<td>large field detector</td>
</tr>
<tr>
<td>liq.</td>
<td>liquid</td>
</tr>
<tr>
<td>M</td>
<td>molar (moles L(^{-1}))</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>µm</td>
<td>micron (10(^{-6}) m)</td>
</tr>
<tr>
<td>ν</td>
<td>stretching vibration</td>
</tr>
<tr>
<td>N</td>
<td>normal (moles L(^{-1}))</td>
</tr>
<tr>
<td>NA</td>
<td>numerical aperture</td>
</tr>
<tr>
<td>NBS</td>
<td>non-Rutherford backscattering</td>
</tr>
<tr>
<td>nm</td>
<td>nanometre (10(^{-9}) m)</td>
</tr>
<tr>
<td>OCP</td>
<td>open-circuit potential</td>
</tr>
<tr>
<td>ORC</td>
<td>oxidation-reduction cycle</td>
</tr>
<tr>
<td>photodecomp.</td>
<td>photodecomposition</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>RRDE</td>
<td>rotating ring-disc electrode</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SE</td>
<td>secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope/microscopy/micrograph</td>
</tr>
<tr>
<td>SERS</td>
<td>surface-enhanced Raman scattering</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion - mass spectrometry</td>
</tr>
<tr>
<td>SLD</td>
<td>scattering length density</td>
</tr>
<tr>
<td>S(_{\mu})</td>
<td>polymeric sulfur</td>
</tr>
<tr>
<td>S(_{n})</td>
<td>sulfur rings</td>
</tr>
<tr>
<td>S(_{n}^{2-})</td>
<td>polysulfide</td>
</tr>
<tr>
<td>sol.</td>
<td>solid</td>
</tr>
<tr>
<td>SR</td>
<td>synchrotron radiation</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunnelling microscope/microscopy</td>
</tr>
<tr>
<td>S(_{\omega 1})</td>
<td>2(^{nd}) fibrous sulfur</td>
</tr>
<tr>
<td>S(_{\omega 2})</td>
<td>laminar sulfur</td>
</tr>
<tr>
<td>S(_{x})</td>
<td>mixture of sulfur rings</td>
</tr>
<tr>
<td>SX/EW</td>
<td>solvent extraction/electrowinning</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>$S_p$</td>
<td>plastic sulfur</td>
</tr>
<tr>
<td>ToF</td>
<td>time-of-flight</td>
</tr>
<tr>
<td>UHV</td>
<td>ultrahigh vacuum</td>
</tr>
<tr>
<td>ULWD</td>
<td>ultralong working distance</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>volts/voltage</td>
</tr>
<tr>
<td>Vis</td>
<td>visible</td>
</tr>
<tr>
<td>VP</td>
<td>vapour pressure</td>
</tr>
<tr>
<td>vs</td>
<td>versus</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XES</td>
<td>X-ray emission spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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1. Introduction
1.1. Preamble

Hydrometallurgical processing offers the possibility of clean and contained mineral extraction, yielding both economic and environmental advantages. The potential for impurity management is good and hydrometallurgical routes tend not to be scale-sensitive (they are economically feasible at small to large sites).

There is a continuing interest in the development of processing routes to avoid smelting. Conventional pyrometallurgical routes have the disadvantages that they are only economic when carried out on a large scale and require the efficient capture of sulfur dioxide gas to avoid environmental impact on the atmosphere. The economic viability of smelting processes is also diminished by the presence of certain impurity elements since custom smelters charge a significant penalty when such elements are present. For these reasons, the world’s minerals industries have seen a need for hydrometallurgical routes that can accommodate these impurities, and be carried out at the mine site on a range of scales. Accordingly, there has been considerable research undertaken into the chemistry of sulfide mineral leaching as better understanding of the factors that control the dissolution processes is sought.

Acid leaching of copper has long been established for oxide ores but is less feasible for the processing of sulfidic ores: few successful full-scale copper sulfide leaching operations exist, and those that do generally involve chalcocite and catalysis by bacteria, which is poorly understood. In particular, ambient leaching of chalcopyrite, the most prolific copper sulfide, is desirable. Sulfate-based leaching processes for chalcopyrite are attractive because of their inherent simplicity (impurity management and control in sulfate media is well understood) and copper winning from sulfate solutions is well established.

Unfortunately, reasonable copper yields from chalcopyrite using sulfate media are not attainable in a practical residence time unless the leaching temperature exceeds 200°C (oxygen pressure leaching) or chalcopyrite is 'activated' by a pretreatment method prior to leaching [1]. The poor yields are acknowledged to be due to the formation of a metal-deficient passivating layer on the surface, but the composition of such a layer, and the mechanisms by which it forms are, as yet, poorly understood. The leaching time required for oxide ores treated via thin layer techniques is usually 6 days, but 5 – 12 months is necessary for mixed oxide sulfide ores [2]. The slow kinetics and low copper yields from
chalcopyrite makes existing hydrometallurgical processes uneconomic for most sulfide ores.

“Commercial” hydrometallurgical processes have so far been feasible for copper recovery at only a handful of sites where fortuitous mineral assemblages are available. Others processes at demonstration, pilot and lab scale have provided no fundamental in situ surface chemistry insights, and thus extensive ore-based testing is required on a site-by-site basis to demonstrate feasibility.

The leaching kinetics and mechanisms of chalcopyrite have been studied extensively over the last several decades, though much controversy remains as to the mechanism of leaching, the extent of passivation in non-chloride lixivants, the properties of the passivating layer, and the effects of additives and different leaching conditions on this surface layer.

1.2. Aims and objectives of this investigation

It will become clear in the ensuing literature review that there remains much controversy around the oxidation and dissolution of chalcopyrite. For instance, anodic dissolution studies of chalcopyrite in the transpassive zone in sulfuric acid solutions have variously proposed the formation of elemental sulfur [3, 4]; the formation of covellite plus elemental sulfur [5-7]; metal-deficient polysulfides [8] \( \text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2, x<<y, x+y≈1 \) [1, 9]; \( \text{Cu}_{0.8}\text{S}_2 \) [6, 10]; and jarosite [11, 12]. Elemental sulfur is not now generally considered to be “passivating” yet the addition of reagents to remove sulfur have been reported to have some effect on chalcopyrite leach kinetics [13]. Other studies have also claimed no effect [8, 14].

The thickness of the oxidative product layer also remains controversial, with early electrochemical studies reporting product layers in the order of 3 nm [6, 15] to more recent experimental reports of non-stoichiometric layers up to hundreds of nanometres thick [16].

Linear kinetics for chalcopyrite leaching in chloride are generally observed, compared to parabolic kinetics in sulfate. This has variously been attributed to different product morphology [17, 18] versus electron-transfer kinetics [8, 19].

The aim of the research project described in this thesis was to determine the mechanisms of chalcopyrite oxidation and the properties of the metal-deficient product layer.
Techniques were developed to investigate sub-monolayers at the mineral surface and identify the reactions such layers undergo in situ.

Specifically, the objectives were as follows:

- To identify the passivating layer composition, distribution, properties and morphology when chalcopyrite is oxidatively leached, using a variety of in situ and ex situ techniques.

- To undertake detailed systematic spectroelectrochemical studies of chalcopyrite oxidation in sulfate or chloride electrolytes.

- To investigate the effects of varying conditions, such as temperature, and ferric versus potentiostatic oxidation.

- To investigate model binary systems and thereby ascertain the suitability of the spectroelectrochemical conditions for the more complex chalcopyrite system.

- To undertake detailed studies of the properties of relevant model compounds as an aid to identifying sulfide mineral oxidation products.

- To develop unique techniques to facilitate sub-monolayer detection in situ on corroding chalcopyrite surfaces.

1.3. Structure of Thesis

This thesis is divided into seven chapters. The remainder of this chapter is devoted to an introduction of the research field, including a detailed literature review on fundamental studies of chalcopyrite oxidation and dissolution, subdivided into electrochemical/kinetic studies and surface structure studies. A brief overview of the development of copper hydrometallurgy and current commercial and demonstration scale processes is then presented.

A review of the instrumental techniques, and specific details of their application in the present investigation is given in Chapter 2. The applications of each technique to similar problems in the literature is also critically reviewed.

Chapters 3 to 6 are devoted to the experimental investigations and discussion of the results. Each chapter contains an introduction to the research area, presentation of results and discussion of their implications followed by a conclusions section. Any deviations
from, or additional information to, the experimental methods of the present investigation presented in Chapter 2 are detailed in the text.

Chapter 3 presents normal spectrophotometric results of chalcopyrite oxidation in acid chloride, sulfate and circumneutral solutions. Potentiostatic studies pre-dominate in this Chapter, although a detailed analysis of the voltammetry as well as various \textit{ex situ} Raman studies are also presented.

Chapter 4 presents surface-enhanced Raman spectrophotometric studies of chalcopyrite oxidation in acidic solutions. Potentiodynamic studies predominate, though \textit{ex situ} results are also presented.

Chapter 5 details studies of spectrophotometric studies of model systems. The first part of the chapter is devoted to normal Raman studies of polysulfides and sulfur allotropes, followed by Surface-enhanced Raman scattering (SERS) studies of model Au-S and Cu-S systems.

Chapter 6 presents \textit{ex situ} non-spectrophotometric studies undertaken to provide both supporting and clarifying information for the spectrophotometric studies in the previous chapters. Results from Environmental Scanning Electron Microscopy (ESEM), X-ray Photoelectron Spectroscopy (XPS), Dynamic Secondary Ion – Mass Spectrometry (SIMS) and Neutron Reflectometry are presented.

Finally, Chapter 7 displays key conclusions and highlights of the experimental findings of this investigation. The results of this study and their implications for furthering the understanding of the chalcopyrite leaching process is considered and discussed.

\section*{1.4. Properties of chalcopyrite}

\subsection*{1.4.1. Structure}

Chalcopyrite [CuFeS$_2$] is the most abundant copper-bearing mineral in the world [20]. Its name is derived from the Greek \textit{chalkos}, meaning copper, and \textit{pyros}, meaning fire (i.e. pyrite [FeS$_2$] ignites when heated in air) [20].

The oxidation state of the cations in chalcopyrite was a subject of debate for some time, though spectroscopic studies indicate copper is present in the copper(I) formal oxidation state [21-23], while iron is present in the high-spin ferric state [24]. There is an absence of a magnetic moment on the copper atom observed in neutron diffraction experiments,
but the iron moment is anomously low (3.82 µB) and has led to proposals of an oxidation state intermediate between Fe$^{2+}$ and Fe$^{3+}$ ([24, 25], and references therein). Extensive direct covalence between the anions in the structure is not observed, but there is considerable covalence between the cations and anions [25]. Chalcopyrite is found together with other sulfides among primary ores of magmatic origin. It is also a common mineral in the secondary enrichment of many ore deposits.

Chalcopyrite is tetragonal with c=525 pm and a = 1032 pm. It’s structure is analogous to that of sphalerite [ZnS] with four zinc atoms being replaced two copper and two iron atoms. Thus, the chalcopyrite unit cell is twice the volume of the unit cell of sphalerite. Each metal atom is coordinated by a tetrahedron of sulfur atoms and each sulfur atom by a tetrahedron of metal atoms (2 copper and iron). [25]. The structure belongs to the D$_{2d}^{12}$ space group, and the Raman bands represent lattice vibrations. The main peak at ~293 cm$^{-1}$ is assigned to the A$_1$ mode [26] (a symmetric anion-only vibration [27]).

![Figure 1.1: Chalcopyrite crystal structure (d$_{FeS}$ 2.25 Å, d$_{CuS}$ 2.30 Å, d$_{SS}$ 3.68 and 3.80 Å [25]).](image_url)

There are three known “stuffed” derivatives of chalcopyrite: talnakhite (Cu$_9$Fe$_8$S$_{16}$), mooihoekite (Cu$_9$Fe$_9$S$_{16}$) and haycockite (Cu$_4$Fe$_5$S$_8$) [28, 29]. They are based on a sphalerite-type unit cell, with the additional atoms located in the unoccupied set of tetrahedral sites of the cubic close-packed sulfur lattice [24]. A first-order tetrahedral coordination to sulfur atoms is maintained for these additional metal atoms, with a
second-order octahedral coordination to normal atoms such that the six surrounding ‘normal’ metal atoms are displaced away from the additional metal atom [24]. The stuffed derivatives of chalcopyrite are known to be more reactive than stoichiometric chalcopyrite [30, 31].

1.4.2. Physical properties

Chalcopyrite is predominantly found massive and sometimes botryoidal [20]. The crystal habit is generally disphenoid (which is like two opposing wedges) and resembles a tetrahedron [20]. Crystals are sometimes twinned. It has a metallic, brassy lustre and is moderately hard (3.5-4.0 Moh scale). It has poor cleavage habits and tends to fracture conchoidally. The resistivity of chalcopyrite ranges between $150-9000 \times 10^{-6} \Omega\text{m}$ [32] and the Néel temperature is 657 °C [20]. Stable $\alpha$-chalcopyrite undergoes a transformation to a cubic form ($\beta$-chalcopyrite) accompanied by a minor loss of sulfur (<1%) at 550°C [20]. This phase is isostructural with sphalerite. The system is complex, with bornite ($\text{Cu}_5\text{FeS}_4$) and talnakhite ($\text{Cu}_9\text{Fe}_8\text{S}_{16}$) appearing at intermediate transition temperatures [20].

1.4.3. Electronic properties

The band structure of a semiconductor is characterised by the forbidden band (the band gap) between the filled valence and empty conduction bands [19]. There are two types of charge carriers in a semiconductor: electrons in the conduction band, and holes in the valence band [19]. The probability of any quantum state of the bands being occupied by an electron or a hole is governed by the Fermi-Dirac law [19]. Unlike a metal, there is excess charge density in the surface of the semiconductor, called the space-charge layer. Thus, the charge-density at the surface increases as a result of lattice structure termination and results in a bending of the bands at the interface.

The effect of impurities and defects on resistivity and magnetic properties, and consequently the semi-conductor band model is substantial at low temperatures [24]. Antiferromagnetic ordering is observed up to a Néel temperature: neutron diffraction studies show that the spins on the two iron atoms tetrahedrally bonded to a common sulfur atom are opposed and directed along the c-axis [24]. Chalcopyrite behaves as a typical semiconductor and exhibits intrinsic behaviour above ~623K (i.e. a filled valence band is separated from a vacant conduction band by a narrow energy gap) and extrinsic behaviour below 223K (electrons move across the band gap and conduction increases). As
chalcopyrite is heated though, it loses sulfur and a consequent irreversible increase in conductivity is observed [24]. Room-temperature determinations on chalcopyrite nearly all show n-type conduction (i.e. electron donation to the conduction band) and band gap values of 0.5 eV, 0.33 eV and 0.6 eV have been reported [24, 25].

*Ab initio* full potential and density functional calculations were carried out for chalcopyrite [33] indicating chalcopyrite is a conductor with no band crossings at the Fermi level. X-ray Emission Spectroscopy (XES), XPS and self-consistent-field Xα scattered wave molecular orbital (MO) calculations indicate that the highest occupied orbitals are of Cu 3d-S 3p antibonding character [34]. Strong mixing of the Fe 3d orbitals with the Cu 3d and S 3p orbitals is observed across a broad range of binding energies. The lowest empty orbitals are computed to be Fe 3d-S 3p antibonding orbitals with <2 eV separation from the highest occupied orbitals [34].

The semiconductor properties of the mineral can be critical in mineral processing and leaching. When two different materials are in contact and in thermal equilibrium, the Fermi levels will be equal when the free energy of the system is a minimum. For example, in the adsorption of oxygen at the surface of a semiconductor, if the work function of the semiconductor (the energy required to remove an electron from the Fermi level of the solid and place it at infinity) is less than the electron affinity of the oxygen, it is energetically feasible for an electron to be transferred to the oxygen and adsorption will occur. The semiconductor, in this case, acts as a reducing agent and is more likely to have the Fermi level close to its conduction band (i.e. it is an n-type semiconductor). On the other hand, a p-type semiconductor, like pyrrhotite, is more likely to act as an oxidising agent by accepting electrons. An n-type semiconductor should favour chemisorption of a cation and a p-type semiconductor would favour sorption of an anion. It is possible to modify the surface of a mineral and form an n-type surface on a p-type mineral or vice versa [24].

Crundwell [19] noted that mixed potential models have been used to represent leaching kinetics, assuming the potential across the solid side of the interface (the space-charge region) remains constant so that the applied difference appears across the Helmholtz layer. This is metal-like behaviour and the dissolution reaction is predicted to have a charge-transfer coefficient of 0.5 for an ideal single-electron reaction. However, as many sulfide minerals are semiconductors, most of the applied potential drop occurs across the space-charge region, with a charge transfer coefficient of 1 for the ideal case. Because
chalcopyrite is an n-type conductor, and the oxidation of sulfide minerals occurs as a result of the consumption of two holes, slow dissolution rates can be expected, limited by the diffusion of minority carriers (holes) to the surface [19]. Fundamentally different behaviour is therefore expected for the dissolution kinetics described by the mixed-potential and semiconductor models.

Electron transfer can only occur between states of the same energy level, thus $E_{\text{redox}}^0$ must be sufficiently close to the conduction- or valence-band edges [19].

### 1.5. Oxidation and dissolution of chalcopyrite

Non-oxidative solubility of chalcopyrite in water is low: $2.35 \times 10^{-6}$ M at 100°C [20]. In the presence of acid reaction is slow, and can be expressed as follows:

$$\text{CuFeS}_2 + 2\text{H}^+ \rightarrow \text{CuS} + \text{Fe}^{2+} + \text{H}_2\text{S}$$

(1)

In the presence of an oxidising agent, chalcopyrite dissolves readily. The anodic dissolution of chalcopyrite can be represented:

$$\text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2\text{S}^0 + 5\text{e}^- (>90\% \text{ under ambient conditions [1, 15]})$$

(2)

$$\text{CuFeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 17\text{e}^- \text{ (aggressive conditions)}$$

(3)

While sulfur is indisputably the major end product under most conditions, the oxidation of chalcopyrite is noted to be somewhat slower than the rate of pore diffusion of oxidant through a sulfur product layer [15]. Elemental sulfur is not generally thought to be the “passivating” product, yet the addition of sulfur solvent (such as CCl$_4$) has been reported to have some effect on chalcopyrite leach kinetics [13]. Other studies have also reported no effect [8, 14].

In addition to the above, there are many published reports of a difference in leaching rate in chloride vs. nitrate, sulfate and perchlorate media. Attributing this to a sulfur layer seems unlikely, though some researchers have proposed that chloride leads to the production of a more porous sulfur product, though do not state why [17, 18].

#### 1.5.1. Kinetic and electrochemical studies

Generally, parabolic kinetics are reported for chalcopyrite leached in non-chloride media [3, 15, 35-38] with linear kinetics reported for chloride leaching [39-41]. However, results are variable with parabolic kinetics also reported in chloride media [42] and, more rarely, linear kinetics for sulfate leaching [3]. At 95°C, euhedral crystals of sulfur have
been noted on chalcopyrite leached for 24 hours in ferric chloride, suggesting that sulfur is deposited from the leaching medium, indicating the involvement of a soluble species (non-oxidative dissolution of chalcopyrite and oxidative deposition of sulfur on the corroding surface) [18, 40, 43]. Discrete sulfur globules have also been noted in ferric sulfate leaching [4]. Jones and Peters [39] observed that chalcopyrite leached in ferric chloride solutions showed overall attack, while, when leached in ferric sulfate, attack was only manifest in fissures or grain boundaries. They also found that ferric chloride leaching was enhanced by smaller particles while ferric sulfate leaching was not.

Most researchers studying chalcopyrite dissolution in ferric solutions have recorded copper release as a function of time. Very few have investigated the stoichiometry of the initial dissolution reaction. Linge [15] investigated chalcopyrite dissolution kinetics and mechanisms using potentiostatic titration of ferric nitrate solution and analysis of leachant titres. The dissolution did not depend on stirring rate and showed parabolic kinetics. Chalcopyrite dissolves stoichiometrically except at very early stages of the reaction (t < 150 minutes at 25°C, SA = 0.22 m² g⁻¹). A pre-treated powder was used to study the stoichiometry of the initial reaction and it was shown that iron was released from the sample at twice the rate copper was. Linge proposed a metal-deficient or proton-stabilised phase to explain the early dissolution results, and showed that the congruent period of dissolution was not due to pore diffusion through a sulfur product layer. Other long-term studies have found congruent dissolution over time [1, 44].

In another study, monitoring of Fe²⁺/Cu²⁺ in sulfate and chloride leaching experiments showed preferential iron release initially which stabilised to stoichiometric release after 15 days leaching in 1M Fe³⁺ sulfate solution at 90°C for a massive specimen, and 2 days for a particulate (-400 mesh, 37 µm) powder [39]. Levels of 0-18% sulfate (calculated) [4, 36, 39] as product have been reported in ferric sulfate leaching studies. The oxidation kinetics in ferric sulfate solution were found to be independent of pH, rotation speed and [Fe³⁺] (above 0.005 M) but have been reported to depend strongly on [Fe²⁺] concentration [3, 36, 38] or not to depend on [Fe²⁺] concentration [37, 45]. The effect of ferrous iron appears to be related to associated cupric concentrations [44, 46, 47] (such that Fe³⁺/Fe²⁺ has an E_H maintenance role while Cu²⁺ interacts with the surface). Chloride leaching has shown a dependence on ferric concentration and less of a temperature dependence [38, 41].

10
Electrochemical studies of chalcopyrite dissolution are numerous. In general a small anodic pre-wave is observed on a fresh surface in the potential region 0.4 to 0.6 V vs. SCE in acid solution prior to the onset of the main anodic wave [6, 7, 9, 14, 48-50], and absent on subsequent sweeps unless the potential is swept sufficiently negative. Polishing the chalcopyrite affects the surface, leading to observation of additional waves attributable to the oxidation of copper-enriched sulfide phases [6]. Quite a number of investigators polished their electrodes, so their initial results (such as observations of the initial release of Cu\(^{2+}\) on anodic scanning [7, 51]) must be treated cautiously. Rotating ring-disk studies have variously demonstrated non-stoichiometric release of iron and copper [7, 49, 50], and it was found that, under non-oxidising conditions, selective iron removal occurred, resulting in a passivated surface [49, 50]. Other notable observations include: the pre-wave area is roughly independent of the sweep rate or stirring [6]; the pre-wave product is stable for long periods at ambient temperature but decomposes at measurable rates at elevated temperatures [6, 8]; comparative studies of covellite and bornite indicate they are not intermediate phases in chalcopyrite oxidation [9, 49, 50, 52]; potentials < -0.2 V vs. SCE result in reduction of chalcopyrite and the product layer to form chalcocite [6, 9]; dipping oxidised chalcopyrite electrodes in CS\(_2\) has no effect on the subsequent redox behaviour [8, 14] (though studies of ferric chloride leaching indicate otherwise [13]); periods of relaxation at open-circuit potential (OCP) facilitate reduction in passivation, depending on temperature [8, 14]; the concentration of H\(^+\) has little effect on the pre-wave, but does affect the main anodic wave [6, 49].

The relative charge passed in anodic and cathodic sweeps, as well as a knowledge of the initial stoichiometry of solutes released into solution and the properties of the pre-wave process, led Biegler and Horne [6] to propose the following reactions to explain the pre-wave process:

\[
\text{CuFeS}_2 \rightarrow 0.75 \text{CuS} + 1.25 \text{S}^0 + 0.25 \text{Cu}^{2+} + \text{Fe}^{2+} + 2.5\text{e}^- \tag{4}
\]

\[
\text{CuFeS}_2 \rightarrow \text{Cu}_{0.75}\text{S}_2 + 0.25 \text{Cu}^{2+} + \text{Fe}^{2+} + 2.5\text{e}^- \tag{5}
\]

Voltammograms undertaken in acid sulfate solutions and chloride solutions have variously reported little difference in the pre-wave region [6] to enhancement of the pre-wave current in the presence of chloride [14, 17]. Parker et al. [8] investigated anodic and cathodic currents generated by potential sweeps to ±0.05V of the corrosion potential of chalcopyrite in various solutions of electroactive substances at 80°C. They found that
electron transfer rates decreased: \( \text{Br}_2, \text{I}_3^- > \text{CuCl}_2 > \text{FeCl}_3 > \text{Fe}_2(\text{SO}_4)_3 \). Similar findings were found by other researchers [39, 45]. The difference in rates argues against a simple resistive film (such as sulfur) being responsible. Jones and Peters [39] undertook mixed potential experiments in ferric chloride and ferric sulfate solutions at 90°C and found equilibration on addition of ferrous iron to be much more rapid in chloride solutions. Ferrous concentrations had little effect in chloride solutions, compared to a significant effect in sulfate solutions, indicating in ferric chloride leaching, ferric reduction is not the main cathodic reaction [39].

A number of models have been proposed to explain the observed leaching behaviour and kinetics of chalcopyrite in acid-sulfate solutions, including:

- A mixed diffusion/reaction model [1];
- A semiconductor energy level model (Fermi-level pinning) [19];
- Potential-dependent models [53];
- Diffusion at the interface [36]; and
- Diffusion processes in the bulk chalcopyrite [15].

Behaviour in circumneutral and alkaline systems is not very different from that in acid, with iron oxide phases formed concurrent with the passivating phase in the transpassive zone, and copper oxide formed in the main anodic wave region [54-59]. In alkaline solutions, a monolayer process, in which iron left the chalcopyrite lattice prior to the anodic pre-wave process, was observed with thicker iron-deficient layers evident in the pre-wave region [55, 56]. This accords well with the rotating ring-disk electrode (RRDE) observations of Lazaro and Nicol in acid solutions [49]. Iron oxide layers produced on chalcopyrite tended to be more porous than those on pyrite [60]. Chalcopyrite showed a predominantly anodic surface at OCP, compared to cathodic for pyrite, and the metal-deficient layers produced on chalcopyrite during oxidation were more stable than those on pyrite [60].

Under aggressive leaching conditions (oxygen pressure leaching) much greater proportions of sulfate are produced [1, 61] with linear leach kinetics independent of acid concentration and partially dependent on oxygen partial pressure.

Synthetic metal-excess chalcopyrite did not show behaviour consistent with that of natural chalcopyrites [62]. \( \beta \)-chalcopyrite (CuFeS\(_{1.83} \)) showed preferential copper dissolution
until approx. 17.5% Cu dissolution, at which time the composition approached \( \text{CuFeS}_2 \). Leaching subsequent to this produced more iron. The leaching occurred in three stages. \( \alpha \)-chalcopyrite \((\text{Cu}_{1.12}\text{Fe}_{1.09}\text{S}_2)\) resulted in the segregation of a fast-leaching copper sulfide phase, after which the remaining chalcopyrite phase leached slowly and stoichiometrically. Natural chalcopyrite is of the \( \alpha \) form. This may help to explain some of the activation and pre-treatment mechanisms (non-oxidising roasting, ultrasonication, ultrafine grinding and mechanical activation) for enhanced chalcopyrite hydrometallurgy [3, 63].

The effect of impurities, based on studies conducted with natural and synthetic chalcopyrite doped with various amounts of metals in galvanic contact with other sulfide minerals has been examined [64, 65]. Pyrite, molybdenite \([\text{MoS}_2]\), cinnabar \([\text{HgS}]\), orpiment \([\text{As}_2\text{S}_3]\), synthetic SnS, synthetic CoS and stibnite \([\text{Sb}_2\text{S}_3]\) accelerate the chalcopyrite dissolution rate, while high-Fe sphalerite \([\text{ZnS}]\) and galena \([\text{PbS}]\) retard the dissolution of chalcopyrite [35, 64, 66]. Cubanite \([\text{CuFe}_2\text{S}_3]\) appears to have no effect, while bornite \([\text{Cu}_5\text{FeS}_4]\) and low-Fe sphalerite accelerate the rate only slightly [64]. Silver is also a known catalyst of chalcopyrite dissolution [67-70].

McMillan et al. [45] studied the anodic dissolution of predominantly n-type (Timmins, Canada) and p-type (Messina, Transvaal) chalcopyrites. They did not find a significant difference in the behaviour of the two types, except as regards the reversibility of \( \text{Fe}^{3+}/\text{Fe}^{2+} \), which was more inhibited on the p-type chalcopyrite, though interpretation was compounded by differing impurity levels in the two samples.

Crundwell [19] interpreted the anodic reaction in terms of electronic structure. Computational studies suggest that the lower part of the conduction band of chalcopyrite is Fe 3d in character and that upper part of the conduction band is Cu 3d and S 3p in character. The location of the bands at the flatband potential and the redox potentials of various oxidants are displayed in Figure 1.2. If the oxidant substantially overlaps the conduction-band edge then electron capture readily occurs. Likewise, if the oxidant couple sufficiently overlaps the valence-band edge then hole injection occurs.
Figure 1.2: The energy level diagram for CuFeS$_2$, indicating the Cu 3d contribution to the valance band and the Fe 3d contribution to the conduction band (from Crundwell [19]).

Crundwell [19] explains that since the dissolution current for the contribution of holes from oxidant Fe$^{3+}$ is greater than the contribution of electrons to Cu$^{2+}$ in solution then it is assumed that the initial step in the dissolution of chalcopyrite progresses via hole transfer:

$$
\text{CuFeS}_2 + 3h^+ \rightarrow \text{Fe}^{3+} + \cdot \text{CuS}_2
$$

This is followed by hole or electron transfer to yield Cu$^{2+}$ and elemental sulfur.

1.5.2. Surface studies

A number of techniques have been used to investigate the corroding surface of chalcopyrite, of which X-ray photoelectron spectroscopy has been the most prevalent. Brion [71] studied air-oxidised chalcopyrite surfaces and identified iron-enrichment (in the form of iron oxyhydroxides), which aged to a basic sulfate. Copper remained in the Cu(I) valence state as the sulfide. An increasing signal from higher binding energy S(2p) components indicated the possible formation of S$_2$ groups in the iron-deficient sulfide lattice. No elemental sulfur was observed. Exposure of fresh chalcopyrite surfaces to water led to the formation of a thin film of iron oxyhydroxide.
Luttrell and Yoon [5] studied a chalcopyrite surface oxidised in pH 10.5 buffered water and found higher binding energy components in the S(2p) spectrum that were consistent with the presence of CuS and S\textsuperscript{0}, though the ratio was much greater than 1:1, which is not consistent with either Gardner and Woods [57], who proposed a mechanism based on electrochemical studies (requiring a 1:1 ratio), or Biegler and Horne [6], who’s mechanism which would require a ratio of 0.75:1. However, since the studies were conducted at room temperature, loss of elemental sulfur to the spectrometer was possible. Buckley and Woods [10] undertook XPS studies at 150K, where loss of sulfur to the spectrometer does not occur, and also found that exposure of chalcopyrite surfaces to air resulted in an iron enriched surface, in the form of iron oxyhydroxides. The S(2p) spectrum showed a high binding energy shoulder on the peak arising from unaltered chalcopyrite. The shift was similar to that reported for covellite (CuS) and bulk elemental sulfur, though the spin-orbit splitting ratio was not consistent with this interpretation, a 1:1 ratio of CuS:S was not observed (the analyses were conducted at 150K) and the spectrum did not alter with warming \textit{in situ} to 298 K (which it would be expected to do if elemental sulfur were present, though perhaps not if only a monolayer were present). Cu was present as Cu(I), and the altered chalcopyrite phase was interpreted as consisting of ~CuS\textsubscript{2} [10]. CuSO\textsubscript{4} was observed after extended periods of exposure. Alkaline media yielded a similar surface to air oxidation. Oxidation in acetic acid showed that the surface became deficient in iron and copper, and the XPS spectra and quantitative results indicated the surface layer had composition Cu\textsubscript{0.8}S\textsubscript{2}, which is similar to Biegler and Horne’s interpretation of the electrochemical pre-wave process [6]. No evidence of iron bonded to oxygen was evident in the spectra.

Numerous other studies have indicated a metal-deficient reactive surface, with spectra variously interpreted as indicating products containing polysulfides [1, 16], sulfur [1, 5, 11, 54, 72, 73], disulfides [11, 72, 74], covellite [5], metal-deficient sulfides [55, 56], electronic defect structures [16] and iron-sulfate phases [11, 75, 76]. Mikhlin \textit{et al.} [16], for instance, interpreted their XPS spectra, obtained at room temperature, in terms of sulfide (~161 eV), disulfide/polysulfide end atoms (~162 eV) and polysulfide mid-atoms (162.8-163.8 eV), assuming elemental sulfur was lost to the spectrometer under such conditions, and that the ratio of the ~162 eV components to ~163 eV components yielded details on polysulfide anion length. In some respects, this was reasonable because studies of polysulfides tend to show undistributed charge with low binding energy S\textsuperscript{−} atoms at the chain end and stoichiometric higher binding energy mid-chain sulfur atoms approaching
elemental sulfur binding energies [77-79]. Klauber et al. [72] caution against this approach noting that, at temperatures >200K, multilayer sulfur will readily evaporate, although monolayer or submonolayer sulfur will not, and that the binding energies of such sulfur will tend to be influenced by the substrate, as per sulfur studies on gold [80] at which multilayer sulfur was observed at binding energies of 162.9 eV, as opposed to 163.5-164.0 eV for bulk elemental sulfur [80]. Thus the ability to distinguish between sulfur monolayers and polysulfides via XPS alone is not possible. The variation in results and interpretation may also be attributed to sample preparation techniques, analysis techniques and spectral referencing (for instance, Klauber et al. [11, 72, 74, 75] assign the lowest binding energy component of the S(2p) spectrum at sulfide at 161.15 eV, while others reference against C(1s) adventitious carbon [16, 54]).

Smart et al. [81] note the necessity of using complementary techniques (extended x-ray absorption fine structure (EXAFS) and vibrational spectroscopy) to assign higher S(2p) binding energy components on oxidised mineral surfaces, though elemental sulfur can generally be identified via evaporative loss at 295 K. X-ray effects and induced-thermal damage must also be considered in such analyses, as must prevention of S_n species from evaporation by the presence of iron oxyhydroxide overlayers. Klauber [74] also points out that some of the ambiguity around XPS spectral interpretation may also arise from lack of comparison spectra for pristine surfaces (chalcopyrite being impossible to cleave under vacuum). He fractured chalcopyrite under a nitrogen atmosphere and transferred the sample to the XPS entry chamber without exposing it to oxygen. A loss feature was observed at ~2.6 eV on the high binding side of the 2p peaks of Cu, Fe and S (S(2p) 163.7 eV) which Klauber attributed to an S 3p→Fe 3d interband transition. A disulfide feature was also observed in the S(2p) spectrum which Klauber proposed was due to restructuring of the surface and formation of a two-layer surface phase containing pyritic FeS_2 at 50% of the bulk density of pyrite [74]. The Fe(2p) spectrum is notoriously intractable and multiplet analyses of the Fe(2p) spectrum were not attempted.

Surface preparative techniques are very important in studies of mineral oxidation. For instance, Biegler and Horne [6] noted voltammetric oxidation peaks prior to the chalcopyrite anodic pre-wave peak on polished electrodes that were absent on electrodes that were merely ground on SiC paper. Holloway et al. [82] used XPS and microreflectrometry techniques to study chalcopyrite surfaces after polishing with diamond paste. Polishing caused surface contamination with silicone oxide oil, and
substrate altered to form iron sulfate, iron oxide and copper-rich sulfide compounds (probably Cu₅FeS₂ and/or Cu₂S) over thicknesses of up to 100 Å.

Raman spectroscopy has been used to investigate sulfide mineral oxidation, primarily pyrite [83-89]. Only Li et al. [87] investigated chalcopyrite oxidation in situ though they investigated the main anodic wave region (E +1.0 V vs. SCE, pH 2.7, pH 6.5, pH 9.2) in chloride solutions. They observed sulfur within relatively short timeframes. All researchers (except Sasaki et al. [89]) claimed to observe polysulfides on oxidised sulfur minerals [83-85, 87] though, in truth, evidence of non-octasulfur S-S bonding is not proof of polysulfides (amorphous sulfur, or other sulfur rings are also possible). Indeed, the spectra obtained showed lower-frequency bands (~450-460 cm⁻¹) not entirely consistent with polysulfides which tend to exhibit splitting at both high (>475 cm⁻¹) and low frequencies as well as bending modes when they are beyond dimeric length [90-95]. However, a polysulfide formed on a mineral surface may be constrained and so lead to these observations. Sasaki et al. [89] noted that a 460 cm⁻¹ band in the product layer formed on pyrite during oxidation, observed in conjunction with octasulfur bands (~470 cm⁻¹, ~220 cm⁻¹ and ~150 cm⁻¹) vanished on submersion in cyclohexane, and they assigned it as “noise” although allotropic chains and rings would also be soluble in non-aqueous solvents. Using XPS, Mycroft et al. [86] observed S(2p) binding energies between 163.3 eV and 163.7 eV on oxidised pyrite surfaces, which falls into non-bulk sulfur and polysulfide territory. With Raman spectroscopy, a distinct band at ~454 cm⁻¹ was observed in addition to octasulfur. It failed to volatilise under vacuum or on heating to 390 K (though vibrational bands became unresolved, thereby indicating an amorphous phase), and did not vanish until heated to 493 K. Mycroft et al. [86] also noted a laser effect under continuous irradiation (acceleration of oxidation) which other researchers failed to note or address.

Fourier-transform infrared spectroscopy (FTIR) is a technique that has been frequently used to investigate flotation collector interaction with sulfide mineral surfaces (e.g. [96-98]). Secondary Ion Mass Spectrometry (SIMS) has also found an application in this respect [99-102], with a study also published of oxidation mechanisms of galena and pyrite using time-of-flight SIMS [103]. The results indicated for air-oxidised galena that initial oxidation took place preferentially at S sites and that alkaline solution oxidation yielded increasing presence in surface layers of Sₙ and oxy-sulfur species, with polymerisation length increasing as oxidation progressed.
Non-Rutherford backscattering spectrometry (NBS) has been used to investigate pyrite, chalcopyrite and bornite oxidation (in H\textsubscript{2}O\textsubscript{2}, 35% vol.) [104]. Pyrite and chalcopyrite were observed to be strongly affected by the oxidising treatments (even after only 100 s) while bornite was little affected.

England et al. [105] undertook surface studies of chalcopyrite and pyrite using Fe-K- and Cu-K-edge glancing-angle X-ray absorption spectroscopy (REFLEXAFS). The development of both Fe-O and Cu-O was observed on chalcopyrite surfaces. The XAS spectrum can be divided into two regions, the X-ray absorption near edge structure (XANES), which is sensitive to the coordination environment of the absorber atom, and the EXAFS, which provides information about bond lengths and coordination number. Glancing incident angles of the X-ray beam were used to selectively sample the surface (20-25 Å) (REFLEXAFS).

Surprisingly the distinction between bulk and lightly oxidised chalcopyrite (1 M HClO\textsubscript{4} at 0.6 V vs. SCE for 2.5 hr) was negligible, although as the samples were polished, the bulk sample is likely to have been oxidised [105]. Spectral fitting indicated that, in bulk and lightly oxidised samples, the metal ions were surrounded by a tetrahedron of sulfur atoms (d\textsubscript{CuS} 2.29 Å and d\textsubscript{FeS} 2.26 Å). For the most heavily oxidised sample (0.1 M Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} at 1.5 V vs. SCE for 7 mins), one oxygen atom was required to obtain the best fit for both Cu-K and Fe-K edges, while for the moderately oxidised sample (0.1 M Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} at 0.4 V vs. SCE for 2 hr), one oxygen atom was required to obtain a fit for the Fe spectrum but not for the Cu spectrum. This is in contrast to pyrite in which even the lightly oxidised samples required the addition of two oxygen atoms to obtain a good fit. Data collected at higher critical angles revealed that, for the most oxidised chalcopyrite sample, the Cu-O association did not extend so deeply as the Fe-O. They also note that change in the XANES Fe pre-edge feature of the oxidised chalcopyrite can be related to an increase in coordination, possibly reflecting the loss of long-range order in chalcopyrite as it suffers oxidative breakdown.

The authors note that the XANES analyses were a sensitive indicator of oxidation and accurate bond distances of reaction products were obtained from the EXAFS analyses [105]. However, the identification of surface species proved difficult due to the inability to differentiate between species in mixed systems. XAS is best used in systems where the surface species are distinct from the substrate (such as sorption, activation or replacement). Indeed, EXAFS has been successfully used to investigate the activation of sphalerite with Cu(II) [106].
Mikhlin et al. [107] also used EXAFS, in conjunction with cyclic voltammetry and XPS to investigate chalcopyrite oxidation. Ferric leaching prior to voltammetry lead to a change in OCP though little change in the voltammogram, possibly due to relaxation (the leach solutions were maintained at 50°C). As per the results of England et al. [105], the metal XANES spectra indicate that the metals maintain their oxidation state and tetrahedral coordination. EXAFS spectra indicate that, after ferric chloride leaching, the Cu-S distances in the surface increase by 0.06 Å and that the Cu and Fe atoms are bonded to polysulfide anions. Based on these results, Mikhlin et al. [107] proposed that passivation is not caused by the metal-deficient layer as such, but rather its specific qualities such that the charge carrier mobility in the disordered structures are less than their ordered (crystalline) counterparts. Positive centres arise as a result of holes to be effectively trapped at particular metal and/or sulfur atoms, orbitals of which comprise the upper valence band and are most readily oxidised. If these sites become abundant, Mikhlin et al. note that they are expected to give rise to large potential fluctuations in the solid and Anderson localisation of the electronic states near the VB edge, thereby sharply impeding carrier transport. This fails to explain the different behaviour of sulfate versus chloride leaching.

In another study, Mikhlin et al. [16] used a range of techniques to investigate chalcopyrite oxidation, including electrochemical, XPS, Mössbauer spectroscopy, Fe Lα,β and Cu Lα,β X-ray emission spectroscopy (XES) and Fe L-, Cu L-, S L-edge and O K-edge XAS. XAS probes the unoccupied electronic states, whereas XES probes the occupied states as electrons fall into the empty core levels of the excited state. The Mössbauer spectra showed a weak signal with a chemical shift 0-0.03 mm s⁻¹ for oxidised samples, which was assigned to ferric iron in the non-stoichiometric subsurface in which the antiferromagnetic structure of chalcopyrite disappeared. The signal intensity was greater for samples leached in chloride solutions compared to sulfate solutions [16].

In their XES studies, spectra gathered at different X-ray tube voltages indicated that compositional deviations extended some way into the sample matrix (analyses were conducted under vacuum, hence sulfur product layers were expected to have volatilised) indicating that the depleted layers neither decompose nor remain essentially passive. After leaching in chloride solution, the Fe Lα line was centred 0.7 eV higher than that for bulk chalcopyrite and was broadened in that direction. Samples leached in sulfate showed a peak shift but it remained narrow. The Cu Lα spectrum from the sample leached in
chloride solution broadened on the high-energy side to a large extent while that leached in sulfate was narrow. This was interpreted as hybridisation of the Me 3d orbitals with the orbitals of disulfide and tetrasulfide anions in the metal-depleted layers, with the extent of mixing dependent on the highest occupied molecular orbitals (HOMO) of the sulfur atoms (and therefore on the number of sulfur atoms connected). The data suggested S₄ anions were present in the reacted layers of chalcopyrite leached in chloride, whereas trisulfide anions whose density-of-states (DOS) are lower than monosulfide under these conditions, were formed on sulfate leached samples [16]. No model compounds were investigated for comparison. They proposed another reason for the broadening on the high energy side of the metal Lα bands may be due to Anderson localisation of states caused by disordering of the metal-deficient layer [16].

The XAS Me L spectra remained almost unaffected by leaching, except for a slight broadening on the high-energy side of the Fe L₃,2 peak on leaching in either ferric sulfate or chloride. The S L₃,2-edge spectra showed some differences in the post edge features, attributed to the splitting of the S 3d band and to multiple scattering with more distant atom shells. However, the features consistent with S-S bonding characteristics were largely absent. This was interpreted in terms of the amorphous metal-depleted layers which are quite thick, as opposed to electrochemical studies which indicate ~3 nm or less [6, 15]. They noted that the electronic structure of the metal-deficient layers is similar to that of chalcopyrite, except for the DOS in the upper portion of the valence band, which depends strongly on the specific polysulfide anion formed. The role of the solution electrolyte is to facilitate cation solubilisation, with chloride facilitating copper dissolution and the consequent dissolution of chalcopyrite as a whole.

Todd et al. [76] also used XAS and XES to examine chalcopyrite oxidised in nitrate solutions (pH 2-10) and their XAS spectra supported a lack of change in oxidation state for copper and formation of ferric oxyhydroxide phases at pH > 3.28. At lower pH, the O K-edge spectra indicated a species on the surface which Todd et al. attributed to ferric sulfate since it could not be an oxide at low pH. They did not wash their samples in clean acid prior to analysis hence the potential for formation of evaporite phases that may not have been present in solution, and nitrate contamination is high.

1.5.3. Commercial processes

While pyrometallurgy has a long history (4,000 B.C.), hydrometallurgy has relatively recent origins, with first application to copper in the 17th and 18th centuries [108-110].
Solvent extraction has evolved markedly in the last 50 years and facilitated a range of novel leaching technologies for the recovery of copper from complex solutions, though relatively few have, as yet, attained the status of commercial viability [108].

Currently, approximately 90% of copper is produced via sulfide smelting [109]. The benefits of hydrometallurgical alternatives include:

- Lower capital and operating costs. The capital cost of smelter and refinery complexes is high, typically $3,000-$5,000 per annual metric ton of copper production [111].
- Impurity elements incur considerable penalty costs from custom smelters.
- Smelter economics are more scale-sensitive than hydrometallurgical alternatives, with potential for modular incremental project development of the latter [111].
- Perceived environmental improvement. In many cases elemental sulfur is a product of the hydrometallurgical process, which is easily handled and transported compared to sulfuric acid produced through SO₂ scrubbing in smelters.
- Gold is frequently associated with copper concentrates. In some cases, high recovery of gold by flotation is accompanied by high levels of pyrite flotation, resulting in a low-grade copper concentrate for treatment [111].

The requirements of a successful hydrometallurgical process for copper are as follows [112]:

1. Recoveries of copper and precious metals equivalent to those achieved in smelting;
2. Recovery of sulfur and iron in useful forms, or their rejection in innocuous solid products; and
3. Flexibility in treating a variety of sulfide accessory minerals.

Obviously, the choice of a hydrometallurgical process for treatment of a particular ore feed is going to depend on a wide variety of factors, and significant amounts of time and money are therefore required to be spent by a potential user to assess the recoveries and costs. The most attractive processes will be those with low initial capital costs, competitive operating costs, high metal/bullion recovery, minimum environmental impact and ability to absorb rapid changes to plant grade changes and/or throughput capacity [113].

While hydrometallurgical processes will not ever totally replace pyrometallurgy, the inevitable lowering of mined ore grades and requirements of treating tailings and other wastes in the future make it probable that copper hydrometallurgy will continue to grow in importance [108].
Dreisinger recently reviewed new developments in the field of commercial hydrometallurgy [111]. He categorised hydrometallurgical processes into sulfate and chloride groupings, noting that the latter are becoming more popular as advances in chemistry, equipment and process technology develop. Within the sulfate category, processes can be subgrouped based on pressure (atmospheric, super-atmospheric) and leach process (chemical, biological) [111]. Historically, numerous hydrometallurgical treatment processes have been developed to treat copper concentrates but none have achieved sustained commercial production for chalcopyritic ores [111].

Summary points of some commercial processes is given below:

**Intec Mt Gordon Copper Process (Qld, Australia)**
- Low-pressure autoclave oxidation (77-90°C for 60 mins) to leach copper from milled ore, followed by solvent extraction/electrowinning (SX/EW) of copper from leach solution [111].
- With chalcocite ores the plant operation achieved 50,000 tons Cu (LME grade) in 2002. Site operating cost for ore through metal was ~$0.31/lb copper, one of the lowest cost operations in the world [111]. Not proven for chalcopyrite ores [113, 114].

**Phelps Dodge Total Pressure Oxidations (Bagdad Plant, Az, USA)**
- High-temperature (~225°C) high-pressure oxidation to leach sulfide minerals to sulfates and sulfuric acid, then SX/EW [111, 115]. Iron precipitation as hematite [111].
- 16,000 ton per annum Cu recovered from concentrations [111]. Used for chalcopyrite concentrate. Potential to cyanide leach residue for precious metals [116].

A number of demonstration-scale processes have been developed and are expected to soon emerge as commercial processes with continuing improvements in technologies (particularly advances in engineering that facilitate corrosive chloride processes [112]). Key contenders are detailed below:

**Sepon Copper Process (Laos)**
- Atmospheric acidic ferric sulfate leaching of copper followed by residue washing and then pyrite/elemental sulfur flotation. Autoclave treatment of flotation concentrate producing a basic ferric sulfate product [111]. Designed for a chalcocitic ore but remaining copper minerals may be scavenged in the pyrite float concentrate [111].
- Plant being constructed with initial capacity of 60,000 megatons per annum of copper. Autoclave oxidation of pyrite/sulfur provides meets most acid and ferric sulfate requirements of the copper leaching step [111].
Outokumpu Hydrocopper Process (Pori, Finland)

- Countercurrent leaching of chalcopyrite using air and chlorine as oxidants at 85-90°C [111, 113]. Residue contains goethite/hematite and elemental sulfur from which gold may be selectively leached via potential control. Cupric ion recycled to leach (precipitated by pH adjustment), cementation for Ag removal, base metal precipitation using sodium carbonate. Purified cuprous solution treated with sodium hydroxide to precipitate cuprous oxide for hydrogen reduction to metal [111].
- A 1 tonne per day demonstration plant in Finland has been built. Impurities management present significant issues [117].

Anglo American/UBC Process

- Fine ground chalcopyrite concentrates leached under moderate oxygen pressure at 150°C in an acid-sulfate system. Surfactant added to disperse molten sulfur. Copper recovered by SX/EW [111]. Hematite.jarosite formation.
- Pilot plant trials complete. Cu and Zn extractions >95%, elemental sulfur 60% in 2 hr residence time. Au extraction > 80% [111].

NSC Process (Sunshine Mining and Refining + The Centre for Advanced Mineral Processing, Butte, Montana)

- Nitrogen-species catalysed (sodium nitrite) moderate-pressure oxygen 30 min leach (125-175°C) of ultrafine ground concentrate. Copper recovered by conventional SX/EW [113].
- Cu yields >99%, good precious metals recovery, no chloride used [113].
- Commercial proven for argentiferous-tetrahedrite ores containing chalcocite. Plant closed in mid-1990s due to lack of suitable feed. Further work to test suitability for chalcopyrite-cobaltite feed from the Formation Capital Corporation Idaho Cobalt Project [118].

Activox (Western Minerals Technologies, Perth WA)

- Low-pressure oxygen sulfate leaching (~100°C) of ultrafine ground concentrate, including chalcopyrite and chalcocite. SX/EW for copper recovery. Cyanidation of leach tails for precious metals recovery [113].
- Demonstrated for mixed nickel, cobalt and copper-bearing feeds in Africa [113]. Successfully tested with chalcopyrite. Demonstration Plant in Botswana built [119].

CESL (Cominco, Vancouver, Canada)
- Two-stage acid sulfate-chloride leach at moderate temperature (150°C) and high-pressure of light-ground chalcopyrite-chalcocite concentrate. SX/EW recovery of copper. Sulfur recovery as by-product. Cyanide leach of tails [113].
- High-cost reagents and use of Ti autoclave apparatus necessary. Pilot-plant agreement with Companhia Vale do Rio Doce (CVRD) to operate on feed stock from Alamoa and Salobo, Brazil [120].

**Dynatec Process (Dynatec Corporation Ltd)**

- Pressure oxidation at 150°C for chalcopyrite (100°C for chalcocite) with oxygen sparging of a sulfate medium [121]. Low-grade coal added as molten sulfur dispersant. Fine-grind required. Copper recovery via SX/EW [122].
- Demonstration miniplants built at Las Cruces, Spain, as well as principal investment, development and operation of the Sudbury Joint Venture.

**MIM Albion Process (MIM and Highlands JV)**

- Ultrafine-ground concentrate undergoes ferric sulfate leach (~80°C) at atmospheric pressure with oxygen/air sparging in an agitated tank. Copper recovery by SX/EW. >98% Cu recovery for chalcopyrite indicated. Recovery of precious metals via cyanidation of residue [114].
- Pilot plant run in Brisbane. The Albion Process has entered pilot production producing zinc metal from McArthur River mine concentrate

**Intec Process (Intec Ltd)**

- Leach circuit operates at 85°C with oxygen supplied via air. Three stage leach circuit of fine-ground concentrate, Halex-laden lixiviant (BrCl₂⁻) with purification via conversion of cupric ions to cuprous, silver amalgam removal and Fe removal via pH control. Cu recovery via diaphragm cell EW, in which Halex lixiviant is also generated [113, 114, 123].
- Complex process chemistry [113]. Copper produced as dendrites, requiring remelting to produce LME ingots. Successful pilot plant demonstrations in Sydney and Tasmania.

1.5.4. **Bacterial leaching**

Bioleaching of metal sulfides is undertaken by a diverse group of bacteria: 11 prokaryotic divisions have been identified relating to this process [124]. It is widely applied in base metal extraction and pre-treatment of refractory gold ores [125] with both bioreactor and heap leaching approaches being used.
Most processes involve the use of mesophilic bacteria, such as *Leptospirillum* and *Thiobacillus* in the temperature range 20-45°C [126]. The bacteria primarily facilitate the oxidation of ferrous to ferric ion by oxygen at or near the mineral surfaces, such that the mineral is oxidised chemically by ferric iron (consisting of contact or non-contact submechanisms [124]). It is now generally accepted that the original “direct” mechanism of sulfide biooxidation (i.e. the direct enzymatic oxidation of the sulfur moieties of metal sulfides) does not exist [124].

Chalcopyrite is one of the few sulfide minerals that does not respond well to mesophiles [126] due to its tendency to “passivate”, often exhibiting parabolic bioreaching [125]. Commercial copper bioheap leach plants operate based on chalcocitic feeds [125]. Thermophilic microorganisms (*Sulfolobus, Acidianus, Metallospaeera*) have been shown to leach chalcopyrite to high extractions at temperatures in the range 65-75°C in stirred tanks and shake flasks [125, 126]. Reported rates of chalcopyrite leaching via thermophiles are generally significantly slower than those associated with mesophile leaching at comparable conditions [126]. However, a benefit of thermophilic leaching is that cooling of stirred reactors may not be necessary; cooling is frequently required in mesophilic leaching [125].

The biodissolution of metal sulfides occurs by two pathways: the thiosulfate or the polysulfide pathway [124]. Which pathway occurs depends on the acid solubility of the metal sulfide [124]. Thus, metal sulfides with valence bands derived only from the orbitals of metal atoms cannot be attacked by protons (acid non-soluble) and oxidise via the thiosulfate pathway [124]. Acid non-soluble metal sulfides include pyrite, molybdenite and tungstenite [124]. In this pathway, oxidation commences via electron transfer from the valence band to Fe(III). The sulfur bonds in the metal sulfide do not break until six successive one-electron step have occurred and thiosulfate is liberated [124]. The free thiosulfate produced is oxidised via polythionates to sulfate. Bacteria regenerate Fe(III) ions from the Fe(II) ions produced by the electron-transfer process. Under acidic conditions, chemical oxidation of Fe(II) is very slow, so the bacteria act as a catalyst [124].

Acid-soluble metal sulfides (such as sphalerite, galena and chalcopyrite) are dissolved by the combined action of electron-transfer to Fe(III) and proton-binding to the sulfide moiety via valence band electrons, yielding $H_2S^+$, which polymerises to form polysulfides and elemental sulfur [124, 127]. Sulfur-oxidising bacteria may also dissolve metal sulfides in this group. However, in both pathways, the main role of leaching bacteria
consists of the regeneration of Fe(III) [124]. Acidophilic sulfur oxidisers contribute to the transformation of intermediary sulfur compounds to sulfate [124]. In the absence of sulfur-oxidising acidophiles, the acidity of the leachant can be reduced, and inhibiting sulfur layers may build up on the mineral surface [124]. Rohwerder et al. [124] note that the factors which affect the surface sulfur layer properties and formation are not yet fully understood. Jarosite precipitation may play a role [12].

Most leaching bacteria grow attached to the metal sulfide surface [124]. Attachment is not random, with bacteria tending to prefer imperfect sites (scratches, fractures etc.) and areas of low-crystallisation [124, 128]. Thus, dissolution tends to occur at galvanic sites. Rimstidt et al. [129] claim that the cathodic reaction (electron-transfer from the mineral to an oxidant) on pyrite is rate-limiting due to dissolution dependence on \( \text{Fe}^{3+} \) concentration, hence the bacteria facilitate faster dissolution by maintaining high \( \text{Fe}^{3+} \) concentrations at the mineral surface [124].

Unlike the abiotic rate which decreases with acidity, the biotic rate increases, showing a maximum at pH \( \sim 3.2 \) [130]. Minimum bacterial activity occurs below pH 1.5 and above pH 5. Jaynes et al. [131] linked the pH-dependent activity to pyrite oxidation: below pH 2.5 the rate is limited by bacteria physiology whereas above pH 3.5, pyrite oxidation rate is limited by the decreasing solubility of \( \text{Fe}^{3+} \) oxyhydroxides.

Typically, microbial cultures are pre-grown or adapted for particular ore feeds in the laboratory or pilot plant, such that potential inhibitors select for a suitable population of ferrous-oxidising and sulfur-oxidising bacteria that can tolerate the conditions [125]. Care must be taken to use water supplies that do not contain additional inhibitory agents since acidophiles are sensitive to inhibition by certain organic acids and anions (such as chloride) [125]. Obviously, temperature sensitivity is another factor that can affect biooxidation kinetics, with temperature control in heaps particularly difficult [125].

Oxygen delivery in heaps or stirred-tank reactors is also a critical operational parameter.

Amongst the bioleaching technologies that have shown success at the demonstration plant scale for chalcopyritic feeds is the BIOCOP Process (Alliance Copper JV, Chile), the GEOCOAT process (Geobiotics Inc., Colorado) and the BacTech/Mintek process [125]. The BIOCOP process has high oxygen requirements, and cooling demands for the stirred-tank reactors [111, 113]. A 20,000 megaton per annum prototype Cu plant has been built in Chile to treat arsenical concentrates (as enargite, \( \text{Cu}_3\text{AsS}_4 \)) from the Mansa deposit [111]. The BacTech/Mintek process is also a stirred-tank reactor approach using air and a two-stage thermophilic ferric leach [113]. A pilot plant was built at Monterey, Mexico,
designed to produce 500 kg per day cathode copper [118]. The project focussed on a polymetallic concentrate (chalcopyrite, galena, sphalerite), with recoveries of 96-97% Cu, 99% Zn, 98-99% Au and 40% Ag achieved at a feed rate of 2.7 tonne per day [125].

The GEOCOAT process is a heap leach thermophile approach, in which flotation or concentrate slurry is coated onto crushed/sized barren rock or ore particles and stacked [114]. The heap is irrigated with acidic solutions containing iron and nutrients while air is applied at the heap base [114]. Peterson and Dixon [126] note that commercial application of stirred-tank thermophilic reactors may be limited by factors such as thermophile sensitivity to mechanical strain, relatively long residence times (5-12 days) and hence the requirement of large reactor volumes. With a heap heat conservation model it is possible to achieve optimal temperature distributions within the heap. Column tests with a chalcopyrite concentrate showed copper extractions >90% within 100 days [126].

The effectiveness of silver-bearing catalysts on the bioleaching of chalcopyrite at low-temperatures (30°C) has also been demonstrated [68], resulting in increased copper dissolution from chalcopyrite concentrate (<20 µm particle size, shake-flask, 20 days bioleaching) from 25% when no silver was added, to 75% with addition of 0.32 g Ag per kg of ore. When no bacteria were inoculated, extraction remained below 20% regardless of either the presence or absence of silver [68]. This is believed to occur via the precipitation of Ag₂S and galvanic acceleration of chalcopyrite or through Ag⁺ displacement of Cu⁺ in the lattice [68, 132, 133]. Gomez et al. reported thicker sulfur and silver sulfide layers (based on voltammetric current densities) for samples bioleached in the presence of Ag⁺, as opposed to chemically leached in the presence of Ag⁺ [132]. Mier et al. [133] reported no benefit in adding silver during bioleaching with Sulfolobus sp. presumably due to toxicity. Bismuth has also been noted to accelerate chalcopyrite bioleaching [133].

1.6. Rationale for this research project

The varying proposed mechanisms and “passivation” product/s of chalcopyrite oxidation in the literature is indicative of the failure of the various techniques employed, in isolation, to yield definitive information of both early and long-term leach behaviour. Electrochemical techniques allow in situ investigation of the initial properties of the leached layer but fail to yield structural information. All near-surface structural/compositional studies to-date have been undertaken ex situ and hence risk
alteration of the product layer formed in the leach process prior to analysis. Sample handling and instrumental issues confound the issue further. Add to this the variation in oxidation conditions (for instance Parker et al. [8] demonstrated the “passivating” layer decomposed rapidly at 80°C, while Biegler and Horne [6] demonstrated the passivating layer was stable for long periods of time at room temperature) and it is not surprising that such confusion abounds. The rare structural studies of corroding sulfide surfaces undertaken in situ have utilised bulk analysis techniques and/or aggressive oxidation techniques [62, 86, 87, 134].

Spectroelectrochemical techniques, particularly utilising Raman spectroscopy allow in situ monitoring of mineral surfaces, providing both structural and kinetic information. Water is a poor Raman scatterer, hence investigation of surfaces in aqueous environments is feasible. Normal Raman spectroscopy can, under ideal conditions, detect thin layers of Raman-active substances (5<nm<100) [84, 103, 135] but this is difficult to control and depends on the Raman scattering properties of both the substrate and corroding layer, the wavelength of the incident light, solvent, sample configuration and spectral configuration. The technique of Surface-enhanced Raman scattering (SERS) spectroscopy facilitates sub-monolayer detection and thus is an ideal technique for investigation of thin-films at interfaces [136]. The use of normal Raman or SERS combined with electrochemical techniques allows real-time investigation of both the initial corroding surface of chalcopyrite and a deep metal-depleted layer, should it form. Until now there have been some barriers to undertaking SERS investigations of natural mineral surfaces (such as restriction to specific substrates, notably the noble metals Au, Ag and Cu) but these barriers have been overcome and are discussed in the succeeding chapters.

Unlike most other surface studies reported in the literature, Raman spectroscopy only samples a small area (<1µm² using appropriate microscope objectives) of the surface and therefore enables investigation of specific regions free from inclusion phases. As all natural minerals contain inclusion phases, the benefit of this over other techniques is clear because the larger the area sampled the greater the probability that inclusion phases are contributing to the signal obtained. Imaging, mapping and point analyses may therefore be used to examine the distribution and nature of product phases over the mineral surface. A number of other techniques, including ESEM, SIMS, XPS and Neutron Reflectometry were used to both verify and clarify the Raman results.
1.7. References

44. S.L. Harmer, *PhD Thesis: Surface Layer Control for Improved Copper Recovery for Chalcopyrite Leaching*. Ian Wark Research Institute, ARC Special Research
Centre for Particle and Material Interfaces, University of South Australia, 235 pp. (2002).


2. Experimental and Instrumental
2.1. Preamble

A major disadvantage of many techniques used by researchers to investigate mineral reactions to-date is that they cannot yield accurate information on chemical structure or the nature of ionic/molecular species and products at the surface while the mineral is in solution. Spectroelectrochemical techniques provide a powerful tool for \textit{in situ} investigations. Specifically, Raman spectroscopy is particularly well suited to investigating surface phenomena in aqueous systems. Coupled with electrochemical techniques, comprehensive studies of surface species under specific potentiostatic/dynamic conditions are possible.

Aside from spectroelectrochemical techniques a range of \textit{ex situ} techniques were employed in this investigation to verify and add to the information gathered utilising spectroelectrochemical techniques, including X-ray Photoelectron Spectroscopy (XPS), Dynamic Secondary Ion-Mass Spectrometry (SIMS), Environmental Scanning Electron Microscopy (ESEM) and Neutron Reflectometry.

A brief background to the various instrumental techniques and a critical review of their use in published studies related to the present investigation is given. Also presented is detailed information on the set-up and use of each technique in the present investigation.

Summaries of instrumental capabilities and limitations are given in Table 2.1, and further information can be found in the references cited in the table.
<table>
<thead>
<tr>
<th>Analytical Technique</th>
<th>General Uses</th>
<th>Signal Detected</th>
<th>Elements Detected</th>
<th>Detection Limits</th>
<th>Depth Resolution</th>
<th>Lateral Resolution</th>
<th>Sample Details</th>
<th>Limitations</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman</td>
<td><em>In situ</em> aqueous studies (org. and inorg.), mapping, imaging</td>
<td>Raman scattering</td>
<td>Molecular/lattice</td>
<td>0.1 wt.%</td>
<td>&gt;5 nm to 1 µm</td>
<td>1 µm</td>
<td>Solid, liq. gas. <em>In situ.</em></td>
<td>Weak effect. Powerful laser source required. Possible photodecomp./heating issues. Fluorescence.</td>
<td>[1-4]</td>
</tr>
<tr>
<td>SERS</td>
<td><em>In situ</em> aqueous studies (org. and inorg.), trace analysis, monitoring catalytic reactions, monitoring electrochem. reactions</td>
<td>Raman scattering</td>
<td>Molecular chemical information</td>
<td>Single molecule</td>
<td>&lt;5 nm</td>
<td>1 µm</td>
<td>Solid, liq. gas. <em>In situ</em> investigations at surfaces</td>
<td>Only coinage metals (Ag, Cu, Au) and alkali metals provide large enhancement. Species of interest must be &lt;5 nm from SERS surface.</td>
<td>[2, 5-8]</td>
</tr>
<tr>
<td>Electrochemical</td>
<td><em>In situ</em> redox studies (org. and inorg.), trace analysis</td>
<td>Current</td>
<td>Ions (redox active) &lt;0.1% (submonolayer)</td>
<td>-</td>
<td>-</td>
<td>Conducting solid/liq <em>in situ.</em></td>
<td>No structural information issued. Highly susceptible to interference. Complex systems difficult to interpret.</td>
<td>[9-12]</td>
<td></td>
</tr>
<tr>
<td>XPS</td>
<td>Surface elemental composition and chemical state information (org. and inorg.)</td>
<td>Photoelectrons</td>
<td>Li-U</td>
<td>0.2 at.%</td>
<td>1-10 nm</td>
<td>~300 µm (non-imaging)</td>
<td>Solid, condensing liq/gas.</td>
<td>UHV technique. Charging of insulating samples can be an issue. Low spatial resolution (non-imaging</td>
<td>[4, 13-15]</td>
</tr>
<tr>
<td>Analytical Technique</td>
<td>General Uses</td>
<td>Signal Detected</td>
<td>Elements Detected</td>
<td>Detection Limits</td>
<td>Depth Resolution</td>
<td>Lateral Resolution</td>
<td>Sample Details</td>
<td>Limitations</td>
<td>Refs.</td>
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<tr>
<td>Dynamic SIMS</td>
<td>Elemental depth profiling. Materials trace analysis. Isotope ratios.</td>
<td>Secondary ions</td>
<td>H-U</td>
<td>&lt;ppb</td>
<td>0.2 – 30 nm (profiling)</td>
<td>~50 µm (profiling)</td>
<td>Solid, condensed liq/gas.</td>
<td>UHV technique. Charging of insulating samples can be an issue. Samples must be smooth on the nanoscale. Destructive. Empirical data fitting is complex.</td>
<td>[4, 16-18]</td>
</tr>
<tr>
<td>ESEM-EDX</td>
<td>Topographical and elemental imaging. Qualitative depth and backscattered information. Vapour adsorption studies.</td>
<td>Secondary and backscattered electrons. X-rays</td>
<td>B-U</td>
<td>0.1-1 at.%</td>
<td>&lt;5 nm (SE)</td>
<td>&lt; 5 nm (SE)</td>
<td>High VP and wet solids, condensed liqs, gases.</td>
<td>High-resolution imaging conducted under UHV conditions. Poor detection limits. Only qualitative depth information may be obtained.</td>
<td>[4, 19-21]</td>
</tr>
</tbody>
</table>

Table 2.1: Analytical technique summary (continued)
<table>
<thead>
<tr>
<th>Analytical Technique</th>
<th>General Uses</th>
<th>Signal Detected</th>
<th>Elements Detected</th>
<th>Detection Limits</th>
<th>Depth Resolution</th>
<th>Lateral Resolution</th>
<th>Sample Details</th>
<th>Limitations</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron Reflectometry</td>
<td>In situ composition/density gradients of surfaces, buried interfaces and thin films. Magnetic profiles (polarised neutron reflectometry)</td>
<td>Reflected Neutrons</td>
<td>Isotopic scattering length density (SLD)</td>
<td>-</td>
<td>Atomic scale (2 Å)</td>
<td>$&gt;10$ mm$^2$</td>
<td>In situ</td>
<td>Complex modelling. Complex systems particularly difficult. Provided there is a smooth interface there is little variation in SLD.</td>
<td>[22-25]</td>
</tr>
</tbody>
</table>

SE = Secondary electrons
BSE = Back-scattered electrons
EDX = Energy Dispersive X-ray
2.2. Raman spectroscopy

2.2.1. Background

Raman spectroscopy, a vibrational technique which arose in the early 20th century, was named in honour its discoverer C.V. Raman who, along with K.S. Krishnan published the first paper on this technique [1]. Its major limitation was the weakness of the effect (about $1/10^7$ absorption events results in Raman scattering [26]) and it was not until lasers became available in the 1960’s that Raman Spectroscopy became a useful analytical technique.

Raman spectra can be observed when visible light is scattered by molecules in solids, liquid or gases. The energy of the incident light used does not correspond to an allowed electronic or vibrational transition, as per infrared spectroscopy, and it will not be resonantly absorbed by the molecules. The scattered light is of interest in Raman Spectroscopy, which is of low intensity compared to the initial intensity of the light source. Thus it is typical to view the scattered light at 90° to the initial beam [26]. The information obtained in a Raman experiment can be quite different from the information obtained in an Infrared (IR) study. A vibration will be IR-active if a change in dipole moment occurs, while a Raman-active vibration requires a change in polarisability of the molecule [1].

Raman scattering studies tend to examine the changes in vibrational energy of molecules although it is possible to study changes in the rotational and electronic energy of the molecules as well. Figure 2.1 depicts the energetics of the Raman process, with the dotted lines of normal Raman transitions representing a virtual state, which assists visualisation of the process but is not a tangible concept. The scattered radiation may be of two types: elastic scattering (Rayleigh scatter) in which the scattered radiation is the same frequency as the incident radiation, $\nu_o$; and, Raman scattering in which the scattered radiation has frequency $\nu_o\pm\nu_m$, where $\nu_m$ is the vibrational frequency of the molecule [2]. The $\nu_o-\nu_m$ and $\nu_o+\nu_m$ lines are called the Stokes and anti-Stokes lines, respectively.
Figure 2.1: Vibrational energy level diagram for normal Raman, resonance Raman and fluorescence processes (R=Rayleigh, S=Stokes, A=anti-Stokes) [2](p. 16).

In a classical description of the spontaneous Raman effect, an electric field of strength $\varepsilon$ induces a dipole, $\mu$, in the molecule additional to any dipole the molecule naturally possesses [26]:

$$\mu = \alpha \varepsilon + \frac{1}{2} \beta \varepsilon^2 + \frac{1}{6} \gamma \varepsilon^3 + \ldots \quad (7)$$

where $\alpha$ is the polarisability and $\beta$ and $\gamma$ are the first- and second-hyperpolarisabilities. The first term dominates in the small electric fields of conventional Raman studies using continuous wave lasers.

Since the electric field strength ($\varepsilon$) at time $t$ is given by $\varepsilon = \varepsilon_0 \cos 2\pi \nu_0 t$, in which $\nu_0$ is the frequency of the radiation and $\varepsilon_0$ the amplitude, then for harmonic vibrations [2](p. 15)

$$\mu = \alpha_0 \varepsilon_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 \varepsilon_0 \left[ (\cos 2\pi(v_0+v_m) t) + (\cos 2\pi(v_0-v_m) t) \right] \quad (8)$$

in which $\nu_m$ is the vibrational frequency, $q$, the nuclear displacement, $q_0$, the vibrational amplitude, $\alpha_0$, the polarisability at equilibrium position, and $\left( \frac{\partial \alpha}{\partial q} \right)_0$ is the rate of change of $\alpha$ with respect to the change in $q$, evaluated at the equilibrium position [2](p. 15).
According to classical theory, the first term represents an oscillating dipole that radiates energy of frequency $\nu_0$ (Rayleigh scattering), while the second term corresponds to the Raman scattering of frequency $\nu_0 + \nu_m$ (anti-Stokes) and $\nu_0 - \nu_m$ (Stokes) transitions [2] (p. 16). If $\left( \frac{\partial \alpha}{\partial q} \right)_0$ is zero the vibration is not Raman active.

The vibrational frequency of a diatomic molecule is given by [2] (p. 18):

$$\tilde{\nu} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

(9)

where $K$ is the force constant and $\mu$ the reduced mass. A large force constant does not necessarily mean a stronger bond because the force constant is the curvature of the potential well near the equilibrium position [2] (p. 18).

Theoretically the intensity of a Raman band observed at $\nu_0 - \nu_{mn}$ is given by [2] (p. 54):

$$I_{mn} = \text{constant} \cdot I_0 \cdot (\nu_0 - \nu_{mn})^4 \sum_{\rho\sigma} (\alpha_{\rho\sigma})_{mn}^2$$

(10)

Here, $m$ and $n$ denote the initial and final states, respectively, of the electronic ground state. $(\alpha_{\rho\sigma})_{mn}$ represents the change in polarisability, $\alpha$, caused by the $m \rightarrow e \rightarrow n$ transition, where $e$ is the electronic excited state. $\rho$ and $\sigma$ label the components of the polarisability tensor ($p, \sigma = x, y$ or $z$). This term can be rewritten [2] (p. 54):

$$(\alpha_{\rho\sigma})_{mn} = \frac{1}{h} \sum_{\rho} \left( \frac{M_{me}^EM_{em}}{\nu_{en} - \nu_0 + i\Gamma_e} + \frac{M_{me}M_{en}}{\nu_{en} - \nu_0 + i\Gamma_e} \right)$$

(11)

where $\nu_{em}$ and $\nu_{en}$ are the frequencies corresponding to the energy differences between the states subscribed, and $h$ is Planck’s constant. $M_{me}$ etc. are the electric transition moments, such as

$$M_{me} = \int \Psi_m^* \mu_{\sigma} \Psi_e d\tau$$

(12)

with $\Psi_m$ and $\Psi_e$ the wavefunctions of the $m$ and $e$ states and $\mu_{\sigma}$ is the $\sigma$ component of the electric dipole moment. $\Gamma_e$ is the bandwidth of the $e^{th}$ state, and the $i\Gamma_e$ term is called the damping constant. In normal Raman scattering, $\nu_0$ is chosen so that $\nu_0 << \nu_{em}$. As $\nu_0$ approaches $\nu_{em}$ the denominator in the first term of the expression for the polarisability (equation 11) becomes very small, hence, this term (the “resonance
term”) becomes so large that the intensity of the band $\nu_{f-r} - \nu_{m}$ increases enormously [2] (p. 55). This technique is termed resonance Raman spectroscopy.

There are a number of specialised Raman techniques, though only normal Raman and SERS will be reviewed here in any detail.

### 2.2.2. Techniques

#### Normal Raman

Normal Raman spectroscopy is used to investigate the vibrational properties of bulk materials. The following details some of the features of Raman spectroscopy:

1. Beam diameters are only 1-2 mm, and the appropriate use of microscope objectives can limit the beam to <2 $\mu$m diameter. Thus, only a small sample volume is required. In recent instruments this has been combined with mapping programs that allow detailed observations of lateral surface variations.

2. Solids, liquids and gases can be investigated.

3. Selection rules are markedly different between IR and Raman spectroscopies: thus, some vibrations are only Raman-active while others are only IR-active. Typical examples are found in molecules having a centre of symmetry for which the mutual exclusion rules hold. Totally symmetric vibrations are always Raman-active [27]. Spectra of gases and liquids can be analysed in terms of mathematical group theory [28]. Lattice mode vibrations in solids provide information of crystal structure and can be interpreted in terms of space group symmetry, factor group analysis, site group analysis and nuclear site analysis [2] (p. 59).

4. Water is a weak Raman scatterer. Raman spectra of samples in aqueous solutions can thus be obtained without major interference from water vibrations.

5. Raman spectra of hygroscopic and/or air-sensitive compounds can be obtained by placing the sample under inert atmosphere. High pressure/high temperature conditions can easily be incorporated.

6. Special preparation techniques are not required for analysis.

7. Data gathered complements IR data. In general, vibrations are strong in Raman if the bond has covalent character, and strong in IR if the bond is ionic in nature.
8. Measurements of depolarisation ratios can provide reliable information about the symmetry of a normal vibration in solution where molecules are randomly oriented. This information cannot be obtained from IR spectra.

9. Laser-induced recrystallisation can provide molecular information otherwise not available.

10. Imaging filters allow collection of spatially distinct spectral information over significant areas of a sample surface in a matter of minutes.

11. Raman lends itself to combination with other techniques such as SEM (commercial) and AFM (developmental).

Disadvantages of Raman spectroscopy include:

1. A powerful laser source is needed to observe the weak Raman scattering effect, which can lead to heating and/or photodecomposition if proper care is not taken.

2. Some molecules fluoresce when irradiated by the laser beam. Fluorescence can be reduced using Fourier transform (FT)-Raman instruments.

3. It is more difficult to obtain rotational and rotation-vibration spectra with high-resolution in Raman than with IR spectroscopy. High-resolving power is difficult to obtain in the UV-Vis region of Raman spectroscopy.

4. The limit of detection for surface layers is 5 nm, which is greater than some other surface analytical techniques (e.g. X-ray photoelectron spectroscopy and secondary-ion mass-spectrometry).

**Resonance Raman**

In resonance Raman, the incident radiation frequency is close to the energy of a molecular electronic absorption, leading to resonance between the exciting wavelength and part of the molecule undergoing absorption (the chromophore) and, hence, an increase in Raman scatter signal of up to \(10^6\) \(^{[2]}\) \(^{(p. 54)}\). This makes it useful for selectively studying structural and kinetic aspects of chromophore reactions. Meaningful vibrational analysis requires extensive isotope-substitution studies.

**Surface-enhanced Raman Spectroscopy**

As Raman scattering is a second order process, it has a very low cross section (generally >10 orders of magnitude lower than that of infrared absorption) meaning that the signal-to-noise ratio of the Raman signal expected from a monolayer of
adsorbates is below the detection limit of a conventional Raman spectrometer [8]. Generally $>10^8$ molecules are necessary to generate a measurable normal Raman scattering signal because of the extremely small cross sections [29]. Surface enhanced Raman scattering (SERS), which occurs with metal nanostructures, results in a spectroscopic technique that can analyse layers $<5$ nm.

The first observation of SERS (from pyridine absorbed on an electrochemically roughened silver electrode) was reported in 1974 by Fleishmann et al. [30], who did not recognize it as such and attributed it to surface area effects. Jeanmaire and Van Duyne [31] undertook experiments and calculated that the intense Raman signal was due to an enhancement factor of $10^5$-$10^6$ times the intensity expected for the cross section of bulk pyridine. Albrecht and Creighton independently arrived at the same conclusion [32].

The mechanisms involved, whereby the surface enhancement spectra are obtainable, are still the subject of considerable controversy with no one mechanism able to explain all the observed effects [8]. The intensity of Raman scattering is proportional to the square of the induced electric dipole moment. There has been general agreement that the SERS effect results from two contributions [7]: the electromagnetic effect (EME) such that the electromagnetic field at the surface is enhanced over that of the bulk due to surface plasmon resonances experienced in surface nanostructures; and, the chemical effect such that the polarizability alters involving a resonance Raman-like process associated with chemical interactions between the molecule and the metal surface [33]. For the most noble-metal systems, the EME enhancement generated from metal nanostructures plays a dominant role [8] with the chemical enhancement magnitude estimated to enhance not more than factors of 10-100 [29]. Closely-spaced interacting particles seem to provide extra field enhancement, particularly near the gap sites between two particles in proximity, resulting in electromagnetic SERS enhancement factors up to $10^8$ [29]. If the correct wavelength of radiation strikes a rough metallic feature, the plasma of conduction electrons will oscillate collectively. This oscillation is unable to propagate into the bulk and produces a localised surface plasmon which, if in resonance with the incident radiation, greatly enhances the electromagnetic field around the roughness feature [34].
For the SERS effect to be observed, the molecules must be 5 nm or less from the surface [1]. Only three coinage metals (Au, Ag, Cu) and the alkali metals provide large enhancement, although Tian et al. [8] have developed procedures to generate SERS on Pt, Ru, Rh, Pd, Fe, Co, Ni and their alloys, via roughening and confocal Raman microscopy [8].

The symmetry rules governing molecules in bulk samples may not apply for sorbed molecules, and hence “forbidden” modes may become Raman-active [34, 35]. Information about the adsorption site, orientation of the adsorbed molecule and bonding with the surface may be obtainable [36].

Not surprisingly, the vibrational frequency of an adsorbed molecule may be affected by the local potential field (either applied or formed via local surface charge distributions), known as the vibrational Stark effect [37]. Two mechanisms have been proposed to explain this: one involves molecular orbital considerations and the other relates to the effect of the strong electric field across the double layer on polarisable electrons of the adsorbate. The vibrational Stark shift is dependent on a number of factors, including the force constant of the adsorbate-metal bond and the polarisability of the adsorbate, solution redox potential, ionic strength and pH. Essentially, the more ionic (electrostatic) the adsorbate-surface interaction is, the more it is expected to shift with potential [38].

Two of the techniques by which SERS is accomplished is adsorption onto metal films or onto colloids [1]. There is some precedence for “borrowing” the EME of a SERS-active substrate for the interrogation of a non SERS-active surface. This may be achieved by putting a thin layer of the non-SERS active substance on a roughened SERS surface [39, 40] or by depositing discontinuous thin films of SERS active metals on the surface of surface to be studied, via sputtering, evaporation or colloidal deposition [41-43]. Laser-ablation and nanosphere lithographical preparative methods have also been reported [3, 44].

**Non-linear Raman spectroscopy**

The contributions of $\beta$ and $\gamma$ terms (Equation ) in conventional Raman spectroscopy is negligible, but the contributions become significant when a sample is irradiated with extremely strong laser pulses ($\approx 10^9 \text{ V cm}^{-1}$) created by Q-switched ruby or Nd-YAG lasers (10-100 MW peak power). These pulses lead to novel spectroscopic
phenomena such as the hyper-Raman effect (HRS), the stimulated Raman effect, inverse Raman effect, coherent anti-Stokes Raman Scattering (CARS) and photoacoustic Raman spectroscopy (PARS) [2] (p. 136). These techniques have not been used in this investigation.

2.2.3. Instrumentation

Invention of the laser and its subsequent use as an irradiation source for Raman spectroscopy studies has revolutionised the technique [45]. Previously, Raman measurements were made with a mercury arc as the exciting source, but because Raman is an inherently weak process, the sources were not sufficiently intense for routine use, with many hours often being necessary to acquire a single spectrum.

The laser is an ideal exciting source for Raman experiments: it gives a very narrow, highly monochromatic, coherent beam, which can be focussed onto a small sample to give high-resolution spatial results.

The laser beam is passed through a (glass/quartz) cell or focussed on the sample directly. Scattered light is collected, filtered for Rayleigh scatter, and then passed into a grating monochromator, then detected via a photodiode or charge-coupled device (CCD). When quantitative results are desired, internal standards are generally used, as Raman Spectroscopy is a single beam technique.

Depolarisation ratios, which provide information on the symmetry properties of Raman-active vibrations, can be collected in 90° scattering geometry using a plane polarised laser beam and placing a polarising filter places between the sample and the collecting lens [45]. The depolarisation ratio may be defined:

\[ \rho = \frac{I_\perp}{I_\parallel} \]

where \( I_\perp \) is the intensity of scattered radiation whose plane of polarisation is perpendicular to that of the incident radiation and \( I_\parallel \) is the intensity of the scattered radiation whose plane of polarisation is parallel to that of the incident radiation. If the vibrational motion preserves the symmetry of the molecule, then the value of \( \rho \) will range from 0 to \( \frac{3}{4} \) [1]. If the symmetry of the molecule is reduced by the vibration, then the ratio will be \( \frac{3}{4} \), within experimental error [1].
Coloured compounds may absorb energy of the laser beam and thus can decompose and so present a problem. In such a case, the laser beam may be defocused, the wavelength changed, the sample diluted, the sample cooled or oscillated.

Sample fluorescence may swamp the weak Raman signal. Fluorescence can result from defects and/or impurities in solid samples, and so sample purification can rectify the problem [45]. Alternatively, if the sample itself fluoresces, changing the exciting wavelength to a longer wavelength should assist [2] (p.128).

2.2.4. Investigations of sulfide minerals

Raman studies of sulfide minerals have been extensive but rarely mechanistic. Mernagh and Trudu [46] published an excellent reference work providing spectra of 20 of the geologically important sulfide minerals and comparing the observed bands with those predicted from theoretical analyses. Of note, the spectra were shown to be sensitive to structural and compositional order/disorder. Metal-excess sulfides such as chalcocite, digenite and bornite were unsuitable for Raman investigation due to metallic bonding characteristics preventing laser beam penetration of the crystal and thermal sensitivity. They noted care must be taken examining sulfide minerals with high-intensity laser irradiation to prevent thermal decomposition. Their studies were undertaken using 514.5 nm irradiation at laser irradiation densities of ~32 to 320 kW cm\(^{-2}\) at the sample. Normal Raman spectroscopy will generally not be sufficiently sensitive to definitively show structural impacts of impurities unless the impurity element is present at % concentrations such as in studies of sphalerite where iron substitution yielded vastly different Raman spectra [47].

A general study of metal sulfide oxidation was conducted by Li et al. [48] using Raman spectroscopy and potentiostatic techniques. Oxidation of the minerals under various conditions in chloride media led to the formation of elemental sulfur (diagnostic spectra showing characterising \(\delta(\text{SSS})\) and \(\nu(\text{SS})\) modes were observed). However the \(\nu(\text{SS})\) band at \(~470\) cm\(^{-1}\) was broad in many cases, indicative of additional sulfur products to octasulfur compounds. These, the authors attributed to “polysulfides” despite the facts that they did not closely match published polysulfide spectra and that polysulfides would not be stable in these systems, particularly under acidic conditions. They found covellite to be recalcitrant to oxidation while chalcopyrite oxidation was examined at high overpotentials.
Turcotte et al. [49, 50] conducted circumneutral and acid oxidation experiments with pyrite in chloride solutions and again identified “polysulfides”, though never in the absence of elemental sulfur. No ferric oxyhydroxide was observed in situ by these researchers, despite the conditions being strongly conducive to its formation. Sulfur electrodeposited on platinum for comparison showed a broad band at ~300 cm$^{-1}$, though no significant broadening of the v(SS) band [49]. Electroreduction of the oxidised layer in acidic solutions produced a “virgin” surface spectrum.

A comprehensive sulfide oxidation study was undertaken by Mycroft et al. [51] in which high XPS S(2p) binding energies on oxidised pyrite samples were identified in conjunction with broad v(SS) Raman bands. After short oxidation times, a band at ~454 cm$^{-1}$ was observed at much higher intensity than bands corresponding to elemental sulfur. They also noted that laser irradiation (514.5 nm, ~0.56 kW cm$^{-2}$) catalysed pyrite oxidation, being about 15 times faster under irradiation with “polysulfide” product being more extensive on irradiated samples. Oxidised surfaces held under vacuum showed reduction of Raman bands attributable to elemental sulfur, although “polysulfide” bands were retained. Heating that sample to 120°C (below the octasulfur polymerisation temperature of 159°C [52]) led to the observation of “polysulfide” alone as a broad amorphous band, compared to discrete sharp bands observed in situ. Also, curiously, v(SS) bands at ~380 and ~340 cm$^{-1}$ attributable to sulfur stretches in the pyrite lattice were not observed, despite their prominent presence prior to heating. This was not discussed in the text by the authors. Heating to 220°C led to the loss of all sulfur on the surface, and re-emergence of the pyrite Raman bands. Unfortunately, experiments on electrodeposited or thin layers of sublimed sulfur on inert substrates were not undertaken.

Similar studies undertaken on modern instruments have shown that sulfur forms heterogeneously on the surface and, possibly, that chloride ions accelerate thiosulfate oxidation and prevent decomposition to elemental sulfur on the surface [53, 54]. Lehmann et al. [53] attributed the broad v(SS) band on oxidised pyrite to thiosulfate (S$_2$O$_3^{2-}$) type species despite the lack of accompanying v(SO) bands. They explained this in terms of sorption of the thiosulfate (complexation through the oxygen leading to downshifting of the v(SO) mode, supported by literature studies) and subsequent peak broadening. Sasaki et al. [55] claimed v(SS) modes at ~460 cm$^{-1}$ (which appeared as a weak shoulder of the major elemental sulfur mode) were noise and
noted they were eliminated with elemental sulfur after treatment with cyclohexane. However, the shoulder was very weak to begin with and still appears slightly evident after the cyclohexane treatment.

It is also worth noting here that Zou and Weaver [39] undertook SERS investigations of CdS/CdSe superlattice films formed on gold by electrochemical atomic-layer epitaxy. However, it is unlikely that the properties of ultrathin films would be representative of mineral specimens. This is supported by the red-shifting of phonon frequencies observed for CdS indicating significant crystallographic strain.

2.2.5. Investigations in this thesis

Raman spectroscopy was used in this investigation to explore the nature, properties and distribution of oxidative product/s on the corroding chalcopyrite surface in situ and ex situ. Both solid- and solution- phase molecular products were examined in chloride and sulfate media.

Normal Raman spectra were primarily collected on a Renishaw Raman 2000 microprobe spectrometer that has a rotary encoded grating stage and an internal two stage Peltier cooled (-70°C) CCD detector. A 442 nm Kimmon 1K series He-Cd laser (Model 5161R-G-S) was used as the excitation source. The laser power varied and is indicated in the text associated with spectra published in this thesis. 442 nm laser power was measured at the stage using a photoprobe:

- 20x objective (spot size ~5 µm)
  - 100% power: 9 mW
  - 25% power: 2.45 mW
  - 10% power: 0.82 mW
  - 1% power: 0.08 mW

- 50x objective (spot size ~2 µm)
  - 1% power: 0.06 mW

The spectral resolution varied between 2.5 and 4 cm⁻¹. The spectra were not corrected for instrumental effects. The grating was calibrated using the 520 cm⁻¹ silicon band. Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed with GRAMS32 software (Galactic Industries, Salem, NH, USA).

Samples for leaching and mapping were encased in clear polyester casting resin (1:100 V/V FGI resin (Batch # BJ211037): methylethylketone peroxide hardener), cut with a diamond saw to produce an even surface for mapping and wet ground on P600,
P800 and P1200 silicon carbide paper. Epoxy resin (Polymer Daystar LC3600 3:1 V/V resin (Batch # 3488); polyamide hardener (Batch #060J)) was not used in long-term leach tests due to lack of stability. Samples were rarely polished due to the possibility of thermal alteration of the sample surface, although, when polishing was required, a Struers polishing machine using 3 µm and 1 µm diamond paste was utilized, after which ultrasonication in isopropanol followed by doubly de-ionised (DDI) water was undertaken.

Spectra of mapped surfaces were corrected for baseline and integrated over the Raman bands of interest. Maps were generally collected over approximately 3500 µm² in 1 µm steps. Raman maps and spectra were also collected on an InVia Raman spectrometer at Renishaw, UK. The excitation sources were 785 nm diode and 514.5 nm Ar ion lasers, operating at 1 mW and 2.5 mW respectively at the sample. Maps were collected in linefocus mode (X50 Leica lens, NA=0.75) with 5s accumulation at each point.

Referencing of sample points was undertaken so that specific sites on the surface could be revisited after continued leaching (time-series gathering). A reference point grid was imposed on the polyresin using high-density laser (442 nm) irradiation (~50 kW cm⁻²) well away from the mineral grains to prevent thermal decomposition. This grid allowed the reference point to be reestablished using the digital microscope stage software each time the sample was put under the objective, and key points on the sample surface could then be reviewed by entering their coordinates into the software. Maps taken of a particular area over time were thus configured by the coordinates of their edges.

Mineral electrodes for use with the Renishaw 2000 electrochemical cell were prepared by attaching a mineral crystal/specimen to a titanium “slug” with silver-conducting epoxy resin and fitting to a Teflon coated support. The joint and electrode support were encased in epoxy resin such that only the mineral surface was exposed to solution. Electrochemical experiments were conducted in a specially designed borosilicate electrochemical cell with an optically flat transparent window. A conventional three-electrode configuration was used, consisting of a platinum counter electrode, a Ag/AgCl reference electrode and the mineral working electrode. Potential control was maintained using an ADInstruments potentiostat controlled by a Maclab/4e analog-digital converter interfaced with a PC running ADInstruments.
Echem software V1.5.2. The cell, electrode assembly and electrolyte were assembled under a nitrogen atmosphere, though the experiment could not be conducted under nitrogen due to the spectrometer-cell optical configuration. The mineral surface was ground and rinsed with degassed doubly de-ionised (DDI) water under nitrogen immediately prior to submersing in the electrolyte. Figure 2.2 displays the Raman cell used for electrochemical investigations on the System 2000.

![Figure 2.2: Electrochemical cell arrangement for electrochemical mineral studies on the System 2000 microscopy stage. The working electrode is inserted from the base of the cell (connects to the potentiostat under the microscope stage).](image)

Real-time electrochemical studies and SERS studies with gold were conducted on a Renishaw 100 system Raman spectrometer using 632.8 nm red excitation from a HeNe laser. The laser spot size was ~ 50 µm with power at the sample measured at ~ 6 mW (100% power). The scattered light was detected with a Peltier-cooled CCD detector with spectral resolution ~ 2cm⁻¹. The laser and scattered radiation were focused through an ultralong working distance x20 Olympus Plan Fl lens (NA=0.4). Spectra were collected for 5-10 s during potentiodynamic scans with a rest time of 1-2 s between scans allowing an acquisition range of 20-50 mV per scan.
For SERS studies of mineral surfaces during electrochemical investigations, surface enhancement was induced by vapour-deposition of gold island films onto the mineral electrode surfaces. Fine gold (99.9% Au) was thermally evaporated at 15 mA for 2-4 minutes yielding discontinuous gold films. Coverage was in the range of tens of nanometres as evidenced by the colour of the gold layer deposited simultaneously on glass slides.

Electrodes for use with the Renishaw 100 electrochemical cell were prepared by attaching copper wire to chalcopyrite with silver loaded epoxy, encasing the join with epoxy resin and the support with glass. The cell was assembled with reference (Ag/AgCl) and counter electrode in place and the electrolyte was purged in the cell for at least one hour prior to immersion of the mineral electrode. The mineral electrode was ground on P1200 mesh SiC paper and rinsed with DDI water immediately prior to immersion in the degassed electrolyte. The electrochemical cell configuration used on the Raman 100 spectrometer is displayed in Figure 2.3.

![Electrochemical cell configuration for use on the Renishaw Raman 100 spectrometer. The laser beam enters horizontally through the transparent window.](image)

Figure 2.3: Electrochemical cell configuration for use on the Renishaw Raman 100 spectrometer. The laser beam enters horizontally through the transparent window.

Some non-mineral SERS experiments are also reported in this thesis. Such experiments were conducted using the same cell configuration as the mineral studies on the Raman 100 system. Fine gold electrodes (99.9% Au) were employed and fresh surfaces for each experiment were generated by grinding on P1200 SiC paper, ultrasonicating in DDI water, submersing in 2 M HNO₃ for 24 hours, then heating at 400°C in a furnace for at least 1 hour followed by multiple rinsings in DDI water.
Once the electrode had been through the cleaning process, a surface suitable for SERS was generated by oxidation-reduction cycling in 1M KCl and 0.1M HCl (the procedures for this are well established in the literature e.g. [7, 8, 29]). The cycle program used in this investigation is displayed in Figure 2.4 below and has been demonstrated to generate surface structures suitable for SERS observations on gold electrodes [56].

![Figure 2.4: Oxidation-reduction cycle used to generate a roughened surface on gold electrodes, suitable for SERS studies.](image)

After completion of the cycle program, the electrode was rinsed with DDI water and, depending on subsequent experimental considerations, further cleaning by applying a potential of 1 V vs. Ag/AgCl (henceforth denoted V/Ag/AgCl) in pH 11 carbonate buffer for 1 minute was undertaken. The electrode surface was checked for contamination via Raman spectroscopic examination prior to commencing experiments.

### 2.3. Electrochemistry

#### 2.3.1. Background

This section will focus on voltammetry, an electrochemical technique based on the measurement of current (i) as a function of voltage (E) [10]. It is the most widely used technique for acquiring quantitative information about electrochemical reactions.
A three-electrode configuration is generally utilised for electrochemical measurements, involving a polarisable working electrode, a non-polarisable reference electrode and a counter electrode.

As the potential is varied, the electron flow in the external circuit is measured and relates stoichiometrically to the extent of the electrochemical reaction/s. Clearly the potential at which a redox current commences relates to the onset of a chemical reaction. As the reaction progresses the environment at the working electrode changes. In general, the current is governed by the rates of processes such as [57]

- Mass transfer (e.g. of oxidant from the bulk solution to the electrode surface);
- Electron-transfer at the electrode surface;
- Chemical reactions preceding or following the electron transfer (homogeneous or heterogeneous); and
- Other surface reactions such as adsorption, desorption, precipitation or crystallisation.

The rate constants for some of these processes (e.g. electron-transfer at the electrode surface or adsorption) depend on the potential.

If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be reversible i.e. the rate of electron transfer is rapid compared to the voltage sweep rate. In other words, if the surface concentrations of O (oxidised form of species) and R (reduced form of species) are maintained at the values predicted by the Nernst Equation then equilibrium is achieved [27]:

\[ E = E^0 + \frac{RT}{nF} \ln\left(\frac{[O]}{[R]}\right) \]  (14)

The situation is very different when the redox reaction is not reversible, when chemical reactions are coupled to the redox process or when adsorption of either reactants or products occurs. In fact, it is these "non-ideal" situations which are usually of greatest chemical interest and for which the diagnostic properties of cyclic voltammetry (CV) are particularly suited. The cyclic voltammogram is a complicated, time-dependent function of a large number of physical and chemical parameters.

2.3.2. **Investigations of sulfide minerals**

Electrochemical techniques have been used extensively to investigate the oxidative mechanism of chalcopyrite, and are reported in detail elsewhere in this thesis. It is the
most sensitive technique for studying oxidative mechanisms of minerals, but the
complexity of the system and low reproducibility of the electrochemical techniques
when applied to natural minerals has led to a variety of interpretations. Some of the
more salient findings are listed below:

- An anodic pre-wave (0.2-0.7 V/SCE) is observed during the first sweep of an
  unoxidised chalcopyrite surface and is absent on subsequent sweeps unless the
  potential is swept sufficiently negative (<-0.1 V/SCE) [58-63].
- The charge passed during the pre-wave process does not depend on the negative
  potential limit of the previous sweep [59].
- The pre-wave area is roughly independent of sweep rate, stirring and acid
  electrolyte at room temperature [59]. At higher temperatures (70°C) acid
  electrolyte effect becomes significant [64, 65].
- The pre-wave layer is thermally unstable, and can also be decomposed by the
  application of higher potentials (main anodic wave) [59, 60, 62].
- Polished and ground chalcopyrite surfaces behave differently [59] with the charge
  passed in the anodic pre-wave being between 0.02-0.06 C cm$^{-2}$, relating to a
  product layer of 20 nm or less [59, 66].
- Rotating ring disc electrode (RRDE) studies, in conjunction with surface studies,
  indicates iron leaches preferentially from the unoxidised chalcopyrite [59-62, 67-69],
  which is expected as ferric ion has a much higher charge/size ratio than
cuprous ion and hence would migrate more rapidly under an applied electric field.
- A knowledge of solution species, reduction products and relative charges passed
  during first sweep anodic and cathodic processes led to the proposal of the
  following stoichiometry for the pre-wave reaction [59]:

\[
\text{CuFeS}_2 \rightarrow 0.75 \text{CuS} + 1.25 \text{S} + 0.25 \text{Cu}^{2+} + \text{Fe}^{2+} + 2.5 \text{e}^{-} \quad (15)
\]

\[
\text{CuFeS}_2 \rightarrow \text{Cu}_{0.75}\text{S}_2 + 0.25 \text{Cu}^{2+} + \text{Fe}^{2+} + 2.5 \text{e}^{-} \quad (16)
\]

The second was closely supported by XPS data [63, 68].

- Interruption of potential programs in the pre-wave region and re-commencement
  led to consistent total charges for the pre-wave process at 25°C [59], although at
  80°C the surface film was not stable for long periods at open-circuit [70] and
  reactivation was independent of sulfur solvents.
• Acidity had no significant effect on the pre-wave, though the main anodic wave moved to less positive potentials with increasing pH [59], in agreement with kinetic studies (e.g. [71, 72]).

• The kinetics of dissolution of chalcopyrite are consistent regardless of whether the oxidising potential is maintained potentiostatically or via ferric ions [60, 70].

• Electron transfer rates on corroding chalcopyrite at 80°C were determined to occur in the following order: Br₂, I⁻, CuCl₂ > FeCl₃ > Fe₂(SO₄)₃ [70].

• A soluble sulfur species was indicated in RRDE sulfate leaching studies at 45°C [60, 61]. However, electrode preparation techniques cannot be discounted in causing this observation.

• Bornite and covellite oxidation in sulfate have been shown to be faster [58, 60, 61] than chalcopyrite; however, similar rates have been found for covellite in some cases ([67] and references therein). Again, electrode surface preparation may be responsible for the diverse observations.

• Non-oxidative dissolution occurs, with the formation of a passivating phase with time, indicating increased rates of leaching reported in ferrous containing lixiviants are short-lived [60].

• Analysis of current-time curves indicates a rate of 10⁻¹⁶ to 10⁻¹³ cm² s⁻¹ for chalcopyrite oxidation, which is comparable to the self-diffusion rate of Cu⁺ in chalcopyrite at 45°C [60].

2.3.3. Investigations in this thesis

Electrochemical techniques were mainly used in this investigation to maintain a controlled potential at the corroding chalcopyrite surface during Raman spectroscopic investigations. The electrochemical data was used to estimate the volume of chalcopyrite corroded and kinetic information.

CVs and current-time potentiostatic data were gathered under varied conditions, and parameters are given in the figure captions throughout this thesis. All CVs and current-time curves were gathered using a conventional three-electrode configuration, consisting of a platinum counter electrode, a Ag/AgCl reference electrode and a working electrode. Potential control was maintained using an ADInstruments potentiostat controlled by a Maclab/4e analog-digital converter interfaced with a PC running ADInstruments Echem software V1.5.2. The range of all experiments was set at 2000 mV (resolution 1 mV). CV scan rates of 2 mV s⁻¹ to 20 mV s⁻¹ were
commonly used, with a 5 ms sampling period in the last 75%-100% of the potential step. Initial rest time was set at 2 s and a ramped staircase waveform was used. The procedures for working electrode construction, preparation and cell assembly procedures were described previously.

Reference electrodes used included a Cypress Systems miniature Teflon Ag/AgCl electrode (66-EE008) consisting of a Teflon barrel (OD 2mm), chloridised silver wire with copper contact, 3.0 M KCl electrolyte and a single-junction glass frit. Ag/AgCl electrodes were also made in-house using fine Ag wire which was chloridised in a pH 1 1M KCl solution by applying 5V vs. a fine Ag cathode wire. 4 mm vycor frits were sealed in a Teflon shrink tube barrel and cleaned at 100°C in peroxide, then soaked at room temperature in 2 M HNO₃ acid solutions overnight. The barrel was filled with 3M KCl electrolyte, the Ag/AgCl wire and dried frit emplaced and the electrode unit sealed. Electrodes were checked against a dedicated reference electrode prior to each experiment, and reference electrolyte was replaced and the frit cleaned as necessary. The reference electrodes were kept in reference electrolyte between experiments and rinsed with doubly de-ionised water prior to use in experiments. Potential reference electrode leakage was unlikely to impact experiments and no further interface to the leach solution was employed.

2.4. X-ray Photoelectron Spectroscopy

2.4.1. Background

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique in which the sample is irradiated by monochromatic X-rays which cause photoionisation of surface atoms in the specimen and emission of a photoelectron. When X-rays of energy \( h\nu \) are used, the kinetic energy of the resulting photoelectron can be related to the binding energy of the core electron as follows [15]:

\[
E_b = h\nu - E_k - \Phi_{sp}
\]  

where \( \Phi_{sp} \) is the spectrometer work function, and is a combination of the sample work function, \( \Phi_s \) and the work function induced by the analyzer. The binding energy is characteristic of the core electron shell (and hence element) from which the electron was ejected, and is subtly shifted with chemical environment (relating to bonding and
A number of factors contribute to chemical shift and so interpretation is generally accomplished on an empirical basis [13].

### 2.4.2. Investigations of sulfide minerals

XPS is a technique that has found extensive use in investigating the oxidation of sulfide minerals. In particular, for the oxidation of chalcopyrite, high binding energy components of the S(2p) spectra have been attributed to metal-deficiency [66, 68], covellite with sulfur [73], polysulfides [51, 74], elemental sulfur, disulfide [75-77] and electronic defect structures [66]. Many of the reported XPS studies have been conducted to investigate flotation issues. Details of these studies were reported in Chapter 1.

Early XPS studies focussed on the valence of the metals in sulfide minerals, notably binary copper sulfides [78-80]. A series of copper sulfides were investigated, including synthetic phases not found naturally, such as pyritic CuS$_2$ (formed at pressures of 1.5 GPa [78]). It was concluded copper maintained a univalent oxidation state in all the minerals studied, and that it does so in chalcopyrite [78-81].

Due to the empirical nature of fitting core electron binding spectra, it is impossible to absolutely specify which of the possible chalcopyrite oxidation products may have formed, although the presence of elemental sulfur can be confirmed via evaporative loss under vacuum. Smart et al. [82] noted that other techniques are necessary to confirm S-S bonding, such as vibrational techniques or EXAFS. Smart et al. also noted that multilayer deposits of sulfur anodically deposited on gold from sulfide solution also produce apparent “polysulfide” binding energies, as distinct from elemental sulfur [82, 83].

Klauber [84] noted that the wide variation in reported surface species using XPS could be due to the following:

- The difficulty in collecting an XPS S(2p) spectrum of a clean unreacted fracture surface because chalcopyrite is brittle and fractures conchoidally making it difficult to expose a clean, reproducible virgin surface under vacuum;

- Lack of true surface-selectivity (only 10-25% of the signal derives from the uppermost layer in conventional XPS studies). Synchrotron based XPS (SR-XPS) can be tuned to provide greater surface selectivity;
• Loss of elemental sulfur through evaporation unless the sample is cooled to 150K;
• Radiation damage from induced thermal effects (lessened at lower temperatures). However, the main factor in radiation damage with XPS is the secondary electron flux which is temperature independent;
• Inappropriate calibration; and
• Inappropriate data treatment.

Vaughan, Becker and Wright [85] caution against the interpretation of XPS spectra using bulk standards and noted examples wherein they calculated very similar shifts for specific S-O-surface complexes that have no bulk equivalent.

To add to the confusion, the range of treatments of minerals has been inconsistent, from leaching of freshly ground relative pure massive specimens to leaching of concentrate with significant quantities of inclusion phases. A range of leaching temperatures has also been employed, and certainly much of the XPS data gathered to-date has yielded topographically averaged data, which almost certainly encompasses signals from inclusion phases.

In studying a chalcopyrite surface ground under high-purity nitrogen, Klauber [84] noted a high binding energy (BE) feature at ~2.6 eV that he attributed to an S 3p → Fe 3d transition. He believes that, in many published hydrometallurgical studies, the intensity on that side of the S(2p) peak has sometimes been erroneously interpreted in terms of oxidised species such as polysulfides. He also identified a second prominent S(2p) feature that was attributed to the presence of the $S_2^{2-}$. He proposed that a fractured chalcopyrite surface underwent reconstruction and redox reaction to form a stable pyritic structure. Earlier studies show that Cu is in the monovalent state in chalcopyrite and iron is present as ferric ion so such a reconstruction is complex and contrary to expectations [78, 86, 87]. The evidence for the loss feature and reconstruction is not definitive.

2.4.3. Investigations in this thesis

XPS studies were undertaken to provide ex situ quantitative elemental and valence-state information of species present on the corroding chalcopyrite surface. The
interaction of Au, deposited on chalcopyrite to facilitate SERS, with the corroding surface was also investigated.

X-ray photoelectron spectra were recorded on a Kratos Ultra Axis instrument with an Al Kα monochromated source, 180° hemispherical electron energy analyser of 165 mm mean radius and an 8-channeltron electron multiplier detector. Charge neutralisation was undertaken via the Kratos patented charge neutralisation system where necessary (e.g. epoxy-encased samples). Spectra were obtained at a source power of 150W (15 kV x 10 mA) from a nominal incident spot of 300 x 700 µm. Survey scans were run at a constant analyser pass energy of 80 eV using 0.5 eV channel widths and a 100 ms dwell time per channel. High-resolution spectra were collected at a constant analyser pass energy of 20 eV, 0.1 eV channel widths and 200 ms dwell time. The spectrometer was calibrated using the C1s (285 eV) line provided charging was not an issue.

2.5. Secondary Ion Mass Spectrometry

2.5.1. Background

Secondary Ion Mass Spectrometry (SIMS) is an ion beam analysis technique useful for surface characterisation. Primary ions of energy 0.5-20 keV (usually O₂⁺, Cs⁺, Ar⁺) impact the sample surface, yielding secondary ions of the target atoms [16]. The secondary ions are extracted from the surface by an electric field and subsequently energy and mass analysed. The ions are then detected by a Faraday cup or electron multiplier and the resulting secondary ion distribution displayed as a function of mass, surface location or depth into the sample [16]. SIMS has been available for 30 years or so, but technological advances and increased demand for sensitive surface probing in the last decade have led to increasingly sophisticated instrumentation.

There are two main variations of SIMS analysis:

1. Static SIMS – low primary ion doses are used to yield mass spectra that are representative of the top monolayer of the surface.

2. Dynamic SIMS – higher current beams are used to monitor selected elements as a function of sputter time (erosion of the sample, hence depth profiling).
In either case, the sputtering phenomena are exceedingly complex and difficult to interpret. The sputter yield depends on a number of parameters: primary ion beam density, primary ion beam species, angle of primary beam incidence, matrix surface composition, surface density of atoms of element A, ionisation efficiency of atom A, transmission of the spectrometer system for ions of element A, acceptance width in energy of the spectrometer system, acceptance angle of the spectrometer system, sample charging, sample homogeneity, sample topography, etc. [17].

2.5.2. Investigations of sulfide minerals

Static SIMS has rarely found successful application to the study of sulfide mineral oxidation products. Time-of-flight (ToF) SIMS has been used in several cases to examine flotation reagent interaction with galena surfaces [88-90], chalcocite [90] and chalcopyrite surfaces [91]. ToFSIMS was able to differentiate hydrophilic/hydrophobic ratios on particles that correlated with flotation response and demonstrated that the products of interaction were the same on pre-oxidised and fresh surfaces indicating ion-exchange was the mechanism for product formation on the pre-oxidised surfaces [88-90].

An “academic” dynamic SIMS investigation of back-scattered sputtered O$_2^+$ kinetic distribution and the relationship with bulk sulfide mineral composition has also been reported, but was not particularly revealing, possibly because of polishing effects [92].

Smart et al. [93] used ToFSIMS to examine oxidised surfaces of iron sulfide minerals, and found that the S$_n$/S fragment ratio correlated well with observed kinetics and XPS S(2p) spectra, with the ratio being highest for pyrite. Likewise, consistent results were found for galena oxidation in neutral aqueous solutions. They found that the ToFSIMS results reflected surface chemistry and they did not believe sputtered species fragmentation or recombination compromised the results. However, this data was unable to resolve, satisfactorily, whether polysulfide species or disordered rings were present. STM [94], SERS [95] and XPS [83] studies of sulfur on gold have shown that a gold surface impacts on sulfur ring structures under-potentially deposited from aqueous sulfide solutions. It is possible, indeed expected, that in the case of the mineral sulfides, the oxidised layer structure will be affected by the former
mineral lattice structure and by charged species, such as cuprous ions, remaining in
the lattice.

2.5.3. **Investigations in this thesis**

Dynamic SIMS was used to investigate the depth of the leached layers, the
stoichiometry of the various species present and how these varied with depth.
Various leach conditions were examined.

Dynamic SIMS investigations were undertaken using the Cameca 5f SIMS at ANSTO
Lucas Heights Laboratories. Vacuum pressures of $0.2 \times 10^{-9}$ Torr were maintained in
the analysis chamber. A Cs$^+$ ion primary source was used at 30°/N and the sampled
area was 50x50 µm$^2$ from a rastered area of 250x250 µm$^2$. The maximum primary
beam current was ~13 nA, with an excitation voltage of 10 kV. A 120 kV offset was
maintained at the sample.

Samples were set in LC3600 and cured at 70°C for 24-72 hours. Samples were then
cut with a diamond saw and ground on P400, P800 and P1200 grit SiC paper
successively. Some samples were then successively polished with 6µm diamond paste
on a metallurgical polishing base, 3µm diamond paste and 1µm diamond paste.

2.6. **Environmental Scanning Electron Microscopy**

2.6.1. **Background**

Electron microscopes operate on the same principle as their optical counterparts, but
instead of using light they use a focussed beam of electrons to image the specimen
[20]. All scanning electron microscopes (SEM’s) include an electron column that
creates a beam of electrons (collimated and focussed via electrostatic lenses), a
sample chamber where the electron beam interacts with the sample and detectors that
monitor a variety of signals resulting from the beam-sample interaction.

The electrons exit the column and interact with the sample surface. As the beam
electrons penetrate the sample they give up energy – there are three major emission
pathways for this energy:
• **Secondary electrons** (SE) are emitted from the sample on interaction with the primary beam. They generally have low energy (<50 eV [20]) and are thus eminently suited to offering high-image resolution [21].

• **Backscattered electrons** (BSE) are elastically scatter primary beam electrons. They have high energies, ranging from 50 eV up to the beam accelerating voltage. They thus derive from a significant depth in the sample and do not offer high image resolution [20]. Contrast derives primarily from average atomic nuclei density in the sample, with high-density regions yielding greater quantities of BSE’s and thus appearing quite bright.

• **Characteristic X-rays** are also emitted whenever a core electron is ejected, and not only from atoms near the sample surface, but with Auger electron emission more probable than X-ray emission for low atomic number elements [20]. The emitted X-rays will have significantly greater escape depth than the Auger electrons. These can be monitored and yield information on elemental composition. Such an analysis is termed Energy Dispersive X-ray (EDX) analysis.

The Environmental Scanning Electron Microscope (ESEM) was developed in the mid-1980’s and its primary advantages over the SEM lie in permitting the analyst to observe the sample surface over a range of pressure, temperature and gas compositions [19, 21]. The ESEM retains all the advantages of the conventional SEM while eliminating the high-vacuum constraint. In ESEM, instead of using a single high-vacuum pressure-limiting aperture as in conventional SEM, a series of pressure-limiting apertures are used [19]. Thus the electron column, which is under vacuum, is separated from the sample chamber in which pressures as high 50 Torr can be sustained [19]. Detectors have been developed that operate without vacuum requirements and thus sensitive samples may be examined without the need to compensate for charging effects.

### 2.6.2. Investigations of sulfide minerals

The SEM has found little application in studying the oxidation of sulfide minerals as it is unable to distinguish elemental composition of thin films, though it is used frequently to characterise natural materials and identify inclusion phases. Dutrizac [71] used SEM to identify the morphology of sulfur formed on chalcopyrite samples.
when leached in ferric sulfate solutions at 95°C. SEM-EDX investigations of chalcopyrite samples leached in alkaline ammoniacal systems [96] showed the formation of ferric oxides and that leaching occurred preferentially at defect sites and grain boundaries. Euhedral sulfur crystals were noted on samples that had been leached in ferric chloride solutions, suggesting solution-phase species may be responsible [97-99].

2.6.3. Investigations in this thesis

ESEM was used to obtain qualitative depth information, to investigate oxidative product distribution and morphology as well as the distribution of mineral inclusion phases which are not Raman-active, such as chalcocite.

Scanning Electron Micrographs were collected using an FEI Quanta 200 instrument with a 10-12 mm working distance, a spot size of 3 µm and beam energy of 15 kV and various detectors (Everhart Thornley secondary electron detector, large field SE detector and SSD-BSE detector). Standardless EDX spectra were collected using a thin-window Si(Li) X-ray detector. Environmental SEM were collected using the Quanta 200 with a 10-12 mm working distance, spot size varying between 3-5 µm, accelerating voltage varying between 7 and 20 kV and recorded using LFD and BSE detectors and pressure at 1 Torr of water vapour. For sample analysis in low-vacuum mode, sputtering was not conducted. Ground, polished and cleaved mineral samples were examined.

2.7. Neutron reflectometry

2.7.1. Background

Neutron reflectivity has become a major technique for investigating the structures of surfaces, interfaces and thin films at the molecular level in recent years. The technique is based on the differing reflection properties of neutrons at the interface of two media having different refractive indices. This kind of information is also yielded by X-ray reflectivity, but neutrons yield greater resolution due to their smaller wavelength, can distinguish between isotopes (notably hydrogen and deuterium), can measure magnetic profiles layer-by-layer (polarised neutron reflectivity, PNR) and can penetrate through many engineering materials [22]. Specular neutron
reflectometry probes variation in the neutron scattering length density (SLD) normal to a flat surface at depths of up to several hundred nanometres, with resolution of several angstroms [24].

The technique is thus ideally suited to studying corrosion phenomena of thin films and experiments described in this thesis were undertaken using the SURF reflectometer at the ISIS pulsed neutron source, Rutherford Appleton Laboratories, Didcot UK. It is a pulsed ToF instrument in which \( \lambda \) is measured at fixed \( \sigma \).

The refractive index, \( n \), of a material can be written [23]:

\[
n = 1 - (\delta - i\beta) \tag{18}
\]

The imaginary component derives from absorption of the material. The real part of \( 1-n \) is generally of the order \( 10^{-5} \) to \( 10^{-6} \), and because \( n < 1.0 \) there is a critical angle of incidence below which total internal reflection of X-rays and neutrons occurs [23].

The real and imaginary components of the refractive index of a material for neutrons are given [23]:

\[
\delta = \frac{\lambda^2}{2\pi} N b = \frac{\lambda^2}{2\pi} N A \sum_i \frac{\rho_i}{A_i} (b_{0,i} + b_i) \tag{19}
\]

\[
\beta = \frac{\lambda \mu_n}{4\pi} = \frac{\lambda^2}{2\pi} N A \sum_i \frac{\rho_i}{A_i} \left| p_i \right| \tag{20}
\]

where \( N_A \) is Avogadro’s number, \( \lambda \) the wavelength of the incident radiation, \( \rho_i \) is the physical density in the sample of element \( i \) with atomic weight \( A_i \) and \( \mu_n \) the neutron attenuation coefficient. The neutron refractive index depends on the bound coherent scattering length, \( b_0 \), and the real and imaginary dispersion terms \( b' \) and \( b'' \) [23].

Dispersion corrections are often negligible and \( \beta \) can often be ignored. The variation of neutron scattering length is apparently random, even between isotopes of the same element [23].

The geometry for a reflectivity experiment is illustrated in Figure 2.5.
Because the wavevectors, $k_0$ and $k_1$, are equal in magnitude for a specular reflection experiment, the magnitude of the scattering vector is [23]:

$$Q_z = |Q_z| = |k_0 - k_1| = \left(\frac{4\pi}{\lambda}\right)\sin\sigma$$

(21)

Thus, specular reflection yields information on the variation of composition through the interface and normal to it [23].

A neutron reflectivity experiment thus involves the measurement of sample reflectivity, $R$ ($I_{\text{reflected}}/I_{\text{incident}}$) as a function of the scattering vector magnitude $Q_z$. Reflectivities can vary by 6-8 orders of magnitude and thus the ability to resolve a reflectivity profile is limited by how quickly the reflectivity falls to background (in neutron experiments background becomes significant at $Q_z$ about 0.25-0.35 Å$^{-1}$) [23].

A critical angle exists below which total reflectivity is observed, and this depends on scattering length density and hence refractive index.

The effect of another film on the interface gives rise to modulations in the reflectivity known as ‘Kiessig fringes’ [23]. When the neutron wavelength satisfies the Bragg condition, $\lambda = 2d_i \sin\sigma$, constructive interference occurs [22]. This leads to:

$$d_i = \frac{2\pi}{\Delta Q_{z,i}}$$

(22)

where $\Delta Q_{z,i}$ is the difference between successive minima. The oscillation depths depend on the magnitude in differences in scattering length densities of the air and film and between the film and interface and thus relates to refractive index [23].

A vastly different scattering length density (SLD) can be observed by substituting isotopes for contrast enhancement. The large difference in the scattering length
densities of hydrogen and deuterium are important in many of the applications of neutron reflectivity in surface chemistry and polymer science [25]. Table 2.2 displays the scattering length densities of some common solvents. Thus, deuteration enables highlighting of a particular component in a complex system. While primarily of use in polymer and surfactant studies, hydrated/protonated thin films may also be of interest.

Table 2.2: Scattering length densities of some solvents [25]

<table>
<thead>
<tr>
<th></th>
<th>Protonated form $\delta \left(10^{10} \text{cm}^{-2}\right)$</th>
<th>Deuterated form $\delta \left(10^{10} \text{cm}^{-2}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-0.56</td>
<td>+6.38</td>
</tr>
<tr>
<td>Octane</td>
<td>-0.53</td>
<td>+6.43</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-0.28</td>
<td>+6.70</td>
</tr>
<tr>
<td>Toluene</td>
<td>+0.94</td>
<td>+5.67</td>
</tr>
<tr>
<td>Chloroform</td>
<td>+2.38</td>
<td>+3.16</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>+2.81</td>
<td>+2.81</td>
</tr>
</tbody>
</table>

2.7.2. **Investigations of sulfides**

No neutron reflectivity studies of sulfides were found in the literature.

2.7.3. **Investigations in this thesis**

Synthetic copper sulfide was selected as a model sulfide material for studying sulfide oxidation processes due to the difficulty in synthesising single-phase stable chalcopyrite films and particles. CuS has been postulated as an intermediate phase in chalcopyrite oxidation [59, 73, 100] and the Cu-S system has been frequently investigated in the literature, so it makes an excellent model system. There are reports in the literature of chalcopyrite nanoparticle synthesis [101-107] but characterisation of the resultant colloidal suspensions was generally poor and the systems were extremely unstable. Chemical bath deposition (CBD) of binary sulfide thin films is reported extensively in the literature. The method used in the this work was analogous to that of Nair *et al.* [108, 109] involving mixing the following solutions (made up with AR-grade chemicals and DDI water), in the order stated, at room
temperature and making up to 100 mL with double-deionised water:

- 10 mL 0.5M CuCl$_2$.2H$_2$O
- 5-8 mL 50% triethanolamine
- 8 mL 30% ammonia
- 10 mL 1M NaOH
- 6 mL 1M thiourea

Substrates were cleaned with concentrated nitric acid and, in the case of silicon were heated at 150°C in the oven prior to CBD to promote a suitable surface for nucleation. Glass microscope slides or silicon wafers/blocks were then set off-vertical in the bath solution at 25-45°C.

Thin films and substrates were submerged entirely in various leach solutions (made up with AR-grade chemicals) over various timeframes.

Neutron reflectivity (NR) data was collected on the SURF reflectometer [110] at the ISIS pulsed neutron source at Rutherford Appleton Laboratories, Didcot, UK. SURF is a time-of-flight station with a horizontal geometry. Specular reflectivity data was obtained from either the interface between the air and the film or from the interface between the film and the substrate with the neutron beam incident on the interface at an angle of between 0.25° and 0.8°. Data collection at the air/film interface was quite straightforward. To collect data at the film/substrate interface the thin Cu$_x$S film was deposited on a silicon disk with the neutron beam passing through the silicon to impinge on the silicon/film interface. The transmission of the silicon substrate was measured to correct the data for the variation in transmission of the neutrons with wavelength. The data was modelled using the optical matrix formulism [111]. This method entails describing the interfacial structure as a series of slabs, each of which has three parameters which can be fitted: that is, the layer thickness, scattering length density (SLD) and the Gaussian interfacial roughness of the layer [112]. All films were adequately fitted with models that consisted of one, or at most, two layers.
2.8. References


3. Normal Raman investigations using minerals
3.1. Preamble

This chapter presents investigations of the oxidation of chalcopyrite, and other selected sulfide minerals, utilising spectroelectrochemical techniques. The chapter opens with detailed compositional data of the various research samples used throughout this thesis and the presentation of Raman spectra of relevant mineral and potential product phases. It then moves onto electrochemical characterisation of the various samples. Electrochemical techniques provide information on the kinetics of the initial leaching process and therefore complement the Raman structural studies. Massive specimens were used in all spectroelectrochemical experiments (except in the case of sphalerite where mineral resistivity was too high) and results were remarkably reproducible.

Oxidative potentiostatic studies combined with normal Raman Spectroscopy allowed \textit{in situ} investigations of oxidative product layers. Normal Raman Spectroscopy is considered a bulk technique but quite thin product layers (5<nm<100) \cite{1-3} are detectable under ideal conditions depending on the identity of the substrate, the nature of the corroding layer, wavelength of incident light, etc. Various factors, including temperature, pressure, leachant counter-ion and potential were investigated and the results presented herein. \textit{In situ} investigations of product distribution were difficult to undertake as the digital microscope stage was impeded by the electrochemical cell, so various \textit{ex situ} mapping and imaging studies are also presented.

Natural samples were used in this investigation: synthetic chalcopyrites tend to leach faster and are prone to instability and segregation \cite{4-6}. Natural chalcopyrites invariably contain inclusion phases, and the large surface regions investigated by \textit{ex situ} techniques and electrochemical methods will likely encompass inclusion phases. With the appropriate microscope objectives Raman spectroscopy can sample regions as small as 1 µm, thus reducing the contributions from inclusion phases. In addition, mapping and imaging yield information on surface distribution and properties of products.
3.2. Research sample characterisation

Research-grade samples were sourced as follows:

- Chalcopyrite – Mt Isa Mine; Ward’s Natural Science Establishment; Messina, Transvaal
- Pyrite – China; Peru
- Covellite – Butte, Montana; Moonta, SA
- Sphalerite – High-Fe (Mt Isa Mine); Low-Fe (Broken Hill)

Pre-oxidation characterisation of various samples was undertaken via Raman spectroscopy, ESEM, XPS and wet chemical analysis. A four-acid (HF-HCl-HNO₃-HClO₄) near-total digest and ICP-MS/AES (inductively coupled plasma – mass spectrometry/atomic emission spectroscopy) determination for 47 elements was undertaken by the ALS-Chemex Mineral Laboratory at Stafford, which is NATA registered for analysis of ores and minerals by ICP-MS/AES techniques. Acid digest will result in loss of sulfur, hence the apparently poor stoichiometry in Table 3.1.

Table 3.1: Ore and trace constituents of sulfide samples (four-acid digest, ALS-Chemex).

<table>
<thead>
<tr>
<th></th>
<th>CuFe₂S₄</th>
<th>CuFe₂S₂</th>
<th>CuFe₂S₂</th>
<th>CuFe₂S₂</th>
<th>CuFe₂S₂</th>
<th>FeS₂²⁻</th>
<th>CuS⁻</th>
<th>ZnS⁻</th>
<th>ZnS⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Mt Isa</td>
<td>- Messina</td>
<td>- Messina</td>
<td>- Mt Isa</td>
<td>- Mt Isa</td>
<td>Ward’s</td>
<td>Moonta</td>
<td>Australian</td>
<td>Broken</td>
</tr>
<tr>
<td>(research-grade)</td>
<td>(SIMS samples)</td>
<td>(bulk piece)</td>
<td>(ore-grade research)</td>
<td>(ore-grade)</td>
<td>(China)</td>
<td>cubes</td>
<td>Moonta</td>
<td>(BK Minerals)</td>
<td>high-Fe</td>
</tr>
<tr>
<td>Ag ppm</td>
<td>37.3</td>
<td>6.81</td>
<td>6.44</td>
<td>40.6</td>
<td>36.5</td>
<td>10.75</td>
<td>1.45</td>
<td>91.3</td>
<td>576</td>
</tr>
<tr>
<td>Al %</td>
<td>0.16</td>
<td>0.61</td>
<td>0.49</td>
<td>0.37</td>
<td>0.5</td>
<td>0.09</td>
<td>0.15</td>
<td>0.02</td>
<td>7</td>
</tr>
<tr>
<td>As ppm</td>
<td>7670</td>
<td>26.4</td>
<td>2.5</td>
<td>8650</td>
<td>16300</td>
<td>59.9</td>
<td>738</td>
<td>92.3</td>
<td>57.9</td>
</tr>
<tr>
<td>Ba ppm</td>
<td>90</td>
<td>20</td>
<td>10</td>
<td>&lt;10</td>
<td>20</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
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<td>1.76</td>
<td>963</td>
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<td>37.4</td>
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<td>0.03</td>
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<td>2.07</td>
<td>1.09</td>
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Table 3.1 continued.
The Mt Isa samples appear to be higher in iron, while the Messina and Ward’s samples returned higher copper stoichiometries. The Mt Isa material is enriched in arsenic, cobalt, silver, nickel, lead and rare earth elements. Messina and Ward’s chalcopyrites are largely similar, with the Ward’s sample having a little less cobalt, nickel and zinc.
EDX and Raman spectroscopic investigation indicated the darkest phase is quartz (a), aluminosilicate (b), pyrite (FeS$_2$, c), chalcopyrite (d) and small patches of cobaltite (CoAsS; e).

Polished samples generally gave poor Raman spectra, with the signal “smeared”. Electrochemical studies undertaken by Biegler and Horne [7] showed a differing response in polished versus ground samples, with polished samples exhibiting additional anodic processes at 0.28-0.38 V/SCE and reduced chalcopyrite pre-wave activity at ~0.55 V/SCE. Gardner and Woods [8] and Parker et al. [9] also found that polished chalcopyrite was substantially more “passivated” than cut/ground surfaces. This indicates thermal alteration and/or pre-oxidation. Electron spectroscopy and micro-reflectometry showed that Fe$_3$O$_4$ or FeOOH together with a copper-rich sulfide (either bornite, Cu$_5$FeS$_4$, or chalcocite, Cu$_2$S) formed on chalcopyrite during polishing [10]. Thus polishing of samples was avoided where possible.

Figure 3.2 shows Raman spectra of Mt Isa chalcopyrite matrix and inclusion phases.
Figure 3.2: Raman spectra of Mt Isa ore-grade sample matrix and inclusion phases (excitation wavelength: 442 nm, irradiation density: 0.102 kW cm\(^{-2}\), 10 s accumulations).

Chalcopyrite is tetragonal having a structure analogous to that of sphalerite [ZnS] with the four zinc atoms being replaced by two copper and two iron atoms [11].
There is not extensive covalent interaction between the anions themselves, but there is considerable covalence between the cations and anions [12]. The structure belongs to the D$_{2d}^{12}$ space group, and the Raman bands represent lattice vibrations. The main band at ~293 cm$^{-1}$ is assigned to the A$_1$ mode [13] (a symmetric anion-only vibration [14]), with bands at 321 cm$^{-1}$ 351 cm$^{-1}$ and 372 cm$^{-1}$ also distinguishable and assigned to B$_2$ or E modes [13]. These modes are believed to relate to vibrations of the ferric ion [14].

The cubic cell for the pyrite [FeS$_2$] crystal [D$_{6h}^6$] consists of Fe atoms and S$_2$ pairs that form interpenetrating face-centred cubic (fcc) lattices [13]. The axes of the S$_2$ dumbbells lie in the (111) directions. The spectrum of pyrite shows two large bands at ~340 cm$^{-1}$ and ~380 cm$^{-1}$, with the lower energy band being due to S displacements perpendicular to the dumbbell axis and the higher energy phonon band due to stretching vibration of the S$_2$ dumbbell in phase throughout the crystal [1]. A small feature at 430 cm$^{-1}$ is attributable to lattice modes.

Chalcocite [Cu$_2$S] is a metal-excess sulfide, containing metallic bonds. It is difficult to obtain Raman spectra from metallic compounds because the laser beam only penetrates a few hundred angstroms below the surface [13]. Mernagh and Trudu [13] studied a range of sulfide minerals; they failed to record Raman spectra from chalcocite or digenite, which they considered to be due to their metallic character and thermal sensitivity. Li et al. [15] obtained a spectrum for chalcocite but claimed it only displayed fluorescence background.

Quartz [SiO$_2$] displays A$_1$ phonon modes at 464 and 206 cm$^{-1}$ [16], with the former being the more intense. Most of the vibrational bands for $\alpha$-quartz lie in the region 600-800 cm$^{-1}$, with the low frequency of the main 464 cm$^{-1}$ band due to motion of the Si atoms not being permitted, so the vibration becomes an O-Si-O deformation [17].

Table 3.2 shows standardless Energy-Dispersive X-ray (EDX) analyses of various chalcopyrite samples. It may be observed that matrix compositions are consistent across the various samples, and it appears that iron is slightly in excess, particularly for the Mt Isa specimen. The whole-sample compositional results shown in Table 3.1 indicate that iron and copper compositions are roughly comparative and thus it appears that the values in Table 3.2 are affected by analysis depth (such that an oxide overlayer is biasing the results), poor fitting routines, lack of calibration or a
combination of these factors. However, unlike the digest results in Table 3.1, the results in Table 3.2 do not suffer loss of sulfur and show roughly stoichiometric correspondence of the anion to cation ratio.

The various analyses of the chalcopyrite matrices indicates that the research-grade Mt Isa samples contains quartz, <2% pyrite, 0.025% cobaltite and trace amounts of galena and chalcocite. The Messina and Ward’s material only contains quartz as a significant inclusion phase.

Figure 3.7 displays the Raman spectra of some research minerals and reference samples of interest to these studies. The crystal structure and Raman spectra of chalcopyrite and pyrite have been discussed above.

CuS, which has been proposed as an intermediate phase in chalcopyrite oxidation [7, 8, 18, 19], is hexagonal (D$_{3h}^4$) in the stable covellite mineral form and has a remarkable structure: as in all the copper sulfides, copper is present in the copper(I) formal valence state, and four of the six sulfur atoms in the unit are joined in two S$_2$ groups while two sulfur atoms are isolated [20]. Two of the six copper atoms have triangular coordination while the other four have tetrahedral coordination [20]. The covellite Raman spectrum consists of a S-S stretching band at ~474 cm$^{-1}$ and a smaller band at ~267 cm$^{-1}$ attributed to other lattice modes [21].

Table 3.2: Standardless ESEM-EDX analyses (atomic %) of sample chalcopyrite matrices and inclusion phases.

|----------------|-------------------------------------|---------------------------------|------------------------------------------|---------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Beam energy    | 20 kV 15 kV 20 kV 20 kV 25 kV 15 kV 15 kV 15 kV
| S K            | 41.4 48.8 69.6 46.2 51.4 51.2 43.4 47.7 |
| Fe K           | 8.3 28.6 20.5 25.8 26.9 27.3 18.3 29.0 |
| Cu K           | 4.2 22.6 9.9 20.2 21.6 21.5 38.3 23.2 |
| As K           | 22.6                                             |
| Co K           | 23.5                                             |
| Au L           | 7.9 0.1                                           |
Figure 3.4: BSE micrograph of an unpolished research-grade Mt Isa chalcopyrite specimen used in leaching (normal Raman, SERS), mapping (normal Raman), XPS and electrochemical investigations.

Figure 3.5: BSE micrograph of a polished Ward’s chalcopyrite specimen used in leaching (normal Raman) and SIMS investigations.
Figure 3.6: BSE micrograph of a polished Messina, Transvaal chalcopyrite specimen used in electrochemical, leaching (Raman, SERS), mapping (normal Raman), SIMS and XPS investigations.

Figure 3.7: Raman spectra of research mineral samples and reference samples. The bracketed values refer to the mineral’s relative spectral intensity and thus relates to its Raman scattering efficiency (excitation wavelength: 442 nm; irradiation density: 0.05 kW cm$^{-2}$ (id, sp), 0.10 kW cm$^{-2}$ (py, cv, αS); Accumulation: 10 s (αS), 50s (cv), 100s (sp), 200s (py), 500 s (id)).
The bornite $[\text{Cu}_3\text{FeS}_4; \text{O}_7^+]$ structure falls in the digenite group, being related to sphalerite and chalcopyrite structures, although only $\frac{3}{4}$ of the $T_d$ sites in the anion sublattice are filled [22]. It is also a chalcopyrite alteration phase [7, 10]. Mernagh and Trudu [13] attempted to gather a bornite Raman spectrum but were unable to obtain one, which they ascribed to its metallic character and thermal sensitivity. Attempts to gather spectra in this study yielded only a broad ill-defined band around $300 \text{ cm}^{-1}$, consistent with its lack of covalently bonded sulfur atoms [23].

Idaite $[\text{Cu}_3\text{FeS}_4; D_{6h}^4]$ has a structure like covellite’s except that one-sixth of the copper atoms are replaced by iron. It is clearly another possible intermediate in chalcopyrite oxidation. It belongs to the layer sulfide group with hexagonal close-packing of the sulfur atoms [22]. The Raman band due to sulfur-sulfur bond vibration is evident in the spectrum recorded (Figure 3.7) and is shifted from that in covellite to $464 \text{ cm}^{-1}$.

The sphalerite $[\text{ZnS}; T^2_d]$ structure is directly related to that of chalcopyrite, with cubic close packing of the sulfide ions and $\text{Zn}^{2+}$ in tetrahedral sites [20]. Sphalerite was briefly studied since it is isostructural with chalcopyrite and is potentially a good model compound. Its structure is analogous to that of diamond, with four zinc atoms at the points of a fcc lattice and four sulfur atoms in a fcc lattice displaced one-quarter along the unit cell [13]. The first-order spectrum consists of a single $F_2$ mode which is both Raman and IR active [13]. As there is no centre of inversion in sphalerite the Raman band is split into a transverse optical (TO) mode at $275 \text{ cm}^{-1}$ and a longitudinal optical (LO) mode at $350 \text{ cm}^{-1}$ [13]. Mernagh and Trudu [13] note that a small amount iron in the sphalerite structure does not affect the frequencies of the main sphalerite bands, but enhances the second-order Raman spectrum which consists of a large number of overlapping bands. However, iron can be substituted for zinc in the sphalerite lattice up to $\sim 20\%$, resulting in a large increase in cell volume. Hope et al. [24] found that at 2-10% iron content, the sphalerite TO modes at $298 \text{ cm}^{-1}$ and $330 \text{ cm}^{-1}$ increased (becoming stronger than the LO mode at 10%), in agreement with observations by Mernagh and Trudu [13].
A spectrum of elemental rhombohedral $\alpha$-sulfur ($D_{2h}^{24}$), the ultimate chalcopyrite oxidation product under ambient leaching conditions, is also shown in Figure 3.7. The bands in the region 100-300 cm\(^{-1}\) have been attributed to S-S-S bending (the highly polarised lines being $\sim$152.5 cm\(^{-1}\) ($\nu_8$) and $\sim$218.5 cm\(^{-1}\) ($\nu_2$)) while a band resulting from S-S stretching vibrations is observed at $\sim$474 cm\(^{-1}\) ($\nu_1$) [25, 26]. Torsional and lattice modes are found below 100 cm\(^{-1}\) [26].

The covellite and elemental sulfur $\nu$(SS) stretch bands overlap, so they must be distinguished by the $\delta$(SSS) mode bands, which are absent for covellite and other entities where disulfide groups are present, but are present in the S\(_6\) rings of elemental sulfur. Turcotte et al. [27] found a consistent Raman peak intensity ratio (I\(_{474}\)/I\(_{216}\)) for sublimed rhombohedral sulfur and sulfur formed on oxidised pyrite. This ratio can be used to assess the presence of covellite and sulfur together, or sulfur in isolation. The I\(_{474}\)/I\(_{216}\) peak area intensity ratio for elemental sulfur in this study was 1.3.

Only the high-Fe sphalerite contained significant impurities in the form of galena [PbS] and a manganese mineral.

### 3.3. In situ spectroelectrochemical investigations of chalcopyrite

#### 3.3.1. Voltammetry

The following figures display first and second sweep cyclic voltammograms for chalcopyrite in unstirred 0.1N acid solutions. The general features are similar to those observed elsewhere: a pre-wave is observed with a maximum at 0.6 V/Ag/AgCl on the first sweep and is greatly reduced or absent on the second sweep [7, 28-32] unless the cathodic switching potential is sufficiently negative. In accordance with hydrometallurgical interests, the acidity was maintained at pH $\sim$1 (0.1N H\(^+\)) and no supporting electrolyte was added, hence the low potential onset of the main anodic wave. This is in accordance with observations by Biegler and Horne [7] and Lazaro and Nicol [31]: their studies indicated that the acid concentration had no effect on the pre-wave potential of charge, but effected the main anodic wave onset.
While sulfur is the ultimate chalcopyrite oxidation product for this potential region, the pre-wave has been variously proposed to result from the following reactions:

\[
\text{CuFeS}_2 \rightarrow 0.75 \text{CuS} + 0.25 \text{Cu}^{2+} + \text{Fe}^{2+} + 1.25 \text{S}^{0} + 2.5e^- \quad (23) \quad [7, 33]
\]

\[
\text{CuFeS}_2 \rightarrow \text{Cu}_{0.75}\text{S}_2 + 0.25 \text{Cu}^{2+} + \text{Fe}^{2+} + 2.5e^- \quad (24) \quad [7, 34]
\]

\[
n\text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Cu}_{n-1}\text{Fe}_n\text{S}_{2n} + 2e^- \text{ (slow)} \quad (25a)
\]

then \(\text{Cu}_{n-1}\text{Fe}_n\text{S}_{2n} \rightarrow \text{Fe}^{3+} + \text{Cu}_{n-1}\text{Fe}_n\text{S}_{2n} + 3e^- \quad (25b) \quad [35]

\[
\text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{FeS}_2 + 2e^- \quad (26a)
\]

then \(\text{Cu}^{2+} \rightarrow x\text{Cu}^{2+}_{(\text{ads})} + (1-x)\text{Cu}^{2+}_{(\text{aq})} \) (slow) \quad (26b)

then \(\text{Cu}^{2+}_{(\text{ads})} + \text{FeS}_2 \rightarrow \text{CuS} + \text{Fe}^{2+} + \text{S}^{0} \quad (26c) \quad [29]

\[
\text{CuFeS}_2 + 3\text{OH}^- \rightarrow \text{CuS}^* + \text{Fe(OH)}_3 + 3e^- \text{ (alkaline solutions)} \quad (27) \quad [36]
\]

Figure 3.8: 1st and 2nd sweep cyclic voltammograms of chalcopyrite (Ward’s: electrode ch31) in 0.1 N \(\text{H}_2\text{SO}_4\) showing effect of sweep rate. Initiated in the positive direction from 0 V/Ag/AgCl. Unstirred.

The charge passed in the pre-wave did not greatly depend on the sweep rate: integration of the pre-waves in Figure 3.8, from 200 to 700 mV/Ag/AgCl, yielded charges of 18.8 mC cm\(^{-2}\), 27.0 mC cm\(^{-2}\) and 19.7 mC cm\(^{-2}\) for sweep rates of 20 mV s\(^{-1}\), 10 mV s\(^{-1}\) and 5 mV s\(^{-1}\), respectively. These values might have been reduced further if corrections for surface roughness were applied. These values agree well with published values for ground surfaces, generally reported within the range 15 to 60 mC cm\(^{-2}\) [7, 9, 37].
A redox process at ~0.20 V/Ag/AgCl can be observed in Figure 3.9 on the 20 mV s\(^{-1}\) scan. This is remarkably similar to that observed by Biegler and Horne at 0.16 V/SCE for chalcopyrite electrodes in unstirred 1M H\(_2\)SO\(_4\), which they attributed to the formation of chalcocite (see equation 28) on reduction scans followed by oxidation to CuS on positive-going sweeps. The process is well positive to the Cu\(^{2+}/Cu^0\) potential for the copper concentration likely in solution (around 0.04 V/Ag/AgCl).

\[
CuFeS_2 + 3Cu^{2+} + 4e^- \rightarrow 2Cu_2S + Fe^{2+} \quad \text{(28)}
\]

Figure 3.9: 1\(^{st}\) and 2\(^{nd}\) sweep cyclic voltammograms of chalcopyrite (Ward’s: electrode ch33) in 0.1 N H\(_2\)SO\(_4\) showing effect of sweep rate. Initiated in the positive direction from 0 V/Ag/AgCl. Unstirred. Pre-wave charge passed, 0.2-0.7 V/Ag/AgCl, 23.7, 24.4 and 32.0 mC cm\(^{-2}\) for sweep rates of 20, 10 and 5 mV s\(^{-1}\) respectively.

Figure 3.10 is directly comparable to Figure 3.9 with only the acid electrolyte changed. Biegler and Horne’s assertion that “the shape, position and area (i.e. charge) of the pre-wave depend on the mode of surface preparation but not much on the acid or the sample origin” [7] is borne out by these results, and contrary to those of Lu et al. [28, 38]. However, the data of Lu et al. was collected from significantly more concentrated solutions (0.5M and 1M) and frequently at higher temperature (70°C and 95°C). Like Biegler and Horne’s results, the second sweep is more telling of the differences between the two acid electrolytes, with “passivation” less complete in the case of the chloride lixiviant (Figure 3.10).
Cathodic processes at ~0.15 V/Ag/AgCl and ~0.37 V/Ag/AgCl are also evident in Figure 3.10. Similar features were noted by Biegler and Horne [7] in unstirred solutions, and were absent when the electrode was rotated. Addition of Cu$^{2+}$ or Fe$^{3+}$ to the system indicated that Cu$^{2+}$ in solution enhanced these waves, while Fe$^{3+}$ had no effect [7]. The extra cathodic wave observed in the chloride lixiviant was attributed to the stability of the aqueous CuCl$^{0}$ species.

![Figure 3.10: 1st and 2nd sweep cyclic voltammograms of chalcopyrite (Ward’s: electrode ch33) in 0.1 N HCl showing effect of sweep rate. Initiated in the positive direction from 0 V/Ag/AgCl. Unstirred.](image)

Again, the charge passed under the anodic pre-waves (Figure 3.10) had only a small dependence on the sweep rate: integration of the pre-waves in Figure 3.10 from 0.2 to 0.7 V/Ag/AgCl yielded charges of 14.2 mC cm$^{-2}$, 25.1 mC cm$^{-2}$ and 34.3 mC cm$^{-2}$ for sweep rates of 20 mV s$^{-1}$, 10 mV s$^{-1}$ and 5 mV s$^{-1}$, respectively.

The electrochemical response of solid chalcopyrite electrodes cut from massive material is notoriously unpredictable, leading some researchers to adopt a carbon-paste electrode (CPE) approach for electrochemical studies of these types of systems [28, 30, 32, 39, 40]. The primary focus of this thesis was not an intricate electrochemical analysis, and CPEs were found to be inappropriate for studies under 442 nm and 514.5 nm laser irradiation due to thermal acceleration of volatilisation of the non-conducting binder material. Despite the extensive use of solid chalcopyrite
electrodes throughout this study, these studies demonstrate that the electrochemical behaviour of chalcopyrites from different sources and under different experimental conditions is relatively consistent.

Integration of the pre-waves for Messina material and Mt Isa chalcopyrite in hydrochloric acid solution issued similar results to the Mt Isa samples, consistent with those reported above and comparable to those reported in the literature.

Figure 3.11 displays the evolution of the pre-wave for a Messina sample, followed by subsequent passivation of the surface on Sweep 2. In Sweep 3, a more negative switching potential leads to reduction of the pre-wave product and its reformation on the subsequent positive-going sweep. Some of the chalcopyrite itself was also reduced in the cathodic sweep to $-0.45 \, \text{V/Ag/AgCl}$, to a phase analogous to chalcocite $[\text{Cu}_2\text{S}]$ [7, 8, 28-30, 41, 42], which was then oxidised to a covellite-like phase in Sweep 4 (at $\sim 0.35 \, \text{V/Ag/AgCl}$). The anodic pre-wave magnitude is similar for the freshly ground surface, and that formed after the negative sweep to $-0.45 \, \text{V/Ag/AgCl}$, consistent with a surface-limited process. On the other hand the wave at $0.35 \, \text{V/Ag/AgCl}$ on Sweep 4 depends on the cathodic switching potential [7].

Comparison of Sweeps 1 and 4 show that current between the pre-wave and main anodic wave onset is higher in sweep 1 than in sweep 4. This has been observed by other researchers, though not commented upon, and is possibly related to oxidation of surface products formed during the interval between grinding the electrode surface and emplacement in the electrolyte.
Figure 3.11: Cyclic voltammogram of chalcopyrite (Messina, sample chb01) in 0.1N HCl. Cycled in positive direction from 0.057 V/Ag/AgCl at 10 mV s\(^{-1}\). Unstirred. Charge passed in pre-wave (0.2-0.7 V/Ag/AgCl): 24.2 mC cm\(^{-2}\).

Figure 3.12 (oxidation of Mt Isa chalcopyrite in chloride solution) more clearly shows the electrochemical features of this system. Again a pre-wave is observed, with the surface passivated on subsequent sweeps at high cathodic switching potentials. The cathodic process observed on Sweep 2 is notably different from that observed on Sweep 3, which has a distinct shoulder and substantially greater charge. Further cycling produces similar behaviour to that observed in Sweep 3, with progressive increases in the charges associated with the anodic process at ~0.32 V/Ag/AgCl and the cathodic process at ~0.3 V/Ag/AgCl. The anodic pre-wave at 0.55-0.60 V/Ag/AgCl remains roughly similar in area on subsequent sweeps. In each cycle, apart from the first, there is an approximate balance in the total cathodic and anodic charges.

The cathodic wave on Sweep 2 at –0.3 V/Ag/AgCl is characteristic of the reduction of the anodic pre-wave product, while cathodic waves on subsequent negative sweeps relate to the reduction of both the anodic pre-wave product and the covellite type species formed at 0.32 V/Ag/AgCl (this peak occurs where the oxidation of chalcocite is expected [43]):

\[
\text{Cu}_2\text{S} \rightarrow \text{CuS} + \text{Cu}^{2+} + 2e^- \quad (29)
\]

The surface formed by the process at –0.45 V/Ag/AgCl is therefore chalcocite (or a similar metal-excess sulfide such as bornite, digenite etc. which are known to form at these potentials [7]):

\[
2\text{CuFeS}_2 + 6\text{H}^+ + 2e^- \rightarrow \text{Cu}_2\text{S} + 3\text{H}_2\text{S} + 2\text{Fe}^{2+} \quad (30)
\]

as is:

\[
2\text{CuS} + 2\text{H}^+ + 2e^- \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{S} \quad (31)
\]

In either case, the charges produced by these reduction and oxidation reactions are stoichiometric and account for the charge balancing observed in the voltammetry. The shoulders observed on the cathodic and anodic waves around these processes are due to the complexity of these systems where a number of intermediate metastable phases can exist.
Figure 3.12: Cyclic voltammograms of chalcopyrite (Mt Isa, sample chik2) in 0.1N HCl. Cycled in positive direction from 0.200 V/Ag/AgCl at 5 mV s⁻¹. Unstirred. Charge passed in pre-wave (0.2-0.6 V/Ag/AgCl): 19.7 mC cm⁻².

Figure 3.13 displays the effect of switching potential on the electrochemical response of the Messina chalcopyrite in 0.1 M H₂SO₄. The features are similar to those observed in chloride system. The pre-wave charge is again similar to that observed for other chalcopyrite samples and electrolytes.

Normal Raman spectroscopy is clearly not suited to detecting pre-wave products formed during a voltammetric cycle which are of the order of ~20 nm (based on complete oxidation to sulfur, and the charge passed), hence long-term potentiostatic experiments were conducted.
Figure 3.13: Cyclic voltammograms of chalcopyrite (Messina, chb01) in 0.1 M H$_2$SO$_4$ showing effect of cathodic switching potential. Cycled in positive direction from 0.100 V/Ag/AgCl at 5 mV s$^{-1}$. Unstirred. Charge passed in pre-wave (0.2-0.7 V/Ag/AgCl): 27.7 mC cm$^{-2}$.

3.3.2. Potentiostatic investigations

In situ normal Raman spectroelectrochemical investigations were attempted in both chloride and sulfate media. However, the integrated anodic leaching and Raman interrogation of chalcopyrite in sulfate solutions proved to be too slow (>48 hours) for product to be observable by this technique, and an ex situ approach was therefore adopted. Transpassive anodic leaching of chalcopyrite in chloride systems was amenable to in situ investigative techniques as product was observed within a reasonable timeframe. This difference in behaviour would indicate that leaching in the sulfate lixiviant is either inhibited over that in the chloride system, or that a different, Raman-inactive product is formed in the sulfate system.

Electrochemical investigations by other researchers have demonstrated that chalcopyrite oxidation processes under potentiostatic control or with ferric leachants are comparable [9, 28, 31, 38]. For instance, Lazaro and Nicol [31] found that either potentiostating chalcopyrite in a sulfate solution at the mixed potential found for a ferric solution (0.04 M Fe$^{3+}$ in 0.1M H$_2$SO$_4$) or leaching at open-circuit potential
(OCP) in this second solution achieved comparable rates of dissolution (5 x 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1} at 60^\circ\text{C}). XPS and voltammetric investigations of chalcopyrite leached in ferric lixiviants versus potentiostatic leaching by Mikhlin et al. [37] indicated similar consistency for both chloride and sulfate lixiviants at room temperature. The surface layer does not inhibit the rate of leaching in chloride solutions at moderately elevated temperatures (80^\circ\text{C}); after the layer thickness has reached steady state generally linear kinetics are reported, although the anodic pre-wave still occurs in chloride systems. In aqueous sulfate media, the layer does appear to inhibit leaching as “parabolic” kinetics have been observed through a constantly thickening layer [4, 44], although linear behavior has also been reported [45]. Parker et al. [9] postulated that the oxidation of chalcopyrite is limited by transport of ions through an unstable film of semi-conductor metal-deficient (poly)sulfide. The product film achieves an equilibrium thickness and decomposes thermally. Parker et al. [9] noted that electron transfer rates decrease in the series: \text{Br}_2, \text{I}_3^-, \text{CuCl}_2 > \text{FeCl}_3 > \text{Fe}_2(\text{SO}_4)_3. This may explain why a FeCl_3 leach follows paralinear kinetics, as product CuCl_2 would be generated. Other theories include the formation of cryptocrystalline sulfur in chloride media as opposed to amorphous sulfur in sulfate media [38, 46] because the activation energies reported for leaching in chloride and sulfate media are different [47].

**In situ** examination of chalcopyrite oxidation in the transpassive region in acid chloride solutions was possible, with rhombohedral sulfur product layers evident within 24 hours when using the Mt Isa material. Figure 3.14 displays the chalcopyrite electrode surface in the electrochemical cell at open-circuit potential and after 22 hours oxidation in 0.1 HCl at potentials in the transpassive region (b) and in the main anodic wave (d). The unpolished surface and intervening cell/solution make it difficult to observe the product layer in the transpassive region, although comparison of the micrographs shows some clear differences. Observation of the product layer is clear when the chalcopyrite has been oxidised at a higher potential (c, d).
Figure 3.14: Mt Isa chalcopyrite surface in 0.1M HCl (x20 ULWD micrograph) at open-circuit potential (a,c) and after 22 hours potentiostated at 0.570 V/Ag/AgCl (b) or 0.690 V/Ag/AgCl (d).

Figure 3.15 clearly displays the emergence of product sulfur on the Mt Isa chalcopyrite surface oxidised in the transpassive region, with the distinct stretching ν(SS) band at ~474 cm⁻¹ and bending modes δ(SSS) at ~150 and ~220 cm⁻¹ in addition to the chalcopyrite Raman bands (see Figure 3.2 and Figure 3.7 for reference spectra). The intensity ratio (I₄₇₄/I₁₂₂₀) of the stretching to bending modes is 1.4, in close agreement with the intensity ratio expected for rhombohedral sulfur. Integration of current-time curves, and assuming complete oxidation to sulfur:

\[
\text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}^0 + 4e^- \quad (32)
\]

with a chalcopyrite density of 4.3 g cm⁻³ [48] indicates chalcopyrite oxidation to a depth of ~2.3 µm over 22 hours, producing a ~1.7 µm layer of elemental sulfur.

Bands at ~160 cm⁻¹ and ~180 cm⁻¹ are also evident in Figure 3.15, though these are due to solution and/or cell window interference as they are also observed on the unoxidised surface and in spectra collected for the solution/cell in the absence of the electrode (see Figure 3.16). These bands are not due to chloride species as they are observed in spectra collected from both chloride and sulfate solutions.
Figure 3.15: Raman spectra recorded from Mt Isa chalcopyrite surface in 0.1 M HCl at open circuit potential and held at potential 0.570 V vs. Ag/AgCl over time (excitation wavelength: 442 nm; irradiation density: 0.05 kW cm\(^{-2}\) (22 hour scan) 0.102 kW cm\(^{-2}\) (other scans); 10s x 10 accumulations).

Figure 3.16: Raman spectrum of 0.1M HCl solution and cell window used in the oxidation experiments (excitation wavelength: 442 nm; laser power: 9 mW; 10s x 5 accumulations).

Figure 3.17 demonstrates the appearance of another distinct band at 452 cm\(^{-1}\) under 442 nm irradiation. It should be noted at this point that, unless otherwise indicated, the laser was only focussed on the sample surface for spectra collection, and was turned off at all other times. Such features were observed rarely under 514.5 nm
irradiation. The photo-induced material was not observed under 632.8 nm or 785 nm irradiation.

The photo-induced material gave a Raman band at a frequency of ~452 cm\(^{-1}\), attributable to a \(\nu(\text{SS})\) vibration, distinct from that of rhombohedral sulfur or covellite at ~474 cm\(^{-1}\). It also showed none of the detectable bending modes (\(\delta(\text{SSS})\)), which are observable in polysulfides and ring allotropes. As the ratio between the sulfur bands and main chalcopyrite bands remains approximately constant with the appearance of the laser-induced phase, it would appear that the formation of this phase is not associated with breakdown of the chalcopyrite lattice or elemental sulfur.

No photocurrents were detected with the appearance of the photo-induced phase, though the laser spot size is sufficiently small that detection would be difficult. However, other researchers have found no evidence of chalcopyrite photosensitivity in electrochemical experiments [49, 50]. Indeed, Figure 3.18 clearly demonstrates that ample oxidised product must be present on the chalcopyrite surface in order for the induced phase to form under irradiation since even long periods at high irradiation densities failed to yield detectable induced phase on fresh chalcopyrite surfaces.

Previously published studies demonstrate that the photo-polymerisation of octasulfur under the conditions of the experiment is unlikely. Photodecomposition of sulfur under UV light to form sulfur radicals and polymerisation products is well known [26, 51-54]. However, Geyer et al. [55] reported on the dependence of the polymerisation of sulfur on the wavelength of irradiating light. They found that S\(_8\) molecules condensed onto polycrystalline gold surfaces to form a continuous film desorbed under irradiation (maximum desorption rate occurred at 255 nm) and light-induced polymerisation of the film occurred maximally at 328 nm, with no detectable polymerisation at 418 and 437 nm. Steudel and Eckert [54] note that all sulfur allotropes are light sensitive in both the solid state and in solution. Homolytic cleavage of sulfur bonds and formation of free radicals will occur is the energy of the absorbed photons is sufficiently high. The thermal bond dissociation energy in liquid sulfur is 150 kJ mol\(^{-1}\) corresponding to a wavelength of 800 nm [54]. However, the extinction coefficient of most sulfur molecules is very low at wavelengths >430 nm [56]. S\(_8\) shows an absorbance maximum at 264 nm, and a shoulder at 276 nm with a steep decrease in the absorbance above 290 nm [56]. Thermal Raman studies also indicate a lack of elemental sulfur conversion to yield detectable radicals/chains under comparable conditions [57, 58].
Figure 3.17: Effect of laser power and time under laser on observed spectrum of Mt Isa chalcopyrite held at 0.570 V vs. Ag/AgCl in 0.1 M HCl for 22 hours time (excitation wavelength: 442 nm; irradiation density: 0.05 kW-0.102 kW cm\(^{-2}\); 10s x 10 accumulations).

Figure 3.18: Effect of laser power and time on a freshly fractured Mt Isa chalcopyrite surface in air (excitation wavelength: 442 nm; irradiation density: 0.05-0.5 kW cm\(^{-2}\); 10s x 10 accumulations).

Investigation of the Messina and Ward’s material demonstrated oxidation of these samples is somewhat inhibited over that of the Mt Isa chalcopyrite. For instance, a
rhombohedral sulfur spectrum was not detected on the surface of Messina chalcopyrite after 46 hours oxidation at 0.570 V/Ag/AgCl in 0.1M HCl (current-time data indicate less <300 nm of product). A spectroelectrochemical study using the Ward’s chalcopyrite showed the development of the laser-induced phase in the absence of rhombohedral sulfur (Figure 3.19). This is consistent with the observation that the recrystallized phase on the Mt Isa samples was not due to the composite nature of the sample and confirms it was not due to a decomposition reaction of the rhombohedral sulfur product layer (see Figure 3.20). The ν(SS) band at 452 cm\(^{-1}\) has been normalised against the main chalcopyrite phonon mode at 291 cm\(^{-1}\) in Figure 3.20 and demonstrates that the band continues to grow under 442 nm irradiation until a maximum intensity is reached.

Figure 3.19: Effect of laser irradiation (labels refer to length of irradiation time) on spectra recorded from Ward’s chalcopyrite surface in 0.1 M HCl held at potential 0.590 V vs. Ag/AgCl for 20 hours (excitation wavelength: 442 nm; irradiation density: 0.50 kW cm\(^{-2}\); 10s x 10 accumulations).
Figure 3.20: Section of spectral region presented in Figure 3.19 showing growth of \( \sim 452 \text{ cm}^{-1} \) band (relative intensity, normalised against the chalcopyrite lattice mode at \( \sim 291 \text{ cm}^{-1} \)) with irradiation time.

The recrystallised phase contains no detectable \( \nu(\text{SO}) \) Raman bands, which occur between 900 and 1300 cm\(^{-1}\) [59, 60], or \( \nu(\text{SH}) \) Raman bands, which occur between 2498 cm\(^{-1}\) (pentasulfane) and 2632 cm\(^{-1}\) (hydrogen sulfide)[59, 61-66], as shown in Figure 3.21. Other than the bands expected for chalcopyrite and the recrystallised phase, filter ripple and cell/solution components are observed, since these same features are found in extended spectra of the solution/cell in the absence of the electrode.
Figure 3.21: Extended Raman scan of Ward’s chalcopyrite surface laser-induced phase (oxidised in 0.1M HCl at 0.59 V/Ag/AgCl for 20 hours; Excitation wavelength: 442 nm; irradiation density: 0.50 kW cm$^{-2}$; 10s x 10 accumulations).

Laser-induced phenomena are not unusual and have proved useful in the study of a number of systems. Laser-induced changes have been used to investigate the oxidation of galena which itself has no Raman-active modes [67], as well as the transformations in the iron oxide system – Mazzetti and Thistlethwaite [68] found different thermal transformation behaviour of amorphous 2-line and 6-line ferricydrite via laser recrystallisation combined with Raman spectroscopic detection.

In the present study, irradiation density at the sample surface was $<$1 kWcm$^{-2}$ not accounting for further scattering of incident light via glass and solution. In general, laser-induced transformation of materials is not desirable but, in the present case, valuable information has been obtained. Freshly fractured chalcopyrite surfaces did not display spectral changes with time or laser power (other than linear dependence on incident intensity) in air or solution media at open-circuit potential (see Figure 3.18). Thus the observed spectral changes with time and laser power after anodic polarisation appear to be due to a surface product layer.
3.3.3. **The effect of radiation**

Clearly, 442nm excitation has an effect on the oxidation of chalcopyrite. Other Raman studies of sulfide mineral oxidation have used a 514.5 nm excitation source. While less energetic than 442 nm radiation, a 514.5 nm laser source was noted to have an effect on the oxidation rate and products of pyrite oxidation [69]. It would be expected that 632.8 nm excitation would be the least likely to affect oxidation rate and product development.

Figure 3.22 displays the effect of continuous laser irradiation on the observance of product on a Messina chalcopyrite oxidised in 0.1M HCl under 632.8 nm irradiation. The Messina chalcopyrite was the most recalcitrant to oxidation of the chalcopryites used in this study. Continuous irradiation yielded detectable localised product sulfur in just over 2 hours as opposed to a non-irradiated site in which product took 46 hours to develop. On the non-irradiated sample, product development was somewhat patchy, with sulfur not evident over the most of the surface, although product was present at the edge of fracture sites. This is not surprising as the charge passed indicates <100 nm of product sulfur formed in 23 hours. There was no evidence of ν(SO) or ν(SH) Raman modes. There was no difference in the current observed between irradiated and non-irradiated studies which may be attributable to the laser spot size being only ~0.0055% of the active surface.

Figure 3.23 displays the effect of continuous laser irradiation on the Messina chalcopyrite oxidised in 0.1M H\textsubscript{2}SO\textsubscript{4}. Again, a laser effect is noted, with localised product sulfur evident within 12 hours. In the previous section it was noted that even the more reactive Mt Isa chalcopyrite did not yield observable product when oxidised in a sulfate electrolyte for 48 hours.

Whether irradiated or not, oxidation was much faster in the chloride lixiviant than in sulfate. This agrees well with the literature. For the Messina chalcopyrite at 25°C, the oxidation rate in chloride was approximately three times greater than in sulfate which is similar to the increase in pre-wave current Lu et al. [28] found in the presence of chloride ions at 20°C for Mt Isa chalcopyrite.
Figure 3.22: Effect of continuous laser irradiation on spectra recorded from Messina chalcopyrite (Electrode chb01) surface in 0.1 M HCl held at potential 0.570 V vs. Ag/AgCl (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm\(^{-2}\); 10s x 1 accumulations). The non-irradiated spectra taken at 46 hours relates to different sites and demonstrates product heterogeneity.

Figure 3.23: Effect of continuous laser irradiation on spectra recorded from Messina chalcopyrite (Electrode chb01) surface in 0.1 M H\(_2\)SO\(_4\) held at potential 0.570 V vs. Ag/AgCl (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm\(^{-2}\); 10s x 1 accumulations).
3.3.4. The effect of leachant (counter ion)

Mt Isa chalcopyrite was oxidised (non-potentiostatically) in ferric leachants to compare with data obtained in potentiostatic experiments. Given that current could not be measured, the appearance of sulfur on the surface (obtained using 632.8 nm irradiation) was measured. The potential measured with a chalcopyrite electrode was 50 mV lower in the sulfate leachant compared to the chloride leachant, although the solution E_H measured with a platinum electrode was virtually identical. In the absence of ferric ions, the potential measured at the chalcopyrite electrode was ~260 mV in both cases. Thus, the oxidation potential tends to be lower in sulfate solutions. However, even in potentiostated experiments where the potential is forced to the same value (see Figure 3.25), oxidation is more recalcitrant in sulfate lixiviants than in chloride solutions.

Figure 3.24: Potential measured at a Mt Isa chalcopyrite electrode in equivalent ferric chloride and ferric sulfate solutions (0.1M in acid) with time. E_H measured using a Pt electrode: 0.58 V/Ag/AgCl in the sulfate solution and 0.57 V/Ag/AgCl in the chloride solution.

Similar trends are replicated for ferric solutions as for potentiostated solutions, with a radiation effect also evident in ferric solutions (not shown) and increased oxidation in ferric chloride solutions over ferric sulfate solutions (Figure 3.26). The timeframes for product appearance in ferric solutions versus potentiostated solutions are not dissimilar (compare Figure 3.26 and Figure 3.27).
Figure 3.25: Long-term current-time behaviour for Messina chalcopyrite oxidised at 0.570 V/Ag/AgCl in 0.1M acid solution.

Figure 3.26: Oxidation of Mt Isa (chi01) chalcopyrite in different ferric leachants (0.005M Fe$^{3+}$, ~0.1M H$^+$) under a nitrogen atmosphere. Non-irradiated. $E_H$ measured using a Pt electrode: 0.58 V/Ag/AgCl in the sulfate solution and 0.57 V/Ag/AgCl in the chloride solution. Excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 5s x 10 accumulations.
3.3.5. The effect of potential

Figure 3.28 displays product development at various potentials for a Mt Isa chalcopyrite electrode. At any potential within the transpassive region, product development required many hours, and current densities stabilised to <30 µA cm\(^{-2}\). After 35 minutes, the chalcopyrite oxidised at 0.85 V/Ag/AgCl (i.e. in the main anodic wave) showed a product spectrum and yielded a current >100x that of samples oxidised in the transpassive zone for equivalent time. In the main anodic region ~1.5 µm of product formed in just 30 minutes indicating passivation was not occurring.
3.3.6. **The effect of temperature**

Not surprisingly, given the kinetic effect of continuous 632.8 nm irradiation, raising the temperature speeds the appearance of product sulfur in both chloride and sulfate lixiviants. Elemental sulfur was evident on chalcopyrite in a solution of ferric chloride in a matter of minutes (Figure 3.29) indicating a rate enhancement >10x that at room temperature. Clearly, oxidation in sulfate solutions was enhanced also (Figure 3.30). In this case, the potential was chosen to match the potential measured at the chalcopyrite electrode in ferric sulfate solutions. Relative currents indicate an increase in Messina chalcopyrite’s oxidation rate of 30 times. As per previous studies, no ν(SH) or ν(SO) bands were observed and the primary solid phase product was elemental sulfur. Further studies at elevated temperature were not undertaken due to several factors:
the potential for a change in mechanism at high temperatures (reports have been published indicating a mechanism change in the region to 80°C [7, 28, 70] effectively eliminating the passivation reaction);

- extensive investigations reported elsewhere [28, 47, 71, 72];

- the potential damage to microscope objectives;

- the instability of the epoxy resin casing on chalcopyrite electrodes at these temperatures; and

- uncertain stability of the Ag/AgCl reference electrode at these temperatures.

Figure 3.29: Oxidation of Mt Isa (chi01) chalcopyrite in 0.005M FeCl$_3$ (0.1M HCl) under a nitrogen atmosphere at 75°C (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 5s x 10 accumulations).
3.4. In situ investigations of other sulfide minerals

As noted previously, the oxidation of selected sulfide minerals was briefly investigated. Structurally related minerals, such as sphalerite, were examined and oxidative processes and products compared to those for chalcopyrite. Proposed intermediate phases in chalcopyrite oxidation, such as pyrite and covellite, were examined with a view to clarifying the similarities and differences in their redox processes and products to chalcopyrite.

Pyrite, in particular, has been a focus of literature research due to acid mine drainage implications and, so, is a useful mineral for verifying experimental techniques in these types of systems. Covellite, being a binary copper compound, which is particularly recalcitrant to oxidation, also makes a good model compound for a variety of instrumental techniques.

3.4.1. Pyrite

The electrochemical properties of pyrite have been extensively studied, and hence this mineral was deemed appropriate as both a natural model system to test the
experimental arrangement, and to investigate surface oxidation products under 442 nm irradiation.

Electrochemical studies on the anodic dissolution of pyrite show that oxidation does not occur until a relatively high potential is reached (compared to copper and lead sulfides) [50]. The maximum anodic thermodynamic stability range for pyrite is described by [73]:

$$\text{FeS}_2 \rightarrow \text{Fe}^{2+} + 2\text{S}^0 + 2\text{e}^- \quad (33)$$

The standard potential for this reaction is ~0.34 V/SHE; yet, pyrite’s rest potential is about 0.62 V/SHE and it does not decompose at an appreciable rate on standing in acid [73].

In 1M HClO$_4$ at 25°C, the only electrode reaction of consequence produces sulfate at 0.81 V/SHE [50]:

$$\text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 15\text{e}^- \quad (34)$$

Koch [50] notes that the high potentials required for pyrite oxidation are consistent with the presence of a passive film and also explain its lack of reactivity during oxygenated pressure leaching. In contrast, other researchers note the quantitative oxidation of the majority of sulfide minerals to elemental sulfur under similar conditions [74, 75].

Pyrite is often perceived as being very reactive due to the environmental implications of the above acid-producing reaction (Equation 34). However, pyrite has been described as the most noble of the sulfide minerals, having a high standard electrode potential [75, 76]. Pyrite is a good electrocatalyst for oxygen reduction and hydrogen evolution [77]. Because it provides a facile cathodic process, galvanic coupling between sulfide minerals and pyrite results in an increased rate of oxidation of these minerals. Oxidation rates of pyrite and chalcopyrite alone are comparable (Figure 3.31).
The product sulfur/sulfate ratio depends on oxidation conditions: higher temperatures foster increased elemental sulfur production [79], and elemental sulfur yields are greatest at low pH [77, 80]. There appears to be no significant changes to oxidation mechanism between pH 4.6 and 13 and, at potentials beyond 0.8 V/SHE, elemental sulfur is oxidised to sulfate [77]. Oxidation by more than one path has been postulated [74, 77, 81] which is not surprising given that oxidation of disulfides may require up to 7 elementary steps [82]. Sulfoxy anions have been identified in pyrite oxidation experiments [83] but there is, as yet, little agreement on their role in the oxidative mechanism. In acidic solution, thiosulfate (S$_2$O$_3^{2-}$) decomposition is rapid, in any case [61-63], and is postulated to be a mechanism by which sulfur forms on the surface [84].

Molecular orbital studies have demonstrated that the oxidant binding to the pyrite surfaces occurs through a persulfido bridge such that continued bridging will form S$_2$O$_3^{2-}$ [79]. The mechanism allows for facile pyrite oxidation by Fe$^{3+}$ but not O$_2$ [79] with oxidation being surface reaction limited [79, 80, 82, 85]. Oxygen isotope studies have demonstrated that the oxygen atoms incorporated into the sulfate product derive from water, and not molecular oxygen, thus establishing an electrochemical
mechanism in preference to a molecular mechanism [74]. Chloride ions have been shown to inhibit elemental sulfur deposition on pyrite surfaces under ambient conditions, possibly through the promotion of thiosulfate oxidation to tetrathionate (S$_4$O$_6^{2-}$) [86]. They also remove passive layers containing hydroxylated ferric ions [86]. Key observations in the spectroelectrochemical study of pyrite oxidation by Lehmann et al. [86] included:

- In 1M H$_2$SO$_4$ at 25°C and electrode rotation rates of 1000 rpm, pyrite oxidation commenced at 0.4 V/SCE with no commensurate current observed at a glassy carbon (GC) ring held at 1.1 V/SCE or −0.7 V/SCE. A cathodic current is observed on the ring when held at −0.7 V/SCE but no current was observed when the ring was held at 1.1 V/SCE as the disc electrode is swept beyond 0.6 V/SCE. This indicates the release of ferric ions.

- An anodic ring current (ring held at 1.1 V/SCE) is observed at pyrite potentials >0.7 V/SCE attributable to oxidation of pyrite, and increased with increasing pyrite potential. This is not likely due to ferrous oxidation (the potential being too high). Chloride ions increased the anodic ring current.

- The reduction peak for pyrite at −0.4V/SCE, attributable to sulfur reduction, is smaller in the presence of chloride ions. Calculations involving charges passed indicate chloride represses sulfur formation. Also, anodic collection efficiencies increase at the ring (1.1 V/SCE) with increasing chloride concentration. The reduction peak correspondingly decreases.

- Ring-disc rotation rate did not affect collection efficiencies (ring held at 1.1 V/SCE) indicating a stable product was formed from a solid-state process at the pyrite electrode, rather than an intermediate formed between the ring and disc.

- High overpotentials were required to be applied to the ring electrode to produce anodic current, indicating tetrathionate, as it is relatively stable in acid solutions. As there was no concomitant ferrous ion detection, and direct production of tetrathionate is unlikely, oxidation of thiosulfate catalysed by the pyrite surface is likely.

Lehmann et al. [86] also collected Raman spectra but the results were not appreciably different from those reviewed in Chapter 2 of this thesis [15, 69] other than that sulfur product peak intensities were reduced in chloride containing solutions. High
overpotentials (and therefore possibly different mechanisms) were required to obtain product spectra in reasonable timeframes.

Figure 3.32 displays a cyclic voltammogram for pyrite, collected in acid, with features typical of the system. There is a very small step at ~0.6 V/Ag/AgCl which might be due to ferrous oxidation, and which has been reported absent on rotated electrodes [86]. The corresponding cathodic peak at 0.5 V/Ag/AgCl is also absent on rotation [77]. The cathodic peak at ~0.3 V/Ag/AgCl corresponds to the reduction of sulfur:

\[ S + 2H^+ + 2e^- \rightarrow H_2S \]  

(35)

and on the second sweep a small anodic process ~0.1 V/Ag/AgCl is evident, being the reverse of Equation 35, which is also not observed on rotation [77]. The potentials at which the events occur agree closely with those of Hamilton and Woods [77] in pH 4.6 solution after adjustment is made for the higher acidity of this study. The onset of anodic current occurs at 0.300 V/Ag/AgCl.

Taking account of stoichiometry, using Equations 33 and 34 and assuming oxidation above 0.55 V/Ag/AgCl produces ferric iron, the relative charges passed in anodic and cathodic processes can indicate the amount of sulfate produced relative to sulfur. Thus, the product ratio of sulfate to sulfur under the conditions shown in Figure 3.32 is approximately 1, with sulfur slightly in excess. This corresponds to an oxidation depth of approximately 33.8 nm, using a density value from [22] and making no allowance for surface roughness. The sulfate/sulfur ratio found is similar to that reported in other strongly acidic chloride media [84, 87]. Other researchers have proposed that the oxidation process appears to be nonstoichiometric in acid solution, with loss of iron and formation of a sulfur-rich overlayer. The product layer is frequently claimed to consist of polysulfides [1, 15, 27, 69, 88-90] although, on one occasion, it has been interpreted to be thiosulfate despite the lack of observable ν(SO) modes [86].
Figure 3.32: Cyclic voltammograms of pyrite (Chinese) in 0.5M NaCl (pH 2). Initiated in the positive direction from –0.45 V/Ag/AgCl at 10 mV s\(^{-1}\). Unstirred.

Figure 3.33 displays spectra of oxidation products on Chinese pyrite after 17 hours oxidation. Prior to oxidation, only the bands attributable to pyrite phonon modes at 340 cm\(^{-1}\) and 380 cm\(^{-1}\) are observed, even at higher laser intensities. Once oxidation has progressed sufficiently, the presence of elemental sulfur on the pyrite surface is clearly observed with distinguishing bands at 150, 220 and 471 cm\(^{-1}\). As in the case of chalcopyrite, a laser-induced product formed under 442 nm laser irradiation, showing the same vibrational frequency as the photo-induced product on chalcopyrite (~452 cm\(^{-1}\)). Assuming about half the product is elemental sulfur, the product layer is several µm thick based on the charge passed at the time the spectra were collected. As per the chalcopyrite experiments, laser irradiation of the sample was restricted to spectra collection only, corresponding to irradiation to oxidation time ratios of about 1/50.

Occasionally a broad Raman band at ~610 cm\(^{-1}\) was evident (as observed in Figure 3.33). It was not associated with \(\nu(SO)\) or \(\delta(HOH)\) modes and was not observed on comparable chalcopyrite spectra of the recrystallised product. It is expected that sulfate would be observed in the oxidation of pyrite and, while adsorbed sulfate is not likely to be observed, several millimetres of solution are interposed in the laser path to the sample surface. While sulfate has a weak bending mode (F\(_2\)) at ~610 cm\(^{-1}\) [64], it is about \(1/4\) the intensity of the symmetric A\(_1\) mode at 981 cm\(^{-1}\) [59]. The lack of
v(SO) modes also precludes sulfate salts such as jarosite [91-93], schwertmannite [68] or roemerite [91] being candidates, and the hydrated oxides (ferrihydrite, goethite, lepidocrocite), which are poor Raman scatterers, are also unlikely due to the lack of δ(HOH) modes [68, 94]. The anhydrous oxides (hematite, maghemite) also yield poor Raman spectra, but distinguishing modes are again missing [68, 95]. In addition, anhydrous oxides are highly unlikely products, particularly under the pH conditions of the experiment and the production of sulfate would only increase the acidity with time. A sensible assessment of expected long-term products would lead to jarosite or a similar amorphous sulfate salt under the conditions of this investigation. It is possible that an amorphous sulfate salt would transform under irradiation to yield an oxide product and hence the poor Raman spectrum with lack of v(SO) distinguishing features.

Figure 3.33: Raman spectra recorded from Chinese pyrite surface in 0.5 M NaCl (pH 2) at open-circuit potential and held at potential 0.700 V vs. Ag/AgCl over time (excitation wavelength: 442 nm; irradiation density: 0.2 kW cm\(^{-2}\) (17 hour scans) 0.102 kW cm\(^{-2}\) (other scans); 10s x 10 accumulations).

Figure 3.34 displays a site on the chalcopyrite surface which has been oxidised for 17 hours at 0.700 V/Ag/AgCl then subjected to various laser powers. It is observed that the band at \(~452\) cm\(^{-1}\) increases in intensity with irradiation density, and that the v(SS) band at \(~471\) cm\(^{-1}\) does not change (when normalised to the pyrite phonon mode at
380 cm\(^{-1}\)). Indeed the \(\delta(\text{SSS})\) modes (not shown in this figure) at \(\sim 220 \text{ cm}^{-1}\) and \(\sim 150 \text{ cm}^{-1}\) also remain constant concurrent with the appearance of the laser-induced phase. This further supports observations in the previous section that the laser-induced phase is not a breakdown product of elemental sulfur.

Other Raman studies of pyrite oxidation have used the Argon ion 488 or 514.5 nm line as the excitation source. In each study, broadness in the region 440 to 473 cm\(^{-1}\) was observed and attributed to \(\nu(\text{SS})\) polysulfide modes [1, 15, 27, 69, 89], even though Lehmann \textit{et al.} [86] tentatively attributed it to thiosulfate despite the lack of \(\nu(\text{SO})\) modes. They explained this in terms of adsorption of the thiosulfate (complexation through the oxygen leading to downshifting of the \(\nu(\text{SO})\) mode, supported by literature studies) and subsequent peak broadening. Despite the fact it is extraordinarily unlikely that an adsorbed layer would be observed in a normal Raman investigation, the electrode was rotated at 200 rpm during spectral collection indicating non-electrostatic adsorption if the product is indeed adsorbed. Sasaki \textit{et al.} [90] claimed \(\nu(\text{SS})\) modes at \(\sim 460 \text{ cm}^{-1}\) (which appears as a weak shoulder of the major elemental sulfur mode) were noise and noted they were eliminated with elemental sulfur after treatment with cyclohexane. However, the shoulder was very weak to begin with and still appears slightly evident after the cyclohexane treatment.

Polysulfide assignments in the aforementioned sulfide mineral oxidation studies were based on the Raman studies of crystalline polysulfides by Janz \textit{et al.} [96-98], later revisited and expanded upon by El Jaroudi \textit{et al.} [57, 99, 100]. Of particular note in these studies was that, excepting some of the \(\text{S}_2^{2-}\) and \(\text{S}_3^{2-}\) compounds, the complex polysulfide structure leads to multiple \(\nu(\text{SS})\) Raman bands centred about 470 cm\(^{-1}\), with \(>1\) mode generally being present at \(>480 \text{ cm}^{-1}\) shifts of moderate to strong intensity. The lack of the appearance of such bands in the pyrite and chalcopyrite studies reported to-date would indicate that only low chain length polysulfides were being observed and that such polysulfides were constrained, or that polysulfides were not, in fact, being detected.
Figure 3.34: Effect of laser irradiation power on spectra recorded from Chinese pyrite surface in 0.5 M NaCl (pH 2) held at potential 0.700 V vs. Ag/AgCl for 20 hours (excitation wavelength: 442 nm; irradiation density: 0.05-0.50 kW cm\(^{-2}\); 10s x 10 accumulations).

El Jaroudi et al. [99] noted that, for inorganic polysulfides, the nature of the cation is important in determining the structure and reactivity of the polysulfide anion. Since the inorganic polysulfides are ionic substances [101], the anion geometry is directly related to the cationic electromagnetic field [99, 100]. Steudel [101] notes that polysulfides have been prepared with many different types of cations. Various metal polysulfido complexes (primarily Pt, V, Rh, Nb, Ir, W, Ru, Re, Mo and Sn) have been synthesised: the disulfido complex charge distribution lies between those for \( \text{S}_2^- \) (200 pm, 589 cm\(^{-1}\)) and \( \text{S}_2^{2-} \) (213 pm, 446 cm\(^{-1}\)), with higher complexes showing a range of bond lengths [102].

At low pH, polysulfides in solution will precipitate \( \text{S}_8 \) [101]. Sulfite ions also rapidly react with polysulfide to produce sulfoxy anions [101]. Taken into account, reports of the observance of polysulfides during pyrite oxidation seem unlikely. In this case, the 442 nm laser definitely facilitates the formation of a phase with sulfur-sulfur bonds, but it does not appear to be a polysulfide, nor does it have a distinct cation interaction. Numerous studies have shown that oxidation of both pyrite and chalcopyrite produce metal-deficient product phases (this is demonstrated again later in this thesis). In the
case of chalcopyrite, this phase is more deficient in iron than copper [29, 34, 36, 37, 44, 70, 71, 103-105] while, in pyrite, iron is clearly the major cation present. Even if iron was the polysulfide-complexing cation in both minerals, iron is present in the chalcopyrite structure as ferric iron, versus ferrous iron in pyrite [20], and the minerals structures are substantially different, presumably leading to vastly different electromagnetic fields and, hence, different polysulfide products in both systems.

To allow direct comparison with published Raman studies of pyrite, experiments were also conducted using a 514.5 nm excitation source (Figure 3.35 to Figure 3.37). Samples again showed a response to laser irradiation, although not leading to the same phase as that found under 442 nm irradiation. Normalised spectra of a pyrite sample held at 0.700 V/Ag/AgCl are displayed in Figure 3.35. When oxidation has just commenced, only the standard pyrite bands are observed at 380 and 340 cm$^{-1}$. After oxidation has proceeded for 40 minutes, a band at ~450 cm$^{-1}$ is observed which, at first glance, appears similar to the observations under 442 nm irradiation. Mycroft et al. [69] observed a similar band at 454 cm$^{-1}$ after 2 hours oxidation in NaCl under 514.5 nm irradiation. However, accompanying this band is a shoulder to the pyrite band, located at ~394 cm$^{-1}$. By comparison, the spectra of Mycroft et al. [69] were not sufficiently resolved to note the presence or absence of this. The band at 394 cm$^{-1}$ is accompanied by broad bands at ~268 cm$^{-1}$ (observed in the scan of Mycroft et al. [69]), 662 cm$^{-1}$ and 997 cm$^{-1}$ (Figure 3.36). These are remarkably similar to the major modes of thiosulfate and tetrathionate published by Meyer et al. [59] and displayed in Table 3.3. However, the ν(SO) modes are greatly diminished or absent. This could be attributed to a loss of symmetry, through adsorption or electrostatic field effects as per Lehmann et al. [86], to instrumental interference, for example, cell window/filter ripple, or possibly due to resonance effects, in which case detection of thin layers would be possible. This last seems unlikely as enhanced ν(SS) modes were not noted on other minerals. Thus, it seems that Lehmann et al. [86] attributed the ν(SS) mode to thiosulfate correctly despite the lack of observable ν(SO) modes, and that these modes are reduced due to electrostatic effects or complexation.
Figure 3.35: Raman spectra recorded from Chinese pyrite surface in 0.1M HCl held at potential 0.700 V vs. Ag/AgCl over time (excitation wavelength: 514.5 nm; irradiation density: 1.0 kW cm$^{-2}$; 10s x 5 accumulations).

Figure 3.36: Extended range spectrum of Raman scan taken at 46 minutes in Figure 3.35 (excitation wavelength: 514.5 nm; irradiation density: 1.0 kW cm$^{-2}$; 10s x 5 accumulations).
Table 3.3: Raman shifts and intensity ratios (against most intense peak) of major modes of thiosulfate and tetrathionate. Vibrational mode assignment as per Meyer et al. [59].

<table>
<thead>
<tr>
<th>Species</th>
<th>Raman shift (cm$^{-1}$)</th>
<th>Vibrational mode</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_2$O$_3^{2-}$</td>
<td>451$^1$, 446$^2$, 435$^3$, 445$^4$</td>
<td>$\nu_3$</td>
<td>1.00$^1$, 1.00$^2$, 1.00$^3$</td>
</tr>
<tr>
<td></td>
<td>672$^1$, 672$^2$, 669$^3$, 672$^4$</td>
<td>$\nu_2$</td>
<td>0.53$^1$, 0.36$^2$, 0.17$^4$</td>
</tr>
<tr>
<td></td>
<td>1002$^1$, 996$^2$, 995$^3$, 999$^4$</td>
<td>$\nu_1$</td>
<td>0.31$^1$, 0.37$^2$, 0.43$^4$</td>
</tr>
<tr>
<td></td>
<td>1125$^1$, 1123$^3$, not observed$^2,^4$</td>
<td>$\nu_4$</td>
<td>0.34$^1$</td>
</tr>
<tr>
<td>S$_4$O$_6^{2-}$</td>
<td>148$^1$, 149$^4$</td>
<td></td>
<td>0.43$^1$</td>
</tr>
<tr>
<td></td>
<td>260$^1$, 256$^4$</td>
<td>$\nu_6$</td>
<td>1.00$^1$, 0.15$^{4,^5}$</td>
</tr>
<tr>
<td></td>
<td>390$^1$, 387$^4$</td>
<td></td>
<td>0.93$^1$, 0.80$^4$</td>
</tr>
<tr>
<td></td>
<td>1040$^1$, 1070$^3$, 1041$^4$</td>
<td>$\nu_2$</td>
<td>0.47$^1$, 1.00$^4$</td>
</tr>
</tbody>
</table>

Clearly, the laser affects the product layer and, while the thiosulfate and tetrathionatetype modes remain relatively constant, the laser stimulates the formation of sulfur after oxidation has commenced. This, it might do, through either accelerating thiosulfate/tetrathionate decomposition to sulfur on the pyrite surface, or through direct acceleration of pyrite oxidation to sulfur through heating or through induced recrystallisation of an inactive product phase. Given that transformation under 442 nm irradiation leads to a different product phase, the latter possibility seems less likely unless kinetic factors come into play. In this regard, it is important to note that

1 From Meyer et al. [59] using 514.5 nm and 488 nm irradiation.
2 This study, unpublished spectra of thiosulfate in solution. Excitation source: 442 nm, Power at sample: 9 mW, 3s x 10 accumulations.
3 From Banister et al. [64].
4 From unpublished spectra of 0.1M solutions, courtesy of Kym Watling, Griffith University. Excitation source: 632.8 nm, Power at sample: 6 mW, 10s x 100 accumulations.
5 Filter-edge interference.
the transformation of inactive product phase under 442 nm irradiation was demonstrably quicker.

Figure 3.37 shows laser-stimulated sulfur formation on the pyrite surface under 514.5 nm irradiation after a longer oxidation period. 13 hours of oxidation, in the absence of laser irradiation, produced detectable sulfur; however, laser irradiation increased the sulfur signal markedly. Mycroft et al. [69] also observed accelerated product development under laser irradiation, which they attributed to laser-initiated promotion of electrons from the valence band to the conduction band. They recorded an increase (0.5%) in oxidation current under the laser, although no such enhancement was recorded here.

Figure 3.37: Raman spectra recorded from Chinese pyrite surface in 0.1M HCl held at potential 0.700 V vs. Ag/AgCl for 13 hours. Times refer to laser irradiation time (excitation wavelength: 514.5 nm; irradiation density: 1.0 kW cm\(^{-2}\); 10s x 5 accumulations).

3.4.2. Covellite

The normal Raman study of the oxidation of several other sulfide minerals was initiated. Mineral covellite was selected, as CuS has been proposed as an oxidation intermediate in chalcopyrite oxidation [7, 8, 106]. It proved extremely recalcitrant to oxidation; 16 hours at an applied potential of 0.75 V/Ag/AgCl in 0.1M HCl at room temperature failed to produce any detectable product (Figure 3.38). The current
rapidly fell to zero. Even at high overpotentials (1 V/Ag/AgCl) no product was detected after 5 minutes oxidation. However, sulfur was evident on the surface within 45 minutes when oxidation (0.80 V/Ag/AgCl) was conducted at elevated temperature (80°C). The normal Raman investigation of synthetic analogs of the binary Cu/S system is discussed further in this investigation presently.

Figure 3.38: Raman spectra recorded from Moonta covellite surface in 0.1M HCl under various oxidative regimes (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm\(^{-2}\); 10s x 5 accumulations). New holographic filters have led to deviant spectral background in some of these spectra.

### 3.4.3. Sphalerite

Sphalerite oxidation was also briefly investigated, because it has structural similarities to chalcopyrite; however, its high ohmic resistance (2.7 x 10\(^3\) to 1.2 x 10\(^4\) \(\Omega\) m) prevents its steady-state electrochemical reactions from being easily studied [50]. Chemical experiments at elevated temperatures in oxygen show elemental sulfur is produced in acid solutions [50]. Thiosulfate has been noted in sphalerite oxidation
solutions, but not necessarily attributed to surface reactions compared to solution-phase reactions [83].

Iron substitution for zinc in the sphalerite lattice has a significant impact on the structure and, hence, electrical properties and reactivity of the mineral [24, 107]. Comparable with pyrite, incongruent dissolution occurs, resulting in 90% sulfur production in 0.1M HCl [105]. The rate of oxidation of iron-containing sphalerites is known to be higher than that of pure sphalerite [11]. Thus a carbon paste electrode (CPE) was constructed for the study, using the high-Fe sphalerite (the low-Fe sphalerite proved, not surprisingly, unsuitable). The electrode was constructed by selectively choosing high-Fe sphalerite pieces from Mt Isa ore, crushing and blending with Aldrich graphite in a 1:1 mass ratio, and mixing with Aldrich high-purity mineral oil until a paste-like consistency was achieved. This was pressed into a Teflon electrode mount with an integrated electrical contact. A fresh surface was revealed for each experiment through sanding the surface.

Figure 3.39 displays the products of oxidation after 4 hours oxidation at 0.800 V/Ag/AgCl. Not surprisingly, sulfur is observed, and a similar laser-recrystallised phase to that observed on chalcopyrite at ~452 cm$^{-1}$. The spectra obtained are not particularly resolved as the mineral binder tended to volatilise under laser irradiation and collect on the optical window between the electrode and microscope objective.
Figure 3.39: Raman spectra recorded from high-Fe sphalerite (MIM) CPE in 0.1 M HCl at open circuit potential and held at potential 0.800 V vs. Ag/AgCl for 4 hours (excitation wavelength: 442 nm; irradiation density: 0.10 kW cm\(^{-2}\) - 0.21 kW cm\(^{-2}\) (other scans); 10s x 10 accumulations).

3.5. Ex situ studies of chalcopyrite oxidation

3.5.1. Acid leaching

Mapping

Given the difficulties in observing oxidation product on chalcopyrite in sulfate solutions, unless the sample was heated or continuously irradiated, long-term ex situ studies were undertaken in an attempt to observe oxidation layers formed in sulfate solutions. Raman mapping was undertaken to investigate the potential heterogeneous product displacement on the chalcopyrite surface. Early studies were undertaken using Mt Isa chalcopyrite, with lowest practicable irradiation density (10% laser power: 4.6 kW cm\(^{-2}\); excitation source: 442 nm) allowing for time and resolution.

The irradiation density is so much higher than for spectra reported previously due to the use of a x50 microscope objective (NA=0.75) as opposed to the x20 ULWD objective used for in situ studies (NA=0.4). Maps were collected over ~3,500 µm\(^2\) in
1 µm steps, hence a 25s spectral collection yielded experiment times of >24 hours. A lower power would have yielded untenable collection times. However, this irradiation density is more than 10x greater than that of *in situ* studies and the potential for alteration of the product layer and also the chalcopyrite itself must be considered. Irradiation densities of this magnitude, or higher, have been used in published sulfide studies, although generally with a less energetic photon energy (514.5 nm) [13, 15, 89, 108].

Investigation of unoxidised Messina chalcopyrite surfaces at irradiation densities of 11.5 kW cm\(^{-2}\) with 10 minute exposure exhibited a weak band at ~470 cm\(^{-1}\) which is consistent with the formation of covellite, as no \(\delta(\text{SSS})\) bands of sulfur were observed. No oxide or iron sulfide species were specifically observed although a very broad band at ~700 cm\(^{-1}\) was barely evident, possibly indicative of an amorphous iron oxide species [68]. Because no surface spot was under irradiation for this length of time, it can be concluded that alteration of the chalcopyrite was unlikely. However, alteration of product layers is very likely. Mazzetti and Thistletwaite [68] reported the aging of amorphous iron oxyhydroxides and sulfates (ferrihydrite and schwertmannite) to hematite and maghemite under 10 kW cm\(^{-2}\) irradiation (excitation source 632.8 nm) after ~30 minutes of exposure.

Figure 3.40 displays Raman maps collected from oxidised Messina chalcopyrite surfaces. \(E_H\) values did not appreciably change with leach time indicating \(\text{Fe}^{2+}\) concentration did not become significant. This is to be expected for such a small surface area exposure (surface area < 1 cm\(^2\) in 100 mL solution). Pre-oxidation maps of the same region were gathered and showed no product formation. Clearly, Raman-active product was not detectable in the sulfate-leached chalcopyrite, although Figure 3.41 shows a thin interference film is present. The product formed on the chloride-leached chalcopyrite included elemental sulfur, though more photo-induced product formed than rhombohedral sulfur (Figure 3.40(b)).

The product layer formed in the chloride leach appeared porous and was clearly distributed in conformance with underlying features (see Figure 3.41) thus indicating deposition from solution was unlikely unless it occurred rapidly. Both elemental sulfur and laser-induced product appeared to volatilise or react further to produce a Raman-inactive phase under laser irradiation densities of this magnitude (see Figure 3.42). Following mapping, the irradiated area seemed more recalcitrant to leaching.
because product formation became inhibited in the mapped area. Soaking the oxidised sample in 0.1M HCl for several days prior to mapping appeared to lessen laser-induced inhibition. Presumably, the HCl would leach the Fe$^{3+}$ and Cu$^{2+}$ concentrations in the outermost layers of the oxidised chalcopyrite and the oxidised species that was induced under the laser was responsible for the inhibition (despite the lack of spectral evidence). Oxide minerals would be expected to dissolve under the pH conditions of the subsequent leaching and hence are unlikely culprits for inhibition. However, the high ferric iron concentration of the leach solutions might inhibit this. Given the effect was observed in both chloride and sulfate leached samples, sulfate salts also appear to be unlikely culprits because the chloride leaching conditions would favour re-dissolution.

The small amount of iron likely present on the surface in the pre-oxidation mapping did not appear to lead to an inhibitory effect; thus, oxidation products need to be present for such observations.

Figure 3.40: Raman maps of Messina chalcopyrite oxidised for 5 weeks in 0.005M ferric solutions (0.1M acid). Spectra collected at 1 μm intervals over the mapped area, and integrated over the ν(SS) band at ~450-470 cm$^{-1}$ (a) and the δ(SSS) band at ~220 cm$^{-1}$ (b). Excitation wavelength: 442 nm; irradiation density: 4.6 kW cm$^{-2}$; 25s x 1 accumulation per pixel.
Product formation tended to somewhat heterogeneous, with sulfate leaching of Mt Isa material (Figure 3.43) showing preferential formation of product at the fracture site. Sulfur formation at the chalcopyrite interface with quartz grains was also common. The sulfur layer formed in the chloride leach is also quite patchy and probably occurs preferentially at crystal boundary sites and fractures.

The interference film formed on chalcopyrite leached in sulfate solutions was observed for both Mt Isa and Messina samples. It was not evident on samples leached for 1 week or less, but became evident at longer leach times. Iron oxides/sulfates thin films formed during circumneutral leaching (discussed later) were visibly affected by even low laser irradiation, so the interference film is attributed to a sulfide oxidation product. There was also no observance of v_1(SO) modes common to schwertmannite at 981 cm\(^{-1}\) [68] or jarosite at 1010 cm\(^{-1}\) [91]. δ(HOH) bending modes at 790 cm\(^{-1}\) were not observed either. Interference films are clearly evident on the chloride-leached sample also: this is seen most clearly in Figure 3.42 (b) in which the sulfur coating has been removed.

Figure 3.41: Optical micrograph of Messina chalcopyrite prior to leaching and after leaching 5 weeks in 0.03M Ferric solution (0.1M acid). (a, b prior to and after leaching in chloride solution; c,d prior to and after leaching in sulfate solution).
Figure 3.42: Optical micrograph of mapped leached area of Messina chalcopyrite leached in 0.03M FeCl$_3$ (0.1M HCl) for 5 weeks and after a further 5 weeks leaching.

Figure 3.43: Mt Isa chalcopyrite Raman surface map integrated over the S-S stretch (≈474 cm$^{-1}$) peak: before leaching and after leaching for 2 weeks in 0.03M Fe$^{3+}$ (0.1M H$_2$SO$_4$; excitation wavelength: 442 nm; irradiation density: 4.6 kW cm$^{-2}$; 10s x 1 accumulation per pixel).

The effect of vacuum

*Ex situ* studies were also undertaken using lower irradiation densities. As per the mapping, elemental sulfur is evident on the surface within a week. It can be seen (Figure 3.44) that the elemental sulfur intensity relative to the main chalcopyrite band varies over the surface, and also that a shoulder is apparent at ~454 cm$^{-1}$. A UHV environment is able to remove the elemental sulfur on the surface, but the band at ~454 cm$^{-1}$ remains prominent after such treatment.
Five weeks of leaching at room temperature in ferric sulfate solution was necessary to yield a weak sulfur spectrum on the surface of Ward’s chalcopyrite with even this observation being somewhat heterogeneous. A sample that had been leached for 8 days and subjected to UHV conditions and X-rays showed a sulfur-bonded product on the surface in addition to some bands that may be attributable to iron oxides. Most of the surface showed no detectable product.
Clearly the product layer in both cases consists of elemental sulfur, although UHV treatment indicates the presence of other less volatile sulfur species. This species does not appear to be laser sensitive (under 632.8 nm irradiation) but is remarkably similar to that formed via 442 nm irradiation, with a S-S stretch downshifted from that seen in rhombohedral sulfur and no detectable bending modes. The oxidised sample was kept ex situ some time before analysis, such that metastable surface products would have had ample time to age/reconstruct, and produce similar product to that observed under photo-inducement. In sulfate leached samples, there is evidence that the stretching mode is downshifted further indicating a sulfur product with longer bonds than that observed in the chloride leached sample. In neither case is an idaite-like phase indicated.

### 3.5.2. Circumneutral leaching

Leaching in hydrogen peroxide solution allowed investigation of chalcopyrite oxidation under conditions where no significant counter ion effects would be observed. A 1% H$_2$O$_2$ solution (0.98 M) was sufficient to produce detectable product
within 24 hours. The $E_H$ of the peroxide solution was $\sim 0.365 \text{ V}/\text{Ag/AgCl}$ and pH $\sim 4$. This places it well within the same stability field (in terms of oxygen reduction corrected for pH) as the ferric solutions. The chalcopyrite anodic pre-wave did not show a dependence on acid concentration [7] although a pH-dependence for the main anodic wave was noted [7]. However, in the stability range of iron oxyhydroxides, a pH dependence should become evident. Oxidation studies of chalcopyrite in alkaline and pH 4 solutions indicate that the $E_H$ of the peroxide solution falls within the transpassive region [104, 109].

Farquhar *et al.* [109] investigated chalcopyrite oxidation at pH 4. Unfortunately they polished the electrode (despite having conducted XPS work that showed a difference in chemical form of cleaved and polished chalcopyrite surfaces) and they also used NaNO$_3$ as an electrolyte. They noted that, even at OCP, some copper dissolved. However, this is probably due to dissolution of copper-rich sulfides formed during polishing [10] or due to nitrate being a reasonably strong oxidant ($E^0[\text{NO}_3^- \rightarrow \text{NO}] = 0.96 \text{ V/SHE}$, $E^0[\text{NO} \rightarrow \text{N}_2\text{O}] = 1.59 \text{ V/SHE}$ [110]) and known accelerator of chalcopyrite oxidation [111]. Ferric oxide was the main oxidation product at potentials $< 0.65 \text{ V}/\text{Ag/AgCl}$. Sulfate was a major product above this potential.

Antonijevic *et al.* [112] studied chalcopyrite oxidation in sulfuric solutions containing H$_2$O$_2$. They found that oxidation rate conformed to a shrinking core model and that, while sulfate was the dominant product, some sulfide also oxidised to the elemental form. A 0.3 order dependence on sulfuric acid concentration was determined, indicating that diffusion through a ferric oxide layer becomes prohibitive at lower acid concentrations.

Less than 24 hours in 1% H$_2$O$_2$ produced an interference film on the chalcopyrite surface. The interference film transformed readily under 442 nm irradiation and produced no detectable Raman spectrum under either 442 nm or 632.8 nm excitation. Thick red product layers, formed via leaching chalcopyrite in 30% H$_2$O$_2$ for 24 hours, showed a broad Raman band at $\sim 710 \text{ cm}^{-1}$ under 632.8 nm excitation which was not associated with detectable $\nu(\text{SO})$ bands or $\nu(\text{OH})$ bands except at a few scattered sites (see Figure 3.46). ESEM-EDX (Table 3.4) and XPS analysis indicated the interference film was a mixture of iron oxyhydroxide and sulfates (cupric and ferric). The sulfate salts are not jarositic as the $\nu_1(\text{SO}_4^{2-})$ mode is not at the expected shift ($\sim 1010 \text{ cm}^{-1}$ [68, 93, 113]) and strong modes at $\sim 429-455 \text{ cm}^{-1}$ ($\nu_2(\text{SO}_4^{2-})$ [68, 113])
and broad modes at ~3400 cm\(^{-1}\) (\(\nu\)(OH) [93, 113]) were not evident. Studies of pyrite oxidation in circumneutral solutions only rarely produced Raman evidence of oxidised iron products [27, 69].

Figure 3.46: Raman spectra of product layers on chalcopyrite leached 24 hours in 30% H\(_2\)O\(_2\) (excitation source: 632.8 nm; Irradiation density: 0.31 kW cm\(^{-2}\); 10s x 10 accumulations).

Table 3.4: Standardless ESEM-EDX analyses (atomic %) of Mt Isa chalcopyrite leached 24 hours in 1% H\(_2\)O\(_2\) at various beam energies

<table>
<thead>
<tr>
<th></th>
<th>7 kV</th>
<th>10 kV</th>
<th>20 kV</th>
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<tr>
<td>O K</td>
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<td>24.65</td>
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<tr>
<td>Fe L</td>
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<tr>
<td>Ca K</td>
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<td>0.09</td>
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</tr>
</tbody>
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Figure 3.47: Optical micrographs of Mt Isa (a,c) and Messina (e) chalcopyrite pre-leached and after 24 hours oxidation in 1% H$_2$O$_2$ (b,f) and 30% H$_2$O$_2$ (d).
The standardless ESEM-EDX data show that the iron and oxygen signals increase with decreasing beam energy (and hence decreasing penetration depth), while copper shows higher signals with increasing beam energy.

Figure 3.47 presents the interference films formed on various chalcopyrites leached in H$_2$O$_2$. Extensive characterisation of the underlying matrix via Raman spectroscopy, ESEM-EDX and XPS did not indicate significant compositional/structural variation amongst the different regions, thus the distinct coloured areas (most noticeable on the polished Mt Isa sample (b)) delineate chalcopyrite crystals within the massive matrix. Thus the distinct colour variations are due to the different leaching rates of the exposed mineral faces and the subsequently different thicknesses and refractive indices. Figure 3.48 displays a low-energy BSE micrograph of a leached chalcopyrite surface: at higher beam energies, the variation of the ferric phase was less distinct. While the image shows an apparently uniform topography, BSE images are not able to distinguish such details and the sample surface is probably quite variable. Low-
energy electron beams also showed a thin ferric layer was present over the quartz inclusion – this was not evident at higher beam energies. Thus, it would appear that, as ferrous iron leaves the chalcopyrite matrix and oxidant becomes depleted near the surface (due to diffusion limitations), the ferrous iron must travel into solution a little before it oxidises. Figure 3.49 displays a higher-energy BSE micrograph of a leached Messina sample. As the ferric overlayer has aged, it has dehydrated resulting in contraction and subsequent cracking.

![Figure 3.49: BSE micrograph of Messina chalcopyrite after 24 hours leaching in 1% H₂O₂.](image)

### 3.6. Conclusions

Normal Raman techniques have proven useful in studying thick oxidation layers on sulfide minerals. A selection of minerals were studied and all, except covellite, exhibited an inactive-phase that transformed under 442 nm irradiation, even at low
irradiation densities, to yield a phase with a sharp band at 452 cm\(^{-1}\) indicative of sulfur-sulfur bonding. This band was observed in both the presence and absence of an elemental sulfur product and was not observed on unoxidised surfaces. It did not appear to be a thermal/photo-decomposition product of either octasulfur or the bulk matrix.

UV-Visible spectroscopy studies in the literature demonstrate octasulfur is not subject to either photolytic bond cleavage or thermal desorption at 442 nm [26, 55, 56, 114]. Changes in the crystal structure of octasulfur are known to occur at \(\sim 96^\circ\text{C}\) and \(\sim 115^\circ\text{C}\); however, the Raman spectra change little [58, 115, 116]. The sharpness of the \(\sim 452\) cm\(^{-1}\) band indicates the phase is not amorphous, though given it was initially Raman-inactive, it may have been amorphous prior to laser-induced transformation. A preliminary assessment would suggest it is either an \(S_2^{2-}\) species or polymeric sulfur chains due to the lack of associated bending modes and \(\nu(SS)\) splitting typically seen in inorganic polysulfides and solid sulfur allotropes [26, 57, 96-100, 117]. That the band was observed across a range of different sulfides, with very different cationic environments, would also make attribution to polysulfides less likely as they show very strong shifts with cation environment [99, 100].

Of all the minerals studied in this chapter, only covellite has a structure consisting of hexagonal close-packing of sulfide anions. Further work is necessary to determine whether the photo-induced phase is characteristic of cubic close-packed sulfide minerals only, or indeed, if there are any structural constraints on the formation of the photo-induced phase.

Normal Raman spectroscopy was not well suited to investigating the oxidation of chalcopyrite in sulfate solutions. Despite the observation of interference films on long-term ferric sulfate leached chalcopyrite, no Raman-active product phase was observed except for localised sulfur formation under photo-stimulated areas or large-scale sulfur formation at elevated temperature. It is possible that the oxidation layer formed on chalcopyrite in sulfate solutions is not conducive to laser-transformation or was simply too thin to be observed by the normal Raman technique. Active sites, around fractures and inclusions, tended to display weak \(\nu(SS)\) modes at a lower Raman-shift and indicative of longer sulfur-sulfur bonds than observed in chloride-leached samples.

Chloride-leached samples that had been kept under UHV conditions exhibited a Raman signal under 632.8 nm irradiation that was previously concealed by the
octasulfur signal. Thus, other sulfur species were present on the surface than octasulfur even in the absence of laser-inducement.

Product formation in both chloride and sulfate systems tended to be heterogeneous. The porosity of the sulfur layer on chloride-leached chalcopyrite is perhaps evident of initial solution-phase deposition of sulfur. Long-term chloride leaching studies, in which the porous overlayer was volatilised, showed that dense reacted underlayers (not consisting of octasulfur) existed across the entire chalcopyrite. That they were detectable via normal Raman spectroscopy indicates that such leached layers were reasonably thick.

Leaching of pyrite in chloride solutions showed strong evidence of thiosulfate and tetrathionate production at the surface. No such observations were made with chalcopyrite although it is acknowledged that the sulfate/sulfur production ratio for pyrite is significantly higher than that for chalcopyrite. More sensitive techniques are required to investigate polythionate production at chalcopyrite.

Jarosite, schwertmannite or similar sulfate salts were not observed on acid sulfate or chloride leached minerals. A sulfate-containing product was only evident on chalcopyrite samples leached in highly oxidising circumneutral solutions. The observed sulfate signature was not indicative of a crystalline ferric sulfate salt whose $v_1$($SO_4^{2-}$) shifts tend to be higher than those observed for simple ferrous/cupric sulfate salts due to decreased H-bonding and increased coordinative cationic bonding [113]. The sulfate salt observed was more indicative of an evaporite phase than a stable sulfate phase.

It is proposed that deep leached layers form on chalcopyrite leached in chloride. These layers are probably structured in terms of a remnant crystal lattice that can be restructured under appropriate conditions to give polymeric sulfur chains. This indicates the remnant lattice in chloride-leached samples is severely metal-deficient but can exist for long timeframes at room temperature before recrystallising to elemental sulfur. In addition, the remnant crystal lattice, in this case, does not seem to “passivate” although it could yield diffusion constants lower than that expected for crystalline octasulfur.

For chalcopyrite leached in sulfate solutions, Raman-active product is not detected except at “active” sites. Such sites indicate a somewhat different structure to that of the chloride-leached samples due, perhaps, to greater cation composition of the leached area. It may be that cuprous ion is difficult to remove from the leaching
structure in this case, where chloride complexation in the chloride system facilitates cuprous removal and hence greater oxidative leaching. Because too much cation remains in the lattice, the sulfur structure cannot age to elemental sulfur and hence diffusion is limited by cation diffusion through the bulk chalcopyrite to the leached layer.

3.7. References


[72] S. L. Harmer, Ian Wark Research Institute, ARC Special Research Centre for Particle and Material Interfaces, University of South Australia, 2002, p. 235.


4. Surface-enhanced Raman investigations - natural minerals
4.1. Preamble

Normal Raman Spectroscopy yielded interesting results on the leaching of chalcopyrite and other sulfide minerals in chloride solutions, but was unable to distinguish initial reaction products, or even long-term reaction products in sulfate electrolytes.

The surface-enhanced Raman scattering (SERS) technique is particularly suited to \textit{in situ} characterisation of surface species, and as such, would be ideal for investigating the initial oxidation products formed on sulfide minerals. However, only three coinage metals (Ag, Cu, Au) facilitate large enhancement, so the application of SERS techniques to sulfide mineral systems has understandably been limited. It is also limited by requiring a surface morphology with a roughness scale of ~10-200 nm [1, 2].

Researchers continue their efforts to extend SERS to the study of other metallic and nonmetallic surfaces. The plasmon resonance frequency depends on size, shape, and identity of the metallic nanoparticles and their environment. Thus, the extensive use of the coinage metals in SERS studies, whose surface plasmons fall in the excitation range of the visible irradiation sources commonly used in Raman spectroscopy.

There is some precedence for “borrowing” the electromagnetic effect of a SERS-active nanoparticle for the interrogation of a non SERS-active substance. This may be achieved by putting a thin layer of the non-SERS active substance on a roughened SERS surface [3, 4] or by depositing thin films of SERS active metals on the surface to be studied, via sputtering, evaporation or colloidal deposition [5-7]. It should be noted, when taking the first approach, that the SERS-active substrate is damped significantly by the coated film, so that the film has to be ultrathin, normally 3-10 atomic layers [1].

In the present chapter, studies are presented of the leaching of sulfide minerals with emphasis on chalcopyrite and the use of Au-decoration to promote surface enhancement. Similar approaches have been reported in the literature and showed some success in investigating systems not typically the subject of SERS investigations. For instance, silver-island film evapo-deposition onto GaAs semiconductor surfaces facilitated \textit{ex situ} SERS investigation of the interaction of $(\text{Ru(bpy)}_3^{2+})$ with the GaAs surface [6, 7]. In another study, colloidal silver droplets
were applied to the surface of highly-oriented pyrolytic graphite as well as single- and multi-walled carbon nanotubes to facilitate SERS investigation of surface groups, lattice modes and radial breathing modes [8, 9].

4.2. **In situ** acid leaching

Gold overlayers were deposited onto sample surfaces in an attempt to promote surface-enhancement. In this study, gold was selected as the enhancing metal of choice because silver and copper oxidize in the region of interest, and Ag$^+$ and Cu$^{2+}$ are known to promote oxidative leaching of chalcopyrite under the conditions of investigation [10-16].

Solution deposition, evaporative deposition and sputter deposition of gold on chalcopyrite surfaces were all assessed as to their ability to facilitate SERS. Solution deposition was accomplished by adding a little (5 mL) AuCl$_4^-$ containing solution (0.1M KCl and 1M HCl) to the 0.1M HCl electrolyte and maintaining the chalcopyrite electrode at its original open-circuit potential. This led to the appearance of a strong ν(SS) mode at 458 cm$^{-1}$ within an hour, and additional bands due to elemental sulfur (see Figure 4.1). No such bands were observed when the sample was maintained overnight at the same potential in 0.1M HCl without AuCl$_4^-$ addition.

Studies of gold cementation onto sulfide minerals (galena, arsenopyrite, cuprous sulfide and pyrite) under similar conditions indicate that the Au(III) binds to surface sulfide groups and subsequently reduces, producing Au(0) and polysulfides [17-23]. The Au(0) so formed is quite mobile, and readily forms crystallites from chloride solutions [17, 18]. X-ray photoelectron spectroscopic (XPS) Au(4f) data do not provide substantial evidence that gold polysulfide is specifically produced, though small amounts may form at concentrations below XPS detection limits [18, 20, 22]. Au cementation from chloride solutions onto sulfide minerals could be considered a model for oxidation of sulfide minerals, although AuCl$_4^-$ is a significantly stronger oxidant than Fe$^{3+}$ [24]. However, Au cementation from sulfate solutions does not produce Au(0) in excess [17] and so is not useful in studying sulfate systems.
Figure 4.1: Raman spectra of chalcopyrite in 0.1M HCl at open-circuit potential with and without the addition of AuCl$_4^-$ solution (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 1x9s accumulations)

Sputter deposition of Au (~50 nm) on oxidized Messina surfaces under low-vacuum conditions led to excellent enhancement without loss of elemental sulfur. Figure 4.2 shows sulfur was evident when SERS was facilitated (using 785 nm irradiation) and no product was evident when SERS was not facilitated (514.5 nm irradiation). SERS mapping of the oxidised mineral surface revealed sulfur was
present over the entire mineral surface (Figure 4.3) although it was not detectable by normal Raman techniques. However, sputter-coating was not undertaken routinely in this work as it was felt that it was too energetic a process and would likely alter the surface too significantly.
Figure 4.2: Raman spectra of the same site on a gold sputter-coated oxidised chalcopyrite sample surface using different irradiation wavelengths (excitation source: 785 nm, 514.5 nm; irradiation density: 5 kW cm$^{-2}$, 13 kW cm$^{-2}$; 5s, 40s accumulation respectively).

Figure 4.3: Sulfur component map (using spectrum #44 in the mapping sequence, shown in Figure 4.2) collected over gold sputter-coated oxidised chalcopyrite surface. Mapped sections show high intensity sulfur matches in red, moderate intensity sulfur matching in green and poor matches in blue (excitation wavelength: 785 nm; irradiation density: 5 kW cm$^{-2}$; 5sx1 accumulations).

To induce surface enhancement, gold films were vapour-deposited onto chalcopyrite electrode surfaces. Fine gold (99.9% Au) was thermally evaporated at 15 mA for 2-4 minutes yielding discontinuous gold films. Coverage was in the range of nanometres (<50 nm), as determined by simultaneous deposition onto glass slides and comparison to standards (based on weight of gold evaporated). Evaporative gold coating of samples was conducted under conditions of moderate to high vacuum (< 10$^{-6}$ Torr). Unfortunately, because chalcopyrite does not cleave/fracture well, exposure to air was unavoidable between grinding and vacuum emplacement, as well as between the vacuum chamber and electrochemical cell. This was also an issue when using sputtering to enhance the surface. Researchers have used small chalcopyrite particles (ground in a high-purity nitrogen glove box) mounted on a XPS stub and transferred from the glove box to the fast entry lock of the vacuum chamber [25, 26] to avoid surface alteration. Even using such methods, oxidation occurs as demonstrated by
their XPS S(2p) regional scans. Unfortunately, the equipment configuration in this study did not facilitate the use of such techniques. However, electrochemical investigations (which include experiments in which grinding and transfer to solution is undertaken under nitrogen [27]) indicate a minor exposure to air does not entirely passivate the surface during preparation although polishing leads to anomalous data [14, 28-30]. In addition, product elemental sulfur evaporates rapidly (unless the sample is cooled to <150 K [25, 26]) under vacuum, thus facilitating examination of less-volatile species that have a higher probability of being the passivation candidates.

It is possible that the Au condensation energy may lead to alteration of the product layer. In an attempt to identify any interactions, investigations were conducted as follows:

- Gold evaporation onto recrystallised rhombohedral sulfur crystals did not yield Raman spectra like those on the chalcopyrite surface – the gold condensation energy was not sufficient to alter S₈ molecules or lead to bond breakage. XPS spectra did not yield multiple Au(4f) BE fits (see Chapter 6).
- Gold evaporation onto chalcopyrite surfaces and subsequent redox cycling in acid yielded XPS spectra in which a single BE fit, consistent with Au⁰, was obtained for the Au(4f) regional spectra. Freshly decorated surfaces yielded similar data (see Chapter 6).
- Thin Au layers electroless-plated onto freshly ground chalcopyrite surfaces showed similar Raman spectra on chalcopyrite surfaces to evaporated layers. Sputter-deposited Au showed S₈ spectra (with some broadening of the ν(SS) band, as per normal Raman investigations) consistent with the oxidized chalcopyrite surface and low-vacuum conditions.
- Similar Raman spectra of products were observed at “active” sites (cracks and fissures) on undecorated Mt Isa chalcopyrite. It is possible that gold from previous experiments had lodged in the fault zones and remained after freshly abrading the surface. Gold deposition resulted in observation of product across the whole surface rather than only at fault sites.

During *in situ* investigations of enhanced chalcopyrite oxidation, it is possible gold might react to form sulfides and/or chloride complexes depending on the applied potential. The chlorides are easily distinguished, spectroscopically and
voltammetrically; they are only observed at highly positive potentials (>700 mV, active dissolution of \(\text{AuCl}_4^-\)) or as weak Raman bands (255-275 cm\(^{-1}\)) across the entire potential region of interest (chloride sorption). They were not observed in this study. Investigations of this nature are discussed in the following chapter.

\(\text{H}_2\text{S}\) may be released from the chalcopyrite surface during reductive scanning and likely interacts with the Au particles. However, sulfide oxidation studies on Au using Scanning Tunnelling Microscopy (STM), electrochemistry and Raman spectroscopy [31-34] indicate \((\sqrt{3} \times \sqrt{3}) R30^\circ\) coverage of the \(\text{Au}(111)\) crystal surface with further oxidation, as per Equation 37, requiring the continued supply of \(\text{S}^{2-}\) to the surface at higher potentials:

\[
\text{S}_{\text{ad}} + x\text{H}_2\text{S} \rightarrow (\text{S}^{2-}_{x+1})_{\text{ad}} + 2x\text{H}^+ + 2(x-1)e^- \quad (36)
\]

\[
(\text{S}^{2-}_{x+1})_{\text{ad}} \rightarrow (\text{S}^{2-}_{x+1})_{\text{ad}} + 2e^- \quad (37)
\]

The supply of \(\text{S}^{2-}\) from chalcopyrite reduction in acid will not continue at the potentials sulfide oxidation to sulfur occurs on gold (see Chapter 6) and hence elemental sulfur build up on the gold is not likely to occur.

There is some evidence that non-oxidative dissolution occurs when chalcopyrite is first immersed in solution, prior to application of an anodic potential. Lazaro and Nicol [29, 35] used a rotating ring-disk electrode (Pt ring, chalcopryite disk) to study the behaviour of chalcopyrite under anodic and non-oxidising (OCP) conditions. At OCP after immersion in a sulfuric acid electrolyte for various times, the ring was potentiostated at 1 V/SHE at the end of the immersion time to monitor Fe\(^{2+}\) production from the disk. After 30 minutes immersion, the typical chalcopyrite anodic response in the transpassive region was absent (on linear sweeps) and the ring also showed less Fe\(^{2+}\) response with time, indicating the surface had passivated. Presumably, the accompanying anion to the non-oxidative release of Fe\(^{2+}\) was \(\text{S}^{2-}\); otherwise, the reaction could not be non-oxidative. This, unfortunately, was not monitored by Lazaro and Nicol [29, 35]. This type of non-oxidative process may occur during \textit{in situ} studies, and resulting \(\text{S}^{2-}\) may interact with the Au particles although, the preference of sulfide for Cu/Fe sites would minimise this [36]. Thus enhancement of \(\text{S}^{2-}\) oxidation products on Au, rather than oxidation products on chalcopyrite may be occurring. XPS spectra of samples with an evaporative gold
coating that have been repeatedly cycled do not support the presence of Au$^+$ species, but SERS detection limits are somewhat greater than those of XPS. Au-coated chalcopyrite samples were used during in situ SERS investigations in both sulfate and chloride solutions. Because the surface oxidised a little due to transfer between vacuum apparatus and the spectroelectrochemical cell, the anodic pre-wave was not evident on the cyclic voltammogram (CV) unless the surface was swept to a sufficiently negative potential to reduce the pre-wave product (Figure 4.4). The voltammograms displayed in Figure 4.4 and Figure 4.5 are typical of chalcopyrite showing passivation in the transpassive region, until chalocite and chalcopyrite are generated on the surface during a reductive scan, after which the oxidation to CuS and the pre-wave product can be observed.

Figure 4.4: Cyclic voltammogram of Au-decorated Messina chalcopyrite in 0.1M H$_2$SO$_4$. Initiated in the positive direction from 0.1 V/Ag/AgCl at 5 mV s$^{-1}$. Unstirred.
Figure 4.5: Cyclic voltammogram of Au-decorated Messina chalcopyrite in 0.1M HCl. Initiated in the positive direction from 0.1 V/Ag/AgCl at 5 mV s\(^{-1}\). Unstirred.

The “smeariness” of the reduction portion of the CVs, between –0.2 and –0.45 V/Ag/AgCl, clearly varies on different runs. This was also noted in Chapter 3. It is not related to sweep rate, upper potential limit or sample origin. It may be related to total immersion time, including time at OCP which Lazaro and Nicol [29] have
demonstrated leads to a change in surface reactivity; however, more evidence would be needed to be ascertain this. Figure 4.6 clearly displays that a more defined anodic pre-wave leads to a more resolved reductive wave. This indicates that a more “distinct” oxidation product is present when the electrode has less pre-immersion exposure and/or less relaxation time. This is not surprising, and is possibly indicative of cation diffusion to the surface from underlying bulk chalcopyrite. It also demonstrates that the anodic behaviour of the sample is essentially identical with or without a gold coating. Samples with or without Au-decoration commenced anodic current flow at ~0.2 V/Ag/AgCl in positive going sweeps, unless a sufficiently reductive (<-0.15 V/Ag/AgCl) return sweep on the previous run had been undertaken. In that case, anodic current commenced flowing at ~-0.06 V/Ag/AgCl. Cathodic currents on return sweeps commenced flowing at ~-0.44 V/Ag/AgCl. Even when potentials were swept highly positive in 0.1M HCl electrolyte, reduction peaks on the return sweep consistent with AuCl$_2^-$ and AuCl$_4^-$ reduction to Au$^0$ [37] (at ~0.9 V/Ag/AgCl and ~0.66 V/Ag/AgCl respectively) were not observed. Raman spectra to accompany the CVs are displayed overleaf. If the voltammetric sweeps are not swept to sufficiently positive or negative potentials, such as Sweeps 1 and 2 in Figure 4.4, the Raman spectrum remains unvarying, with a broad ν(SS) band centred around ~457 and ~462 cm$^{-1}$ and the suggestion of a δ(SSS) mode at 218 cm$^{-1}$ (see Figure 4.8). This is remarkably similar to observations of Au in acidic solution containing H$_2$S. A broad ν(SS) band is evident at ~415 cm$^{-1}$ on entering the anodic wave, after scanning down to -0.45 V/Ag/AgCl, that increases in frequency to ~470 cm$^{-1}$ as the anodic pre-wave is transgressed, indicative of shortening bond lengths. This is consistent with sulfur atoms moving from lattice positions in chalcopyrite, where the closest sulfur-sulfur distance is >3.6 Å [38], to rhombohedral sulfur or covellite type bond lengths (2.05 Å and 2.07 Å respectively). In Figure 4.7, δ(SSS) bands at ~220 cm$^{-1}$, characteristic of rhombohedral sulfur, are evident only at potentials within the main anodic wave. Raman spectra observed for Au-decorated chalcopyrite in HCl (Figure 4.9 and Figure 4.12) showed similar general features to those observed in H$_2$SO$_4$, with the broadness of the ν(SS) Raman band in both electrolytes indicative of a disordered product. Intriguingly, ν(SS) modes were evident at much lower potentials in H$_2$SO$_4$ than in HCl, despite the anodic current commencing at similar potentials (-0.1 V/Ag/AgCl) in
both systems. As sweep rate was consistent across both sets of results, the different behaviour might be related to ionic strength, or a mechanistic difference between the systems. The strong $v_1$(SO$_4^{2-}$) and $v_2$(HSO$_4^{-}$) modes at $\sim$980 and $\sim$1050 cm$^{-1}$, respectively, were clearly evident on all spectra but were somewhat more intense on spectra taken from “undecorated” samples. No S=O stretching modes attributable to thiosulfate or other sulfoxy anions were observed, although broadening of the $\sim$1050 cm$^{-1}$ band at higher potentials may indicate their presence. Unfortunately, sufficient resolution was not attainable under the conditions of the experiments to definitively identify sulfoxy anions such as thiosulfate.

Figure 4.7: Raman spectra collected from Au-decorated Messina chalcopyrite surface during cyclic voltammogram – Sweep 7 (see Figure 4.4) in 0.1M H$_2$SO$_4$ under N$_2$ (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 1x9s accumulations, 10s cycle).

In H$_2$SO$_4$, the oxidation of the surface proceeded through a series of distinct species. Notably, at low oxidation potentials, a $v$(SS) mode appeared at $\sim$415 cm$^{-1}$, broadening and shifting to $\sim$430 cm$^{-1}$ in the chalcocite oxidation region of the voltammogram. Since it is less evident on sweeps where the negative potential limit was insufficient to
produce chalcocite (Figure 4.8) it may indeed be a chalcocite oxidation product. However, it may also be due to an aged passivation product (due to air exposure during gold deposition) which is reduced during the negative potential scan.

A ν(SS) shoulder at ~471 cm⁻¹, in conjunction with δ(SSS) modes, indicates elemental sulfur is present in the main anodic wave potential region, yet it remains only a minor product. The high intensity of the ~471 cm⁻¹ shoulder, compared to the δ(SSS) intensity, in conjunction with a weak band at ~267 cm⁻¹, suggests a covellite-like phase may also be present on the surface, as expected. Examination of Figure 4.7 indicates a number of small bands are present in δ(SSS) region, though they are not sufficiently resolved to yield structural information. The presence of ν(AuS) modes at ~310 cm⁻¹ [32] are difficult to discern due to the adjacent chalcopyrite lattice modes. Previous studies of the interaction of soluble sulfide with gold are reviewed in this thesis and demonstrate that strong ν(AuS) modes are most clearly observed at potentials <-0.35 V/Ag/AgCl at ~270 cm⁻¹. No such bands were observed in these studies.
Figure 4.8: Raman spectra collected from Au-decorated Messina chalcopyrite surface in 0.1 M H$_2$SO$_4$ at the commencement of each sweep shown in Figure 4.4 (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 1x9s accumulations, 10s cycle).

The spectra collected from a decorated Messina chalcopyrite surface in HCl are displayed in Figure 4.9. The species observed in Figure 4.7 with sulfuric acid, were different from those observed in HCl, exhibiting a broad $\nu$(SS) band evident over the entire anodic region. Occasionally, weak $\nu$(SO) modes attributable to sulfate and bisulfate were observed (as per the spectrum collected at 0.55 V/Ag/AgCl in Figure 4.9 and 0.33 V/Ag/AgCl in Figure 4.12).

![Raman spectra](image)

Figure 4.9: Raman spectra collected from Au-decorated Messina chalcopyrite surface during cyclic voltammogram – Sweep 6 (see Figure 4.5) in 0.1M HCl under N$_2$ (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 1x9s accumulations, 10s cycle).

When spectra were collected from undecorated surfaces, no $\nu$(SS) modes were observed during potential cycling (see Figure 4.10).

Figure 4.11 displays an extended Raman spectrum of a Au-decorated chalcopyrite sample in HCl, showing low-frequency features in accord with other enhanced samples. Clearly no $\nu$(SH) modes are present at $\sim$2500 cm$^{-1}$, nor are $\nu$(SO) modes evident.
Figure 4.10: Raman spectra collected from undecorated Messina chalcopyrite surface during cyclic voltammogram – Sweep 6 (see Figure 4.6) in 0.1M HCl under N$_2$ (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 1x9s accumulations, 10s cycle).

Figure 4.11: Extended Raman spectra of Au-decorated Messina chalcopyrite in HCl solution at OCP, showing $\nu$(SS) modes at ~457 cm$^{-1}$ (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 5s x 10 accumulations)
Results were reproducible across different samples and scan rates - Figure 4.12 displays the spectra collected from a Au-decorated Ward’s sample in HCl, which shows similar features to those observed in Figure 4.9.

Figure 4.12: Raman spectra collected from Au-decorated Ward’s chalcopyrite surface during cyclic voltammogram – Sweep 2 (2 mV s\(^{-1}\); Initiated 0.0 V/AgCl; Lower limit: -0.45 V/Ag/AgCl; Upper limit: 1.0 V/Ag/AgCl) in 0.1M HCl under N\(_2\) (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm\(^{-2}\); 1x10s accumulations, 11s cycle).

4.3. **Ex situ studies**

4.3.1. **Acid leaching**

The difficulty in distinguishing the reactions on Au from that of chalcopyrite led to the commencement of some *ex situ* studies. Chalcopyrite electrodes were emplaced in acid solutions, taken through a sweep (~1 min) of the transpassive region and then removed from solution, rinsed with doubly deionised water, dried under a stream of N\(_2\), and then vacuum coated with gold for SERS activation. Raman spectra were
collected during the sweep and showed no detectable product. Samples were subsequently examined for oxidation products in air.

Figure 4.13 and Figure 4.14 show typical anodic sweeps for fresh chalcopyrite surfaces in chloride and sulfate electrolytes. The total charge passed in the pre-wave is similar in both solutions (being 0.022 C cm\(^{-2}\) and 0.024 C cm\(^{-2}\) respectively, uncorrected for surface roughness).

Figure 4.13: Positive-going linear sweep of Messina chalcopyrite in 0.1M HCl prior to Au deposition (10 mV s\(^{-1}\)).
Figure 4.14: Positive-going linear sweep of Messina chalcopyrite in 0.1M H\textsubscript{2}SO\textsubscript{4} prior to Au deposition (5 mV s\textsuperscript{-1}).

Figure 4.15 displays the spectra obtained from samples treated in this way. The spectra are similar to those observed from sample surfaces \textit{in situ} at transpassive potentials. In the bottom spectra, some recrystallisation of product has clearly occurred between potentiostatic oxidation and Raman spectrum collection, based on the formation of elemental sulfur that is evident on the surface. In the cases displayed below, no chalcocite-type phase was formed in reductive scans; hence, the $\nu$(SS) bands are due entirely to chalcopyrite oxidation products. It could be that the gold condensation energy has led to some product formation, but results in Chapters 5 and 6 demonstrate that Au condensation energies are not sufficient to affect elemental sulfur crystals, thus indicating that if affected, only unstable product phases would react. As per the \textit{in situ} results, no $\nu$(SO) modes were observed.
Observations of Au-decorated Messina chalcopyrite not specifically oxidised in solution (i.e. only air oxidation occurred) showed similar results, at sample fault/fracture sites, to those specifically oxidised. Very little product was observable over most of the sample (see Figure 4.16). Raman bands attributable to $v_1(\text{SO}_4^{2-})$ modes, at a shift in keeping with a poorly crystalline ferric sulfate salt ($\sim$1001 cm$^{-1}$) were observed at “active” sites [39-42].
Figure 4.16: Raman spectra of Au-decorated Messina chalcopyrite samples (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 10 s to 100s accumulations).

Investigations have been made to determine whether an irradiation effect in these SERS studies was being observed. A sample leached overnight in ferric sulfate solution, then sputter-coated with gold for SIMS analysis, showed a laser effect at irradiation densities of 0.31 kW cm$^{-2}$: recrystallisation of a phase with broad Raman $\nu$(SS) modes at ~470 and ~430 cm$^{-1}$ yielded a phase with a sharp $\nu$(SS) mode at ~471 cm$^{-1}$, and a moderate mode at ~270 cm$^{-1}$, consistent with a covellite-like product. At irradiation densities of 0.031 kW cm$^{-2}$, no spectra features were evident at all. In samples leached for longer periods or leached in ferric chloride, an obvious recrystallisation reaction was not evident at high irradiation densities but, at low irradiation densities, the spectra were featureless. These samples had spent an extensive period ex situ prior to Raman analysis, hence may not be representative of fresh product layers.

Figure 4.17 displays spectra collected from oxidised chalcopyrites that were immediately Au-decorated then examined using Raman Spectroscopy ex situ. It can be observed that there is little/no product is under 0.031 kW cm$^{-2}$ irradiation. Curiously, the major chalcopyrite band (evident on the higher intensity ferric leached
samples) was not evident under low irradiation density at the same site indicating that extensive time-frames for collection of spectra under this laser intensity may be required and, thus, the lack of product bands are not due to a laser effect. The similarity of the product layer in the ferric and potentiostatically leached samples should be noted. It seems a laser effect is not evident on these samples either.

Figure 4.17: Raman spectra of Au-decorated Messina chalcopyrite leached in 0.03 M Fe$_2$(SO$_4$)$_3$/0.1 M H$_2$SO$_4$ for 2 weeks, and Mt Isa chalcopyrite potentiostatically leached for $<$2 min (scanned from 0.2 V – 0.65 V/Ag/AgCl at 5 mV s$^{-1}$) then decorated with gold (excitation wavelength: 632.8 nm; 10 s x 20 accumulations). Times refer to irradiation time at the irradiation density indicated.

4.3.2. Circumneutral leaching

Chalcopyrite samples leached in 1% H$_2$O$_2$, then 0.1M HCl to remove iron/copper oxides, were sputtered with gold and examined using Raman spectroscopy. Octasulfur was evident over the entire surface. However, it was noted that there was an effect from laser irradiation. This was observed visibly for thicker layers under radiation of any wavelength but was not detectable using Raman spectroscopy unless SERS was facilitated. In this case, it is observed that even low irradiation densities
led to such observations and that the thermal impact appears to reduce the signal attributable to elemental sulfur (bands at ~220 cm\(^{-1}\) and ~471 cm\(^{-1}\)) with broadening of a band with an intensity maximum at ~461 cm\(^{-1}\) (Figure 4.18). The appearance of this band corresponds to the observation of weak bands at ~270 cm\(^{-1}\) and ~310 cm\(^{-1}\) (Figure 4.19), which are attributable to \(\nu(AuS)\) modes (discussed in the next chapter) \[32\]. The \(\nu(AuS)\) bands are of extremely low intensity, less intense than when a gold electrode is covered with a sulfide monolayer.

![Raman spectra](image)

Figure 4.18: Raman spectra collected from Messina chalcopyrite leached in 1% \(H_2O_2\) followed by 0.1M HCl, and then sputtered with Au (excitation wavelength: 632.8 nm; 1s to 50 s accumulations).
4.4. Conclusions

SERS on chalcopyrite surfaces was facilitated via gold deposited by either electroless plating, sputtering or vapour deposition. Vapour deposition is the least energetic of these processes for depositing gold onto chalcopyrite, and thereby the least likely to affect surface layers. However, the ex situ nature of the technique, like most other techniques used to study the surface speciation of oxidation products on chalcopyrite, means that surface restructuring and aging of product layers is possible.

In situ investigations of Au-decorated chalcopyrite surfaces indicated that a product containing sulfur-sulfur bonds, but distinct from octasulfur, formed on entering the anodic pre-wave on chalcopyrite. Octasulfur also formed as the product aged and the potential was driven higher. The initial product showed ν(SS) maxima at low shifts in sulfate solutions for longer periods than in chloride solutions, indicative of slower restructuring; however, but the oxidation products observed were not overly different in the two solutions, in agreement with voltammetry results. Thus, the substantially faster oxidation rates in chloride solutions must be either due to faster electron-
transfer rates on the corroding surface, or more rapid decomposition of the initial corrosion product, possibly relating to complexation of cuprous ions. There was little evidence of sulfide formation on Au in these solutions (diagnostic \( v(\text{AuS}) \) modes at potentials \(<-0.35 \text{ V/Ag/AgCl} \) were absent). No thiosulfate or tetrathionate was observed although, occasionally, a hint of sulfate/bisulfate was observed in spectra collected from chalcopyrite in chloride solutions. These might indicate the fleeting formation of thiosulfate or might be due to surface contamination as a result of \textit{ex situ} handling.

Sputter-coated samples leached in peroxide solutions showed a laser irradiation effect, with broadening of the elemental sulfur \( v(\text{SS}) \) mode. This is similar to the broadening observed around the octasulfur recrystallisation temperatures [43-45]. It may be deduced that localised heating is occurring at the surface and may be related to the presence of minor amounts of iron oxide remaining after acid washing. Evidence for laser effects at acid-leached sample surfaces with vapour-deposited gold coatings was not conclusive.

The possibility that non-oxidative dissolution resulted in the release of \( \text{H}_2\text{S} \) during \textit{in situ} investigations, with subsequent absorption and oxidation on gold, could not be excluded as contributing to the SERS spectra. Hence, samples were pre-oxidised, decorated with gold then examined \textit{ex situ}, resulting in virtually identical surface products to those observed \textit{in situ}. Some recrystallisation/aging of the surface product to form octasulfur had occurred in both \textit{in situ} and \textit{ex situ} studies. Excluding octasulfur bands, \( v(\text{SS}) \) bands occurred in the absence of \( \delta(\text{SSS}) \) modes and were very broad. The product would appear to be highly disordered in both chloride and sulfate systems.

Only sites within \(~5\) nm of the gold particles would be surface-enhanced. Even the brevity of the oxidative sweep on the pre-oxidised samples might result in layers thicker than this; the charge passed indicated \(~25\) nm of product formed although, if allowance were made for surface roughness, this would be significantly reduced. It is also possible that the handling and coating procedures results in “aged” products which might not be representative of fresh product. The lack of change in Raman signal on anodic sweeps, after prior cathodic sweeps to \(~0.45\) V/Ag/AgCl, during which the oxidation product is reformed, would indicate that fresh oxidation product is either Raman-inactive or too deep to be observed. Given that a remnant lattice is
probably formed on initial oxidation, and that the sulfur atoms would need to move ~1.5 Å before bonding could commence, then it would not be surprising if the initial oxidation layer were Raman-inactive.

Long-term leached samples that had been Au-decorated showed evidence of the formation of jarosite. Freshly leached surfaces showed no evidence of jarosite formation or other crystalline/solid sulfate species. While it seems that amorphous sulfate phases are long-term products of chalcopyrite leaching, they have little to do with initial products and kinetic constraints on these systems.

SERS facilitation through Au-decoration of chalcopyrite surfaces provided a good deal of information on the properties of the initial leached layer. The system is particularly complex, and application of this technique to other, simpler systems would not be plagued with some of the uncertainties inherent in this study and could provide useful information on leaching or solution interactions.

4.5. References


5. Model systems
5.1. Preamble

This Chapter is devoted to spectroelectrochemical studies of key model compounds and systems. A number of model compounds were investigated in an effort to identify oxidation products formed on sulfide minerals, in addition to their properties and stability. In particular, the photo/thermal properties of thin sulfur films were examined in detail. Polysulfides and sulfoxide anions were also investigated as potential intermediates in chalcopyrite oxidation, as they have been proposed as products in a number of sulfide mineral oxidation studies [1-9].

Surface-enhanced Raman scattering (SERS)-voltammetric studies of the interaction of sulfide with gold surfaces were undertaken to identify the forms and vibrational characteristics of the elemental sulfur formed from aqueous solutions under different conditions and to investigate substrate interactions and effects on the sulfur product layers formed. This work was undertaken in an attempt to distinguish the behaviour of sulfur on gold from that on chalcopyrite and assess the impact gold-decoration of chalcopyrite might have on oxidative product formation.

The production of synthetic chalcopyrite is well-known (including via hydrothermal routes) [10-14] but the particles so produced are somewhat unstable, tend to be multiphase (including pyrite and covellite) and are not conducive to Raman/electrochemical interrogation. Conversely, the synthesis of binary copper sulfides is more straightforward, and the materials produced are superbly suited to spectroelectrochemical studies, particularly when formed through chemical bath deposition (CBD) [15, 16].

The copper sulfides were of interest in this work since a covellite-like [CuS] phase has been proposed as an intermediate in chalcopyrite oxidation [17-19]. The covellite structure is significantly different from that of chalcopyrite, with sulfur in hexagonal close-packing, and it can be envisaged that the rearrangement of sulfur atoms necessary to produce the covellite structure from chalcopyrite would lead to slow leaching. However, the chalcocite [Cu₂S] to CuS oxidation sequence (through a number of intermediates) is not greatly inhibited, although still somewhat sluggish at low temperatures, and it nominally goes through a hcp→ccp→hcp sequence during this process [20]. A cubic form of CuS has been reported [21, 22] though evidence of its existence is somewhat scant [23]. Thus, the binary copper sulfide system was
deemed of some interest in this investigation, particularly in regards to amorphous forms and the possibility of them being intermediate in chalcopyrite oxidation.

5.2. Sulfur species

5.2.1. Normal Raman investigations

Polysulfides

A detailed literature review and investigation of polysulfide anions, sulfoxyl anions and elemental sulfur allotropes was undertaken in an attempt to identify the laser-induced phase formed on chalcopyrite, sphalerite and pyrite (see Figure 5.1, which also shows elemental octasulfur modes evident at ~150, ~220 and ~471 cm\(^{-1}\)). Published spectra of the inorganic polysulfides did not yield any contenders, other than \(\beta\text{Na}_2\text{S}_2\) which has a strong band at 451 cm\(^{-1}\) [24-26]. Longer-chain crystalline polysulfides yield bending modes and multiple \(\nu(\text{SS})\) modes due to the undistributed charge along the polysulfide chain [24, 25, 27-29]. \(\text{Na}_2\text{S}_2\) was synthesised in this investigation by mixing stoichiometric amounts of Aldrich anhydrous \(\text{Na}_2\text{S}\) (5mmol, Product # 407410) and elemental sulfur (5 mmol, Laboratory Supplies Australia, 99%) in a pyrex tube. The pyrex tube was sealed under vacuum and fired at 200°C for 4 hours then 500°C for 1 hour [30]. The resulting solid was annealed at 200°C for 10 hours. The \(\beta\text{Na}_2\text{S}_2\) phase belongs to the \(D_{6h}^4\) space group, with four Raman-active modes: the \(A_{1g}\) \(\nu(\text{SS})\) mode at 451 cm\(^{-1}\), a librational fundamental at 135 cm\(^{-1}\) and \(S^2_2\) and \(\text{Na}^+\) lattice modes at 64.5 cm\(^{-1}\) and 27 cm\(^{-1}\) respectively [24].

Figure 5.2 displays the Raman spectra collected from the \(\text{Na}_2\text{S}_2\). Clearly, there was incomplete mixing/incongruent crystallisation of the sodium sulfide and sulfur, as the crystalline product evinced colours ranging from pale yellow to red. The pale yellow crystals yielded the Raman spectrum expected for hexagonal \(\beta\text{Na}_2\text{S}_2\) [24, 29] with a single \(\nu(\text{SS})\) band at 451 cm\(^{-1}\). The broad bands at ~900 cm\(^{-1}\) are likely overtones.

\(\text{Na}_2\text{S}_2\) phases showed no recrystallisation or spectral changes under 442 nm irradiation at irradiation densities of 0.5 kW cm\(^{-2}\) despite the presence of metastable phases (probably \(\text{Na}_2\text{S}_4\) and \(\text{Na}_2\text{S}_5\)). The detailed studies of El Jaroudi et al. [25, 29, 31] demonstrated that the cation electric field directly affects the polysulfide anion geometry, and hence the Raman spectrum. This makes disulfide an unlikely contender for the laser-induced phase on chalcopyrite, sphalerite and pyrite where the
cation electric fields would be expected to be very different. In addition to this, the inorganic polysulfides are not stable in presence of water, even though the kinetics of oxidation are sufficiently slow to facilitate the study of aqueous polysulfide solutions [32].

Figure 5.1: Raman spectrum of Ward’s chalcopyrite oxidised at 0.690 V/Ag/AgCl in 0.1M HCl for 21 hours (excitation wavelength: 442 nm; irradiation density: 0.05 kW cm$^{-2}$; 10s x 20 accumulations).

Figure 5.2: Raman spectra of the synthetic $\sim$Na$_2$S$_2$ phase (excitation wavelength: 442 nm; irradiation density: 0.102 kW cm-2; 10s x 10 accumulations).
Sulfoxyl anions

The sulfoxyl anions were discussed briefly in Chapter 3. The lack of observable S-O stretching bands on corroding chalcopyrite, indicates they were not present, or are present at low concentrations. However, decomposition of thiosulfate (or other sulfoxyl anions) at the chalcopyrite surface may lead to product sulfur formation [33, 34]:

\[
\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{S}_0^{(s)} + \text{SO}_{2(g)} + \text{H}_2\text{O}
\]  

(38)

Elemental sulfur produced by such a reaction is acknowledged to form by way of intermediate polythionate species [33]. Other rings may also be present, though S₈ tends to predominate [33], with HCl promoting reversible precipitation of the S₈ allotrope. Such a precipitate was examined in this study. The reaction of 1M HCl and sodium thiosulfate produced an off-white colloidal suspension that settled overnight. Raman spectra of the precipitate showed only the spectrum typical of elemental sulfur, with no irradiation effects (442 nm).

To explore the possibility that surface-complexed thiosulfate might react to form a Raman inactive phase that crystallises under 442 nm irradiation, or that thiosulfate decomposition is stimulated by laser irradiation, sulfided and non-sulfided platinum was exposed to a 1M Na₂S₂O₃ solution, then 1M HCl was added dropwise until sulfur began to form. No phase induced under 442 nm irradiation was evident. Steudel *et al.* [33] conducted irradiation experiments, using a 40W high-pressure Hg immersion lamp (290-600 nm) and found that, in aqueous solutions of sodium tetra- and pentathionate irradiated for 10 minutes, sulfur precipitated, H₂S was produced and thiosulfate (as well as minor quantities of sulfite and polythionates) were formed. However, wavelength selection experiments showed that radiation of wavelength >350 nm did not stimulate tetrathionate decomposition even after 1 hour of exposure.
Gold, subjected to 1M $\text{S}_2\text{O}_3^{2-}$ and subsequently acidified with HCl, led to observance of the standard rhombohedral sulfur spectrum under 442 nm irradiation.

**Elemental sulfur thin films**

The molecular spectra of the various sulfur allotropes were reviewed by Steudel [35]. The ring structures all showed bending modes and were clearly unrelated to the spectrum observed on the corroding sulfide minerals. Only acyclic $\text{S}_3$ is known to absorb near 442 nm (at 410 nm), with ring species and longer chains absorbing in the near-UV [35, 36].

The only stable form of sulfur at STP conditions is the orthorhombic modification, $\alpha$-$\text{S}_8$. No other element forms more solid allotropes than sulfur, with ~30 well characterised sulfur allotropes currently known [37]. At ambient temperature about 20 crystalline phases consisting of rings are known. Sulfur allotropes consisting of chains are less well characterised.
There are three forms of cyclo-octasulfur that may crystallise under ambient pressure conditions: orthorhombic $\alpha$-S$_8$ (<96°C), monoclinic $\beta$-S$_8$ (<115°C) and monoclinic $\gamma$-S$_8$ (metastable at all temperatures and found as mineral rosickyite) [37].

“Flowers of sulfur” is made by sublimation of sulfur vapours, and is a finely divided form of sulfur containing mainly $\alpha$-S$_8$ though small amounts of polymeric insoluble sulfur ($S_\mu$) and trace amounts of S$_7$ are typically present in addition to organic impurities [38]. It is usually the presence of S$_7$ that leads to the bright yellow colour of commercial sulfur samples; pure $\alpha$-S$_8$ is greenish-yellow. Impurities can be removed by dissolving the sample in toluene or CH$_2$Cl$_2$ and filtering [37]. CS$_2$ is not a good solvent, as traces of it tend to remain in the product. Even after such treatment, traces of carbon compounds tend to remain [37]. Recrystallisation from solvent is an option for obtaining crystals of $\alpha$-S$_8$.

Those forms of elemental sulfur which are insoluble, even in CS$_2$, at 20°C have been termed polymeric sulfur ($S_\mu$) and consist of chain-like macromolecules though the existence of large rings, S$_n$ (n>50) is very likely [37]. Thus, $S_\mu$ is a mixture of chains of differing lengths and rings of differing sizes rather than a pure compound. The nature of the chain-terminating endgroups is unknown [37]. In some cases crystalline phases have been isolated and molecular structures determined by X-ray diffraction: these phases are known as $S_{\omega1}$ and $S_{\omega2}$ (2$^{nd}$ fibrous and laminar sulfur respectively) and consist of helical chains (catenapolysulfur).

Liquid sulfur’s physical properties are very unusual: at the melting point (~119°C) sulfur forms a light yellow low viscosity liquid [39]. On heating, the liquid darkens and the viscosity increases going through a maximum at ~159°C. It is so viscous at this point that it cannot be poured from containers. At this temperature, the specific heat, the density, light scattering, the electric conductivity and other physical properties show a discontinuity [39, 40]. This is due to equilibrium polymerisation of sulfur initiated by ring scission and propagated by a condensation reaction. At higher temperatures, a steady depolymerisation process occurs, resulting in chains of $10^4$-$10^5$ sulfur atoms [37].

$S_\mu$ is a component of liquid sulfur at all temperatures after chemical equilibrium has been established which takes about 10 h at 120°C [41]. The polymer can be obtained by quenching the melt (yielding plastic sulfur) and extracting the soluble rings with CS$_2$ at 20°C. The polymer content of the melt increases from 1% at 135°C to a
maximum of 45±10% at 250-300°C [42]. After quenching and extraction, the sulfur is amorphous but ages to a microcrystalline structure and, finally, $\alpha$-$S_8$ at room temperature. This conversion can be accelerated by mechanical impact, irradiation with UV-Vis light, or by heating (60°C for 1-2 h) [42]. Polymeric sulfur is also formed on decomposition of certain pure sulfur ring allotropes ($S_7$ at 60°C to $S_{12}$ at 140°C) [37].

At least three crystalline allotropes of macromolecular sulfur chains are known at STP: two fibrous forms and a laminar form [41]. The properties and crystal structure of the polymeric sulfur tend to depend on the preparative method [41]:

- Stretching of plastic sulfur (x1000) and extraction of the soluble ring fraction ($S_\psi$, fibrous sulfur);
- Quenching of the liquid melt and extraction of the soluble ring forms with $CS_2$ (mainly $S_{\omega 1}$, second fibrous sulfur, and $S_{\omega 2}$, laminar sulfur);
- Sublimation of sulfur vapour onto a relatively cold substrate ($S_{\omega 1}$, second fibrous sulfur, and mainly $S_{\omega 2}$, laminar sulfur);
- Irradiation of solutions of unstable sulfur rings at room temperature or of solid $S_8$ at low temperature (predominantly $S_{\omega 1}$, with $S_{\omega 2}$);
- Thermal decomposition of metastable allotropes ($S_6$, $S_7$ etc.) (predominantly $S_{\omega 2}$, with $S_{\omega 1}$); and
- Application of high pressure in combination with high temperature or intense light (predominantly $S_{\omega 2}$).

The diffraction pattern of the filaments formed by stretching and extraction of plastic sulfur ($S_\psi$) can be understood in terms of the superposition of the patterns for catenapolysulfur and monoclinic $\gamma S_8$ [41]. Crystalline $S_\psi$ consists of parallel helices (each consisting of S-S bonds of 206.6 pm and torsional angles of 85.3°) which are regularly left-handed and right-handed [37]. It belongs to the monoclinic crystal system and the $C_{2i}$ space group. Second fibrous ($S_{\omega 1}$) and laminar forms ($S_{\omega 2}$) are less well characterised (diffraction lines are somewhat broadened as there is generally a mix of products) though are believed to belong to the orthorhombic ($D_{2h}^{10}$) and tetragonal ($S_4^1$) crystal groups respectively [37]. Thus, $S_\psi$ and $S_{\omega 1}$ have closely related structures while $S_{\omega 2}$ has adjacent layers of helices oriented perpendicularly. The polymer starts to soften at ~90°C [43]. Raman spectra of the various forms of $S_\mu$
are similar and up to now their structures have only been differentiated through X-ray structural analysis [37].

Below 159°C, the octamer is the main component of liquid sulfur, with the reaction-limiting step presumed to be the opening of the ring to a chain radical. The reaction enthalpy has been estimated by electron spin resonance (ESR) and magnetic susceptibility measurements to be 140 kJ mol\(^{-1}\) [42, 44] with propagation thereafter only requiring 10 kJ mol\(^{-1}\). Rings (S\(_6\), S\(_7\), S\(_8\), S\(_{10}\) and S\(_{12}\)) and CS\(_2\) are photochemically active at wavelengths <420 nm [45]. Indeed, photodecomposition of \(\alpha\)-S\(_8\) was found to occur at \(\lambda<400\) nm at 77K, resulting in a yellow-coloured product that further decomposes at 260 K [46].

The S\(_8\) allotrope has been the most extensively spectroscopically studied of the sulfur allotropes. The ring belongs to D\(_{4d}\) point group and has 7 Raman active modes. Force constant calculations showed that the force constants for a particular type of vibration (stretching, bending, torsion) are almost uncoupled [47]. Accordingly, the various types of vibrations are energetically well separated: stretching \(\sim410-480\) cm\(^{-1}\), bending \(\sim150-250\) cm\(^{-1}\) and torsion \(\sim90\) cm\(^{-1}\) [35].

The Raman spectrum of polymeric sulfur is relatively simple compared with other allotropes [35]. It consists of a strong band in the stretching region \(\sim452\) cm\(^{-1}\) accompanied by weak bands in the stretching and bending regions \(\sim415\) cm\(^{-1}\) and \(\sim273\) cm\(^{-1}\). To quote Dultz et al. [48] “since the (fibrous sulfur) sample has the isotropic disorder of a heap of spaghetti, the spectrum does not depend on the polarisation of the incident and the scattered light”. In general, the Raman spectra of polymeric sulfur synthesised by different mechanisms are rather similar with spectra reported for samples that have been sublimed from the gas, quenched from a melt, mixtures of large disordered rings, or produced via commercial processes (“flowers of sulfur” and Crystex, a commercial form of sulfur containing polymer chains stabilised by certain organic olefins) [35]. However, the bandwidths and relative intensities of the spectra from different sources differ, probably due to varying crystallinity of the samples. Highly disordered forms of sulfur prepared from liquid sulfur and containing a mixture of large ring structures (S\(_x\), on average x\(\sim25\)) show similar spectra, though tending to broadened Raman modes.
Table 5.1: Published Raman shifts (cm\(^{-1}\)) and intensity indicators of polymeric sulfur samples (~300 K).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stretching</th>
<th>Assignment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystex</td>
<td>456 vs, 418 w</td>
<td>273 w</td>
<td>[49]</td>
</tr>
<tr>
<td>Fibrous sulfur</td>
<td>453, 418</td>
<td>273</td>
<td>[48]</td>
</tr>
<tr>
<td>Insoluble sulfur</td>
<td>452 s, 416 w</td>
<td>270 m, 261 w</td>
<td>23</td>
</tr>
<tr>
<td>S(_n)(^1)</td>
<td>460 s, 416 w</td>
<td>275 w, 260</td>
<td>65</td>
</tr>
</tbody>
</table>

\(^1\)Spectrum obtained from high-pressure photo-induced sulfur, and extrapolated to ambient pressure Raman shift.

Raman spectra of liquid sulfur (159°C upwards) tend to be overwhelmed by the S\(_8\) spectrum. Broadening of the \(\nu(\text{SS})\) band, due to increasing polymer formation and S\(_8\) deformation, increases with temperature [49, 51-53].

Raman spectra of both sulfur and “plastic” sulfur collected in this study yielded the expected spectra of S\(_8\), with increased broadness of the main \(\nu(\text{SS})\) band evident in the sublimed sulfur (see Figure 5.4).

![Figure 5.4: Raman spectra of elemental sulfur (excitation wavelength: 442 nm; irradiation density: 0.035-3.5 kW cm\(^{-2}\); 1x60s-100x10s accumulations).](image)

It was noted that thin films of sulfur vapour rapidly sublimed onto relatively cool substrates (gold, titanium oxide and glass) would transform under 442 nm irradiation to yield a product (Figure 5.5) identical to that observed on oxidised chalcopyrite (Figure 5.1), and strongly resembling the expected Raman spectrum of polymeric sulfur. Eckert and Steudel [35] note that commercial sulfur contains S\(_7\) (0.5-1.0%) and
organic residue, which is important to remove before any structural determinations. In this case, “flowers of sulfur” was generally used, rather than high-purity sulfur, as the sulfide mineral system on which the recrystallised sulfur was formed is not a high-purity system. The recrystallised product could be formed under a nitrogen atmosphere and was not accompanied by the appearance of any $\nu$(SO) modes. The lack of $\nu$(SO) modes extended to studies in solution indicating that, under air/N$_2$, loss of SO$_2$ was not occurring. Also, to within the limits of observation, the elemental octasulfur intensity remained constant during the polymeric sulfur recrystallisation under 442 irradiation (Figure 5.5). The appearance of this induced phase did not coincide with the appearance of detectable $\nu$(SH) modes.

A broad series of overlapping bands at ~800 - ~950 cm$^{-1}$ were observed to grow with the $\nu$(SS) band at 454 cm$^{-1}$. This is thought to be an overtone mode as it is the same region as the well-known 2$^{nd}$-order phonon modes of rhombohedral sulfur. It is too low in frequency for a $\nu$(SO) mode, and also formed under a nitrogen atmosphere, and too high in frequency for a $\nu$(SC) mode [54, 55]. The rhombohedral sulfur two-phonon processes in the region 800-950 cm$^{-1}$ are due to combinations of stretching mode components and those shown in Figure 5.5 closely match published spectra, with bands at 818, 866, 871 and 932 cm$^{-1}$ [35, 48].
Rhombohedral sulfur crystals were grown by dissolving “flowers of sulfur” in CCl₄, filtering the solution, and allowing the CCl₄ to evaporate. The crystals so formed readily volatilised under high irradiation densities though no recrystallised phase was observed. It could be that the signal of any “recrystallised” phase was simply swamped by the S₈ spectrum, though the studies of sublimed sulfur above indicate this is unlikely, because the intensities of the recrystallised polymeric sulfur in the studies tended to overwhelm the elemental sulfur signal.

Thin deposits around the edge of the beaker from which the CCl₄ evaporated were observed. They were of non-crystalline appearance and issued a Raman spectrum similar to that of polymeric sulfur. The insoluble (polymeric) components of the “flowers of sulfur” were filtered out from the CCl₄ prior to recrystallisation. In addition, the phase did not recrystallise under laser irradiation, was observable under both 514.5 nm and 442 nm irradiation, and the vibrational frequencies are subtly
different from those of the laser-induced phase (compare Figure 5.1 to Figure 5.6). Of note, Raman shifts of ~452 cm\(^{-1}\) and ~415 cm\(^{-1}\) in the laser-induced phase are found at ~458 cm\(^{-1}\) and 425 cm\(^{-1}\) in the solvent-recrystallised thin film. The 2\(^{\text{nd}}\) phonon modes are rather similar to those of the laser-induced phase although the leading edge is shifted up by ~4 cm\(^{-1}\). Steudel [42] notes that if a solution of \(S_8 + S_n\) (soluble sulfur ring components other than \(S_8\)) is evaporated in a vacuum, a yellow resin-like mass is obtained which solidifies as a glass but decomposes at room-temperature to a mixture of \(S_8\) and \(S_n\). Thus, it might be possible that polymeric sulfur has formed where the \(S_x\) evapo-deposited and that this polymeric sulfur has slightly different properties to that of the laser-induced polymeric sulfur (but still consistent with published spectra). Alternatively, Steudel [42] noted that, in recrystallisation experiments with CS\(_2\) cooled to ~78°C, \(\alpha-S_8\) was obtained as large yellow crystals; however, colourless small plates also formed, similar to those observed in this study, which had a \(\nu(\text{SS})\) Raman line at 460 cm\(^{-1}\). Structural analysis/HPLC-MS of the colourless phase they consisted of soluble rings larger than \(S_8\) (>35 atoms). Hendra et al. [50] reported similar FT-Raman spectra for flowers of sulfur, with Raman shifts of purified Crystex consistent with those reported for the laser-induced phase.

Figure 5.6: Raman spectra of thin layer observed on glass after recrystallisation from CCl\(_4\) (excitation wavelength: 442 nm, 514.5 nm; irradiation density: 0.5 kW cm\(^{-2}\) (442 nm), 6.1 kW cm\(^{-2}\) (514 nm); 5s-10s accumulations)
Only 442 nm irradiation produced the laser-induced polymeric sulfur from “flowers of sulfur”, sublimed sulfur or on oxidised chalcopyrite, pyrite or sphalerite surfaces. 514.5 nm, 632.8 nm and 785 nm irradiation did not lead to changes in the spectra of “flowers of sulfur” although the crystal structure of very thin films would collapse under high-intensity irradiation of any wavelength. However, this is a thermal effect rather than a photoeffect and had no significant effect on the Raman spectrum unless SERS was facilitated.

As already discussed, temperature has a significant effect on the properties and structure of sulfur. The effect of temperature on the laser-induced phase was investigated. Sulfur vapour was collected in a capillary tube, which was then sealed. The tube was heated in a small quartz holder which was wrapped in heating (resistance) wire and insulated with fibrefrax and ceramic fibreboard shielding. The resistance wire was heated using a power supply. Temperature was measured with a thermocouple as close as possible to the tube containing the sulfur but it was not possible to obtain an accurate temperature reading of the sample.

![Figure 5.7: Raman spectra of thin elemental sulfur film (and laser-induced phase) in glass capillary tube, collected during a heating cycle (excitation wavelength: 442 nm; irradiation density: 0.005 kW cm\(^{-2}\); 10s accumulations)](image-url)
The laser-recrystallised phase (formed initially at room temperature) and elemental sulfur were heated to >100°C with the laser-induced phase vanishing at ~70°C (see Figure 5.7). At temperatures above this, prolonged laser irradiation would not induce significant amounts of this phase; however, the broadness of ν(SS) band, particularly under laser irradiation, indicates the polymer was still present. Figure 5.8 shows the Raman spectrum of elemental sulfur that had been heated to >100°C and irradiated at the highest irradiation density possible for 30 minutes. The spectrum is similar to others published in heating studies in which the phase change from α-S₈ to β-S₈ and polymerisation has commenced [49, 51, 52]. Thus, it would seem that not only does the polymer breakdown to S₈ more rapidly at high temperatures (as expected, depolymerisation increases with temperature [41, 42]), but that the laser inactive material responsible for its appearance in the first place has decreased by converting to S₈. Once the sample is cooled, the laser-induced phase can be reformed. However, after repeated heating-cooling cycles, the intensity of the laser-induced phase decreased indicating the phase converts to S₈ as the temperature rises and then recrystallises as S₈ when cooled. The thermal history of sulfur samples has been noted to affect polymerisation temperatures [42]. The inability to accurately measure the temperature of the laser-stimulated phase’s transition does not allow identification of the phase, but because it is probably an amorphous phase rather than a well-defined crystalline substance, temperature measurements are not likely to greatly assist.
5.2.2. SERS investigations

Background

In this study, the interaction of sulfide/sulfur with gold has been examined in chloride and sulfate solutions to help discern distinguishing features of gold interactions from SERS studies of chalcopyrite. The behaviour of sulfur on gold has received some attention in the literature. The deposition of sulfur on gold from a sulfide solution occurs at about ~0.4 V/Ag/AgCl more negative than the sulfide/sulfur(0) couple [56, 57], even into the hydrogen evolution region [58]. The underpotential layer was restricted to ~0.4 monolayer close-packed layer coverage [56]. Multilayers were formed above the reversible potential and this led to passivation of the gold surface [56].

X-ray photoelectron spectroscopic (XPS) and rotating ring-disc electrode (RRDE) studies found that sulfide on gold deposited below the reversible potential behaved as gold sulfide (Au$_2$S), with binding energies of 161.2 eV (~65%) and 162.3 eV (~35%), which was attributed to different adsorption sites on gold [59]. Sulfur multilayers

Figure 5.8: Raman spectra of heated and cooled elemental sulfur (excitation wavelength: 442 nm; 5s accumulation for spectrum @100°C, 5sx20 accumulations for spectra of cooled sample)
deposited at higher potentials were of lower volatility (similar to metal-deficient sulfides) and behaved differently than bulk sulfur, with a lower binding energy of 162.9 eV [59]. Polysulfides were formed as intermediates in the oxidation and reduction processes [57-59] and were probably also formed on the gold surface by reaction between the deposited sulfur and solution sulfide with electrochemical data explained by [57, 59]:

\[ S^{2-} \xleftrightarrow{ \text{slow} } S^2_s \xleftrightarrow{ \text{rapid} } S^0 \]  \hspace{1cm} (39)

\( S_6^{2-} \) was the primary polysulfide found at pH 13, while a mixture of polysulfides, with average chain length being \( S_{3.3}^{2-} \) were observed at pH 9.2, and \( S_2^{2-} / HS_2^- \) at pH 6.8 [59].

Ho et al. [60] studied sulfur deposition on rotating gold electrodes from acidic H\( _2 \)S solutions (pH ~5) and found deposition of sulfur on gold was rapid (relative to glassy carbon) as nucleation is facilitated by the underpotential deposition of an atomic layer. An anodic peak at ~0.2 V/SHE related to oxidation of H\( _2 \)S to S\(^0\). Dipping the product so formed into CS\(_2\), and then continuing the cathodic sweep revealed that the cathodic peak at ~0.25 V/SHE (absent after CS\(_2\) treatment) related to sulfur reduction to H\( _2 \)S, and the cathodic peak at ~0.35 V/SHE (still present) was due to monolayer desorption. No associated anodic peak for the monolayer was observed [60]. They also found that, while the cyclic voltammograms of sulfide on gold remained similar in shape when conducted under different pH conditions (pH 0 to 6.8), the peak potentials shifted to more positive values as the acidity increased with a potential-pH plot for H\( _2 \)S concentrations yielding a linear relationship with coefficient -59±8 mV, as expected for the oxidation of H\( _2 \)S.

Gao et al. [61] undertook an electrochemical SERS investigation of sulfur on gold in both acidic (0.01 M HClO\(_4\) + 0.1 M NaClO\(_4\)) and basic (0.01 M NaOH + 0.1 M NaClO\(_4\)) electrolytes. They observed two cathodic and two anodic peaks on cyclic voltammograms (CVs) run between ~-0.6 and 0.5 V/SCE and ~-1.05 and 0.3 V/SCE for acidic and basic studies, respectively. The small anodic peak that occurred at low potential was reversible and the charge passed independent of sweep rate and sulfide concentration (0.5 to 5 mM). In acid solution, this couple occurred at ~-0.4 V/SCE, and ~-0.8 V/SCE in base. The couple was attributed to a deprotonation/protonation reaction, rather than oxidation/reduction of Au associated with sorption, as \( \nu(AuS) \) modes were observed prior to the anodic wave. SERS features accompanying this
phenomenon included the appearance of broad bands at ~270 and ~310 cm\(^{-1}\) which were attributed to \(\nu(Au-S(\cdots-H))\) and \(\nu(Au-S)\) modes respectively. The covalent bond nature of Au-S species (as opposed to Au-Cl species) was proposed to explain the lack of Stark-tuning.

Increasing the upper potential limit of the voltammetric scan led to a broad anodic peak commencing at 0 and –0.4 V/SCE in acid and base, respectively. This coincided with the appearance of \(\nu(SS)\) modes in the SERS spectra associated with polysulfide formation and oxidation to elemental sulfur. A third cathodic peak occurred in basic media which was independent of pH and attributable to the reverse of Equation:

\[
S_{ad} + xHS^- + xOH^- \rightarrow (S_{x+1}^2)_{ad} + xH_2O + 2(x - 1)e^- \quad (40)
\]
\[
(S_{x+1}^2)_{ad} - 2e^- \rightarrow (S_{x+1})_{ad} \quad (41)
\]

They proposed that the two cathodic processes could not be resolved voltammetrically in acidic media. Curiously, despite these proposals, they never examined the spectral region encompassing \(\nu(SH)\) modes. They did comment on the spectral anomalies associated with the \(\nu(SS)\) modes, suggesting both \(S_8\) and other sulfur species were present; however, they did not comment on the different observations in acidic versus basic media. At \(S^2^-\) concentrations <2 mM, only monomeric features at ~300 cm\(^{-1}\) were observed over the potential range of the voltammetric scan [61]. \(S_8\) features at anodic potentials become prominent at \(S^{2-}\) concentrations >10 mM.

These investigations were expanded to include STM observations of sulfide at a Au(111) surface [62]. At potentials below which oxidation commenced, the sulfide was adsorbed as a \((\sqrt{3} \times \sqrt{3})\) \(R30^\circ\) adlayer with ~5 Å spacing, and the sulfur binding site, probably a three-fold hollow. At low potentials where gold-sulfide Raman modes (~270 cm\(^{-1}\)) were observed in the SERS studies, sulfur did not yield an adlayer structure in the equivalent STM studies. Direct comparisons with their SERS work was difficult because the sulfide concentration and pH was lower in the STM studies than in the SERS studies. However, the lower acidity should serve to lower the anodic wave onset, while the sulfide concentration is not reported as having any effect on the underpotential deposition region of the voltammogram [61]. After forming the adlayer, and lowering the potential back to –0.5 V/SCE, Gao et al. [62] noted that the adlayer desorbed although ordered rows of sulfur remained on terrace edges.

At the onset of sulfide oxidation (~0.1 V/SCE and higher), arrays of rectangular close-packed structures formed which consisted of predominantly \(S_8\) rings [62]. In many
cases, long-range rectangular close-packed superstructures were obtained [62]. The ring dimensions and S-S bond distances (2.2 to 2.7 Å) were significantly affected by the gold substrate, being different from bulk-phase polysulfur (bond distance <2.1 Å). Further oxidation yielded multilayers of elemental sulfur species, consisting of $S_8$ rings and larger species exhibiting structural disorder.

Synchrotron high-resolution photoemission spectroscopy and density-functional calculations have been used to investigate the nature of sulfur on gold [63]. $S_2$ gas was sorbed on Au(111) in an ultrahigh vacuum (UHV) environment. It was proposed that, at 100K, at coverage <0.35 monolayers sulfur atoms adsorbed in fcc sites on gold; at 0.35<monolayers<1 sulfur dimers (bond length 1.95 to 2.0 Å) were indicated; and, at greater coverage, larger sulfur aggregates formed. At 300K, sulfur aggregation allegedly occurred from 0.33 monolayer coverage concomitant with a reduction in the strength of the Au-S bond [63]. They also commented that sulfur atoms adsorbed to the Au(111) surface probably have a relatively large mobility which allows them the facile change of adsorption site. Sorption on polycrystalline gold surfaces showed similar general trends, though a greater proportion of atomic S was suggested at monolayer coverage than on the Au(111) surface [63].

Lay et al. [64] investigated both sulfide and thiosulfate interaction with gold surfaces using electrochemical (EC), EC-Scanning Tunnelling Microscopy (EC-STM) and, ultrahigh vacuum X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) techniques. EC-STM and LEED studies revealed a 1/3 coverage ($\sqrt{3} \times \sqrt{3}) R30^\circ$) from both sulfide and thiosulfate solutions. At higher potentials, the ($\sqrt{3} \times \sqrt{3}) R30^\circ$ sulfur adlayer converted to a (3$\sqrt{3} \times 3\sqrt{3}) R30^\circ$ structure in sulfide solutions. LEED indicated a bulk (2x2) unit cell structure formed in both sulfide and thiosulfate solutions near the bulk deposition potential (> ½ monolayer coverage) [64]. These researchers also found terrace structures with a (4x4) periodicity after bulk sulfur deposition had occurred and been stripped which persisted on return scans at potentials below the ($\sqrt{3} \times \sqrt{3}) R30^\circ$ sulfur structure [64]. It remained until potentials at which hydrogen evolution occurred and was attributed to alteration of the underlying gold surface by the strained interaction with the adlayer.

In situ studies
The concentration of H$_2$S in acid was difficult to control without bubbling H$_2$S through the solution. The Raman equipment configuration used in this investigation made it necessary to conduct experiments outside of a fumehood, hence H$_2$S sparging of the solution was deemed unwise. Rather, acid solutions were made up in advance, added to the electrochemical cell and purged for 1 hour. Na$_2$S (Aldrich) was then added to the solution to yield concentrations ~ 0.02 M H$_2$S. The cell was then sealed from the atmosphere for the duration of the experiment. This concentration was selected based on Ho et al.’s [60] observation that H$_2$S bubbling of solutions yielded saturation values of ~0.02 M H$_2$S (primarily pH 4/5 solutions). In the present case, saturation was clearly exceeded as a “salting out” effect was observed with solid suspensions of sulfur evident in the acid, despite that it was well below the solubility predicted by the Henry’s Law constant.

Some representative voltammograms for gold in various sulfide solutions are displayed below. Because 0.1 M acid solutions were used, a slight rise in the pH of the solution would occur in the ~20 mM sulfide solutions. The anodic and cathodic charge passed on the following voltammograms showed a general correspondence, indicating solution species were not formed during the oxidative sweep. Sweep rate did have a significant effect on the charge passed, as expected, since dependence on diffusion rate of sulfide to the electrode surface is expected. However, the features of the CVs obtained at different sweep rates were similar. A broad anodic peak is observed at potentials >-0.1 V/Ag/AgCl with a rise in potential at >0.6 V/Ag/AgCl, which may be due oxidation of sulfur to sulfate, which occurs at 0.8 V/Ag/AgCl in acid [64, 65]. The high-potential current was not significant because the anodic and cathodic charge passed was similar. The oxidative current at high potentials does not appear to be related to gold dissolution in chloride, as it was observed in both hydrochloride and sulfuric acids.
Figure 5.9: Au electrode in 0.1 M HCl and ~20 mM H$_2$S. Initiated in the positive direction from −0.45 V/Ag/AgCl at 20 mV s$^{-1}$. Unstirred.

Figure 5.10: Au electrode in 0.1 M HCl showing effect of varying H$_2$S concentration. Initiated in the positive direction from −0.45 V/Ag/AgCl at 5 mV s$^{-1}$. Unstirred.
Figure 5.11: Au electrode in 0.1 M H$_2$SO$_4$ showing the effect of varying H$_2$S concentration. Initiated in the positive direction from –0.45 V/Ag/AgCl at 20 mV s$^{-1}$. Unstirred.

The double peak at potentials > 0.15 V/Ag/AgCl on the positive-going sweep of the voltammograms is unexpected, and is more defined in hydrochloric than in sulfuric acid although it was observed in both electrolytes. Comparisons with literature do not provide enlightenment on this, as the upper potential limits of literature studies tend to be low. It was less evident in chloride solutions when higher acidities were maintained (0.14 M HCl), at slower sweep rates, and at lower sulfide concentrations. Polysulfides are not stable in acidic solutions [59, 65] and, while the pH may vary locally at the electrode surface, it is difficult to believe this would occur sufficiently (under these conditions) to promote formation of polysulfides near the surface and that these would survive into the negative sweep. A single cathodic peak was nevertheless observed indicating these processes led to a single product. STM studies indicate the formation of sulfur strongly influenced by the substrate prior to bulk sulfur deposition [62, 64]. It may be that these are resolved electrochemically under the conditions of the experiment.

Varying the sulfide concentration yielded voltammograms with similar general shape though the monolayer formation at -0.2 V/Ag/AgCl is more resolved in the ~2 mM solution. The oxidative and reductive processes are shifted with lower sulfide concentrations requiring higher overpotentials for oxidation as expected. Also of note is the higher anodic current at high potentials for the concentrated sulfide solutions.
Cyclic voltammograms obtained in 0.1M H$_2$SO$_4$ were virtually identical to those obtained in 0.1M HCl (excluding anodic wave resolution), thereby indicating that the difference in acidities and ionic strengths of the two systems has little effect on the electrochemical response.

The following figures display the SERS spectra that were gathered during the voltammetric experiments. At low potentials (<-0.35 V/Ag/AgCl), a sharp band at ~270 cm$^{-1}$ is observed. While a $\nu$(Au-Cl$_{ads}$) Raman band is found in this region (~240 to 280 cm$^{-1}$, Stark-shifting with potential) it is generally observed at ~240 cm$^{-1}$ at -0.4 V/Ag/AgCl in acid-chloride solution [66-68]. Because the ~270 cm$^{-1}$ band is also observed in the sulfate lixiviant, it can confidently be attributed to a $\nu$(AuS) mode rather than a $\nu$(Au-Cl$_{ads}$) mode. Furthermore, it is similar to that observed by Gao et al. in perchloric acid solution which they attributed to a $\nu$(Au-S(H)) mode [61]. The spectral region 2100-2800 cm$^{-1}$ was also examined during voltammetry and under applied potential in both chloride and sulfate electrolytes but no $\nu$(SH) modes were detected indicating that the assignment by Gao et al. was not correct or that the S-H interaction is strongly ionic. Since it was present at very low potentials (verging on hydrogen evolution) it may be that the modes are due to strong Au-S interactions at terrace sites which become less strong as the potential is made more oxidising.

Contrary to studies by Gao et al., the ~310 cm$^{-1}$ mode (which they attributed to an Au-S vibration) was not prominent in acid solution, although a weak band at ~315 cm$^{-1}$ was generally evident when the $\nu$(SS) mode appeared. This band remained while the $\nu$(SS) modes were evident and then disappeared at lower potentials.

$\nu$(AuS) modes were much more evident at reduced sulfide concentrations, in which case, elemental sulfur formation was negligible. A broad $\nu$(SS) mode was observed with a maximum at ~461 cm$^{-1}$. This mode was also evident at higher sulfide concentrations but became less prominent at high potentials when the bulk sulfur modes (~218 cm$^{-1}$ and ~471 cm$^{-1}$) became more intense. This indicates that, in the less concentrated sulfide solutions, the sulfur product formed on the surface is constrained; hence, the lack of bending modes. It may also have longer bonds than bulk-phase elemental sulfur, in agreement with STM results [62]. At low sulfide concentrations, bulk elemental sulfur formation is inhibited.
Figure 5.12: Raman spectra of Au electrode in 0.1 M HCl and ~20 mM H$_2$S (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 1x4s accumulations, 5s cycle). Initiated from $-0.45$ V/Ag/AgCl at 5 mV s$^{-1}$.

In chloride-containing solutions, bulk elemental sulfur formation is more inhibited than in sulfate solutions. This is possibly due to competitive sorption of chloride, which is present at higher concentrations than sulfide. Maintaining the potential $>0.9$ V/Ag/AgCl in ~1 mM H$_2$S/0.1 M HCl solutions yielded a pronounced feature at ~326 cm$^{-1}$. This feature was accompanied by distinct shoulders at ~350 cm$^{-1}$ and ~310 cm$^{-1}$ indicative of [AuCl$_2$]$^{aq}$ and [AuCl$_4$]$^{aq}$ species and possibly some mixed chloride-sulfide species [69-72]. Cathodic scanning would then yield cathodic peaks at ~0.9 V/Ag/AgCl and ~0.7 V/Ag/AgCl consistent with reduction of these species to Au$^0$ [73-76] at which point the Raman bands would vanish.
Time

Figure 5.13: Raman spectra of Au electrode in 0.1 M HCl and ~1 mM H₂S (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm⁻²; 1x4s accumulations, 5s cycle). Initiated from –0.45 V/Ag/AgCl at 5 mV s⁻¹ as per Figure 5.10.

The general features of the sulfide/gold system in sulfate solutions are similar to those already observed in chloride (Figure 5.14). A ν(AuS) mode is evident at ~270 cm⁻¹ at low potentials which decreases in intensity as the potential is swept positive. Just prior to 0 V/Ag/AgCl, ν(SS) modes appear in conjunction with a weak mode at 310 cm⁻¹. As the potential continues more positive, the ν(SS) mode intensifies with a maximum at ~460 cm⁻¹ but shifts to the bulk sulfur spectrum as the potential continues positive. On the return sweep, after the sulfur has had sufficient time to crystallise, bulk elemental sulfur is dominant in concentrated sulfide solutions. It remains the major phase on the gold surface until the potential drops below 0 V/Ag/AgCl. As there is no competition for gold surface sites at high potentials, unlike in the chloride electrolyte, bulk elemental sulfur formation is facilitated during the voltammetric scan; the ~460 cm⁻¹ mode remains present throughout.
Figure 5.14: Raman spectra of Au electrode in 0.1 M H\textsubscript{2}SO\textsubscript{4} and ~20 mM H\textsubscript{2}S (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm\textsuperscript{-2}; 1x9s accumulations, 10s cycle). Initiated from –0.50 V/Ag/AgCl at 2 mV s\textsuperscript{-1} to 0.9 V/Ag/AgCl.

At low potentials, a ~270 cm\textsuperscript{-1} mode predominates with a 313 cm\textsuperscript{-1} mode becoming prominent as the monolayer region is transgressed. These modes are only minor compared to the sulfur modes. The ~310 cm\textsuperscript{-1} modes remains on the surface while elemental sulfur formation continues, then diminishes as the main cathodic peak is transgressed, with the ~270 cm\textsuperscript{-1} mode reappearing at greater intensity. These trends were more resolved in basic solution (Figure 5.15). It appears that the ~270 cm\textsuperscript{-1} mode is due to Au-S interaction on terrace sites whereas the 310 cm\textsuperscript{-1} modes relates sulfide adsorption in 3-fold hollow fcc sites on the gold surface. Clearly, the Au-S interaction remains significant in the underlayer even while elemental sulfur builds up. This is different from the interpretation by Gao et al. [61] who attributed the ~270 cm\textsuperscript{-1} mode to Au-S(...H) vibrations. However, the lack of v(SH) modes observed in spectra collected during this study, in conjunction with STM results of other researchers [62, 64], support this interpretation.
**Ex situ studies**

In previous chapters, the effect of laser irradiation on product sulfur produced through mineral oxidation has been observed. Gold was evapo-deposited on recrystallised rhombohedral sulfur, and “flowers of sulfur” were evapo-deposited onto roughened gold substrates. After irradiating for at least 1 minute with 632.8 nm light, no irradiation effect was noted nor were any ν(AuS) modes observed, independent of whether the sites were thinly or thickly coated.

---

Figure 5.15: Low-frequency Raman modes from gold in ~4 mM Na₂S, pH 9.2 (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm⁻²; 1x5s accumulations, 10s cycle). Initiated from −1.0 V/Ag/AgCl at 5 mV s⁻¹; E_max = 0.2 V/Ag/AgCl
5.3. The binary copper sulfide system

5.3.1. Background

The literature investigating covellite oxidation is fraught with controversy, as it is for chalcopyrite. Some key conclusions of published research are listed below:

- Studies of rotating discs in ferric-containing solution show oxidation of chalcocite occurs in several steps through several intermediates involving progressive removal of Cu from the lattice into solution [77-79]. Intermediate phases may include metastable forms of djurleite [Cu$_{1.97}$S, hcp], hexagonal Cu$_{1.83}$S (hcp), digenite [Cu$_{1.83}$S, ccp], anilite [Cu$_{1.75}$S, ccp], blaubiebender covellite [Cu$_{1.40-1.36}$S, hcp] and covellite [CuS, hcp] [80, 81].

Figure 5.16: Raman spectra (in air) of sulfur deposited on roughened gold, or gold evapodeposited on recrystallised elemental sulfur (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm$^{-2}$; 1s accumulation (S evaporated onto roughened gold), 10 s accumulation (Au evaporated onto recrystallised sulfur))
- Covellite oxidation is much more recalcitrant than that of the above phases and shows active-passive behaviour typical of systems yielding a sulfur product [79, 82] with both linear [78, 83] and parabolic [80] leaching kinetics reported. The long-term leaching of covellite is independent of stirring, with ≤ 6% sulfur reporting as sulfate and heterogeneous attack of the surface [78].

- Dissolution rate is strongly affected by electrolyte and concentration [82] with chloride facilitating faster dissolution rates [80, 84].

- Oxidation of chalcocite and reduction of covellite is reversible at slow rates provided there is sufficient cupric ion in solution [81].

- <10% sulfate is produced during ferric leaching [78, 80, 83, 84], with elemental sulfur being the primary product. Sulfur solvents increase the leach rate in chloride-containing lixiviants [84].

- The kinetics are strongly temperature dependent, showing 2-stage leaching from chalcocite/digenite at low temperature (in which virtually complete oxidation to covellite was necessary before further oxidation to sulfur occurred; $E_A \sim 20 \text{ kcal mol}^{-1}$) while at $T>60^\circ\text{C}$ linear kinetics were observed ($E_A 6 \text{ kcal mol}^{-1}$) [77, 78, 85, 86].

- An anodic wave is observed on an initial covellite sweep (~0.5 V/SCE) that decreases with each subsequent sweep. The maximum current density varies with the square root of the sweep rate indicating transport control although there was no variation with stirring rate [80, 82, 84] indicating solid-state/pore diffusion. Biegler and Swift [87] noted the same phenomena in their studies of chalcocite oxidation, indicating the wave Ghali et al. [82] observed was due to an altered surface (they used polished electrodes, which can produce chalcocite-type phases due to thermal alteration [88]) or copper-rich inclusion phases, rather than pure covellite. High anodic peak currents in both sulfate and chloride electrolytes were noted, and circuit resistance became significant at high currents [87]. Secondary peaks at >1V/SCE were observed [82, 87, 89], analogous to the potentials achieved after the galvanostatic jump (discussed below).

- The behaviour of the system varies strongly with current density [90] with non-passivating CuS at low current densities (<1.4 mA cm$^{-2}$) and a sharp potential rise at higher current densities [90, 91]. Increased temperature may suppress the potential jump [91].
In galvanostatic studies, the potential rises sharply after a period, determined by $I^2\tau = \text{constant}$, where $I =$ current density and $\tau =$ transition time, with the constant being much less in sulfate systems than chloride systems. This was originally interpreted in terms of copper diffusion inhibition due to CuSO$_4$ precipitation in pores which formed because of molar shrinkage of the CuS product [87]. This was later re-interpreted in terms of solid-state diffusion and electrochemical reaction in the first stage of reaction product CuS [92, 93].

Reasonable oxidation rates at lower potentials, particularly at elevated temperatures, have been noted for covellite [83, 91, 94]. Chloride increases the rate at even moderate temperatures [86]. Some researchers predict higher oxidation rates for covellite than chalcopyrite [94, 95]. Li et al. [3] claimed, using Raman spectroscopy, that minor amounts of elemental sulfur formed on chalcocite oxidised at 0.3 V/SCE in acid and on covellite at 0.4 V/SCE in acid-chloride solution at 25°C. They also observed an increase in S$_2$ type species on covellite with oxidation.

Chalcocite can allegedly leach by two different paths: in strong ferric solutions, a hcp sulfur path is followed; whereas, in weak solutions ($\leq 10^{-2}$ M), a tetragonal (ccp) leaching path is followed in structures with no natural analogs [22].

5.3.2. Normal Raman investigations

Chalcocite thin film electrodes were prepared by electrodepositing copper onto a stainless steel “slug”. The initial copper film was 0.5 $\mu$m thick, electrodeposited from a copper sulfate electrolyte (45 g/L Cu$^{2+}$, 20 mg/L Cl$^-$, 3 mg/L thiourea and 2 mg/L glue). The thin copper layer was then sulfidised overnight using a 0.1M sodium sulfide solution under nitrogen at a potential of $-0.87$ V vs. Ag/AgCl. Electrochemical experiments were then conducted in the electrochemical apparatus described in the Experimental section of this thesis, using an electrolyte consisting of 0.01M Cu$^{2+}$ in 0.1M H$_2$SO$_4$, after Koch and McIntyre [81].

While the copper sulfides have not been extensively characterised by Raman spectroscopy, they have been characterised electrochemically. Free energies [23] and reduction potentials [81], obtained by constant current experiments on thin film electrodes, have been determined for chalcocite, djurleite [Cu$_{1.95-1.91}$S], digenite [Cu$_{1.86-1.80}$S], anilite [Cu$_{1.75}$S], blue-remaining covellite [Cu$_{1.40-1.36}$S] (spionkopite and yarrowite [96]) and covellite.
Raman spectra of natural samples of chalcocite (Butte, Montana) and covellite (Moonta, SA) were shown in Chapter 3. Chalcocite shows only a broad weak band around 300 cm\(^{-1}\), whereas covellite displays a strong \(\nu(\text{SS})\) band at ~472 cm\(^{-1}\) and a weak lattice mode at ~267 cm\(^{-1}\).

Figure 5.17 shows Raman spectra obtained from a thin layer chalcocite electrode held at varying potentials until current flow became negligible (i.e. equilibrium was approached). Each of the spectra shows a band at 986 cm\(^{-1}\) attributable to sulfate in solution. A potential of 0.14 V/Ag/AgCl is in the stability region of chalcoite (see Table 5.2) and the spectrum observed is equivalent to that obtained from the natural mineral sample. The spectrum at 0.237 V/Ag/AgCl is the same as that at 0.140 V/Ag/AgCl, and is in the region Koch and McIntyre [81] found Cu\(_2\)S to have been oxidised to Cu\(_{1.68}\)S. At 0.262 V/Ag/AgCl the oxidation to blaublündender covellite is approached and a hint of a \(\nu(\text{SS})\) mode can be observed. Once at 0.286 V/Ag/AgCl a Raman band at 474 cm\(^{-1}\) appears indicating that sulfur pairs were present. At this potential, Koch and McIntyre found Cu\(_{1.40}\)S (spionkopite). These findings are in agreement with those of Goble [97] who reported that only covellite and the blue-remaining covellites (spionkopite and yarrowite) contain covalently bonded sulfur. At 0.33 V/Ag/AgCl, in the CuS stability region, a spectrum typical of covellite was observed, with \(\nu(\text{SS})\) at 474 cm\(^{-1}\) and a lattice mode at 267 cm\(^{-1}\).
Figure 5.17: Raman spectra from a thin layer of Cu$_2$S deposited on a stainless steel electrode after holding the potential at different values in $10^{-2}$ M CuSO$_4$ in 0.1 M H$_2$SO$_4$ (excitation wavelength: 442 nm; irradiation density: 0.05 kW cm$^{-2}$; 10s x 100 accumulations).

Table 5.2: Rest potentials for a chalcocite electrode at “steady state” in 0.01M CuSO$_4$, 0.1M H$_2$SO$_4$ (From Koch and McIntyre [81])

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rest Potential (V vs. Cu/Cu$^{2+}$)</th>
<th>Rest potential (V vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>2$S → Cu$</em>{1.95}$S + 0.05 Cu$^{2+}$ + 0.10 e$^{-}$</td>
<td>0.143</td>
<td>0.203</td>
</tr>
<tr>
<td>Cu$<em>{1.91}$S → Cu$</em>{1.86}$S + 0.05 Cu$^{2+}$ + 0.10 e$^{-}$</td>
<td>0.173</td>
<td>0.233</td>
</tr>
<tr>
<td>Cu$<em>{1.80}$S → Cu$</em>{1.68}$S + 0.12 Cu$^{2+}$ + 0.24 e$^{-}$</td>
<td>0.190</td>
<td>0.250</td>
</tr>
<tr>
<td>Cu$<em>{1.65}$S → Cu$</em>{1.40}$S + 0.25 Cu$^{2+}$ + 0.50 e$^{-}$</td>
<td>0.202</td>
<td>0.262</td>
</tr>
<tr>
<td>Cu$_{1.36}$S → CuS + 0.36 Cu$^{2+}$ + 0.72 e$^{-}$</td>
<td>0.268</td>
<td>0.328</td>
</tr>
</tbody>
</table>

The equilibration time in the binary Cu-S system above was significant. Thus an alternative means to study the system using chemical bath deposited (CBD) films was attempted. Using the film mix described in the Experimental section, thin films <0.5
μm on glass, platinum and gold were obtained [15] with prolonged exposure resulting in the films peeling from the surface. The films were generally amorphous when put down, but would readily recrystallise to covellite when annealed at 150°C for 30 minutes (Figure 5.18) or aged for a few days in a copper sulfate solution. Generally, the latter technique was followed for coating of gold/platinum electrodes to prevent decomposition of connectors and holders.

![Raman spectra of CuS thin films as-deposited and after annealing at 150°C for 30 minutes on glass slides (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm⁻²; 10s x 5 accumulations)](image)

Figure 5.18: Raman spectra of CuS thin films as-deposited and after annealing at 150°C for 30 minutes on glass slides (excitation wavelength: 632.8 nm; irradiation density: 0.31 kW cm⁻²; 10s x 5 accumulations)

In order to undertake spectroelectrochemical investigations, a thin CuS film was CBD deposited on a Pt electrode. Figure 5.19 displays a cyclic voltammogram of the film which was previously held at –0.1 V/Ag/AgCl prior to scanning in order to insure chalcocite was present. The CV is typical for chalcocite in a copper-containing sulfate solution and agreed well with the data obtained by Gerlach and Kuzeci [92] and others [82, 87, 89, 98, 99], with oxidation to covellite at ~0.4 V/Ag/AgCl (reversible potential ~0.33 V/Ag/AgCl [92]), the reversible potential for the Cu²⁺/Cu⁰ couple at ~0.055 V/Ag/AgCl, reduction of covellite to chalcocite at ~0.2 V/Ag/AgCl
(CuS + Cu$^{2+}$ + 2e$^-$ → Cu$_2$S) and also −0.2 V/Ag/AgCl (2CuS + 2H$^+$ + 2e$^-$ → Cu$_2$S + H$_2$S). The resolution of the chalcocite to covellite oxidation peak into two processes is unusual, but possibly due to the oxidation of intermediate compounds, which tends to be obscured at higher sweep rates or in stirred solutions where the precipitation of intermediate compounds during reduction is discouraged. At potentials >0.6 V/Ag/AgCl the oxidation of covellite remains recalcitrant (also in agreement with the literature) until potentials >1.1 V/Ag/AgCl are observed. Unfortunately, multiple CVs were difficult to obtain due to the molar density changes, in addition to the reductive release of H$_2$S, leading to the CuS film cracking and falling off the electrode surface.

![Cyclic voltammogram of a CuS film deposited on Pt in 0.01 M CuSO$_4$/0.1M H$_2$SO$_4$. Initiated in the positive direction from 0.10 V/Ag/AgCl at 5 mV s$^{-1}$. Unstirred.](image)

Raman spectra of the CuS thin film on the platinum electrode were collected during the cyclic voltammogram. Remarkably, the ν(SS) modes were discernable even in the absence of surface-enhancement. The spectra are displayed in Figure 5.20. As the main anodic wave is entered, ν(SS) modes become evident. Initially the maximum intensity occurs at a low frequency (~420 cm$^{-1}$) and then shifts to the values expected of covellite (~471 cm$^{-1}$), though remaining somewhat broad. These mirror the spectra above (Figure 5.18) showing as-deposited film and annealed forms, indicating the longer sulfur bonds are initially formed in a somewhat amorphous matrix that
progressively crystallises and becomes more covellite-like. However, a distinct shoulder on the covellite ν(SS) band remains throughout the potential sweep indicating only partial recrystallisation, or that two different forms exist. As the potential continues to rise δ(SSS) modes at ~220 cm⁻¹ become evident, indicating that minor amounts of elemental sulfur are present, but these never become significant indicating CuS remains the major phase within these potential boundaries. The δ(SSS) modes do not correspond with the voltammogram and, so, are possibly due to laser effects and/or interaction with underlying substrate. On the return potential scan, CuS remains on the surface until the cathodic current becomes significant and is not observed below 0.15 V/Ag/AgCl. ν₁(SO₄²⁻) modes at ~981 cm⁻¹ are also evident in the spectra and are due to the electrolyte.

Experiments were also conducted in a chloride electrolyte and were very similar to those displayed for the sulfate electrolyte. Potentiostatic experiments were conducted and revealed a laser effect under 632.8 nm irradiation, as shown in Figure 5.21.
at exceptionally low irradiation densities, recrystallisation of sulfur was noted. This was not noted on spectra collected at OCP, so presumably an unstable Raman inactive phase is present that reacts to yield elemental sulfur. Thus, the laser effect cannot be discounted from the spectra collected during the CV, though in that case Cu$^{2+}$ was present in solution, thereby decreasing the tendency to sulfur formation and increasing the stability of copper sulfide phases.

Figure 5.21: Raman spectra of CuS thin film on Pt oxidised in 0.1M HCl for four hours. The labels refer to irradiation densities and times (excitation wavelength: 632.8 nm; 10sx5 accumulations per spectrum)

5.3.3. SERS investigations

To further explore the model copper sulfide system, the deposition of thin films (via CBD techniques) on gold was undertaken. Emplacement of the film involved immersion of a roughened gold electrode in deionised water contained in a glass cell. The gold surface was brought into focus and monitored continuously using Raman spectroscopy. Thin film constituents were added as required. The emersion of the
gold electrode was based on the observance of Raman bands in the ν(SS) region of the spectrum and the commencement of SERS background drop (<2 minutes immersion). On gold, nucleation centres are readily available, thus care must be taken to ensure that CuS ultrathin layers and not Au$_2$S/Au-S$^0$ are being observed. This is not too difficult to achieve given the greater stability of CuS ($\Delta G^0_f$=−53.2 kJ mol$^{-1}$) over Au$_2$S ($\Delta G^0_f$=47.5 kJ mol$^{-1}$) and elemental sulfur under the deposition conditions [100].

Generally, deposition times of <2 minutes were sufficient to observe ν(SS) modes on gold, as opposed to the 0.5 hours or more required to observe the phase on a glass substrate with a maximum thickness prior to peeling of <0.5 µm [15, 16]. Figure 5.22 displays the Raman spectrum, collected in air, of a CuS ultrathin film on gold immersed <2 minutes and aged overnight in acidic copper sulfate solution. This same electrode and film were used in the following spectroelectrochemical studies. It is compared to a mineral (Moonta) covellite spectrum and displays all the hallmarks of its mineral counterpart, even (surprisingly) showing a lattice mode and combination overtone. This indicates that the film is thick enough to have bulk properties, yet, as shown in the following in situ spectroelectrochemical results, still facilitates SERS. It may be that the film is discontinuous since irregularities on the roughened gold surface are of the order, or greater, than the film thickness, and thus SERS is facilitated.
Figure 5.22: Raman spectrum of thin film on gold aged overnight in 0.01 M Cu$^{2+}$/0.1 M H$_2$SO$_4$ prior to use in voltammetry experiments (Figure 5.23) and comparative mineral covellite spectrum (excitation wavelength: 632.8 nm (thin film), 442 nm (mineral); Irradiation density: 0.31 kW cm$^{-2}$ (thin film), 0.10 kW cm$^{-2}$ (mineral); 50s accumulations).

Cyclic voltammograms of the ultrathin film on roughened gold in 0.01 M Cu$^{2+}$/0.1 M H$_2$SO$_4$ solution are presented below. Clearly, they display no commonality with the voltammograms of clean roughened gold in the presence of sulfide and 0.1 M H$_2$SO$_4$ (Figure 5.14). The potential minimum was chosen to ensure no aqueous Cu(II) reduction to Cu(0), which occurs at 0.064 V/Ag/AgCl in this electrolyte [81]. The voltammogram bears a strong resemblance to that of the CuS film on Pt and compared well with the literature [81, 82, 87, 89, 92, 98, 99].

A surface product was evident in the first voltammetric cycle that was oxidised and did not re-appear on subsequent cycles. This is not unexpected as the chemical bath deposition results in an amorphous phase which, on aging, might lead to formation of elemental sulfur, copper oxides (which would dissolve on immersion in the acid electrolyte), sulfates, etc. In the first three cycles, a potential maximum of 0.55 V/Ag/AgCl was imposed. In such cases, a single broad oxidation peak was evident, coupled with a single reduction peak commencing 0.33 V/Ag/AgCl. As the potential
maximum was increased on subsequent cycles, the cathodic peak was resolved into two (the total cathodic charge passed remained exactly the same) with the second peak at ~0.2 V/Ag/AgCl.

![Cyclic voltammograms of a CuS thin film on a roughened gold electrode in 0.01 M CuSO₄/0.1 M H₂SO₄ solution. Initiated in the positive direction from 0.1 V/Ag/AgCl at 5 mV s⁻¹. Unstirred.](image)

The Raman spectra accompanying the first voltammetric cycle are display in Figure 5.24. At the starting potential, no Raman features are observed, consistent with the presence of chalcocite, which should be present at the starting potential of 0.1 V/Ag/AgCl. As the positive-going sweep continues, ν(SS) modes become evident. A ν(SS) mode consistent with a covellite-like product (~471 cm⁻¹) is observed but a shoulder at ~420 cm⁻¹ remains conspicuous. The spectra remain virtually unchanged until the cathodic current starts flowing, and the low-frequency shoulder vanishes at ~0.2 V/Ag/AgCl. The covellite-like phase then remains until the potential reaches ~0.15 V/Ag/AgCl. No elemental sulfur was observed, as no δ(SSS) modes were evident.

The Raman spectra collected on subsequent cycles with higher potential maxima are essentially identical to that in Figure 5.24, except that the low-frequency ν(SS) bands extended down a little lower (to ~410 cm⁻¹). Even at 1.0 V/Ag/AgCl, no other
product was observed, consistent with published studies on the chalcocite/covellite systems. No bending modes consistent with element sulfur or polysulfides were observed in any spectra. For all cycles, the low-frequency $\nu$(SS) bands vanished at $\sim$0.2 V/Ag/AgCl.

A mechanism consistent with these observations is that, on oxidation of the chalcocite, Cu$^{2+}$ leaves the close-packed sulfur lattice at a slightly greater than stoichiometric amount (i.e. slightly greater than 50 at.% of the total copper is lost). As the sulfur lattice then modifies to produce the CuS structure, a metal-deficient overlayer, is formed that is stable and recalcitrant to oxidation to accommodate the loss of excess copper. The structure of the overlayer/polymorph product yields $\nu$(SS) bands with a lower frequency than those observed in CuS, in accord with longer bonds expected for such a phase. Underlying sulfur layers, where the copper:sulfur
atomic ratio is closer to 1, form a covellite-like product. The overlayer remains present until the cathodic current commences flowing, at which point the copper:sulfur ratio rectifies and the metal-deficient layer reduces to covellite. The resolution of the cathodic peaks after higher potential excursions is due to reconstruction of the amorphous overlying phase in these cases. Another possibility is that chalcocite oxidises to Cu$_{1.4}$S (which also yields the ν(SS) band at 471 cm$^{-1}$) with the low-frequency shoulder being due to a metastable polymorph of CuS.

5.4. Conclusions

This chapter presents a number of studies concerning model systems and compounds in order to clarify the identity and properties of oxidation products of chalcopyrite, and distinguish the behaviour of gold layers in chalcopyrite SERS experiments. In normal Raman investigations, the laser-induced phase (442 nm irradiation) formed on chalcopyrite, pyrite and sphalerite was found to be consistent with a polymeric sulfur compound. The laser-induced phase was not consistent with polysulfide species nor polythionate decomposition products. Polymeric sulfur could also be induced from thin films of vapour-deposited “flowers of sulfur” on a number of substrates under 442 nm irradiation. Polymeric sulfur could not be induced to form from rhombohedral sulfur crystals crystallised from carbon tetrachloride. Polymeric sulfur could not be induced from vapour-deposited thin films under 514.5 nm, 632.8 nm or 785 nm irradiation. However, once present, it was readily observed at these frequencies and was stable to irradiation. This accords well with observations of oxidised chalcopyrite samples kept under UHV conditions. Prior to application of vacuum the octasulfur spectrum overwhelmed other features on the oxidised chalcopyrite surface. However, once octasulfur had volatilised under vacuum, modes consistent with polymeric sulfur became evident on the surface under 632.8 nm irradiation.

The identity of the compound that transforms to polymeric sulfur from the “flowers of sulfur” thin films under laser irradiation is unknown. Recrystallisation experiments showed that octasulfur was not responsible, as expected from known photo/thermal studies. Published UV-Vis spectra of the various sulfur allotropes indicate most ring structures are also unlikely candidates, though S$_7$, a known component of commercial sulfur preparations is acknowledged to be thermally unstable. Temperature
experiments showed that the polymeric sulfur pre-cursor compound transformed to octasulfur at temperatures well below 100°C.

SERS investigations of sulfide interactions with gold electrodes showed that, while the redox behaviour is not easily distinguished from that of chalcopyrite, some spectral features are conspicuous. At saturated sulfide concentrations in acid solutions, the $\nu$(SS) modes approach a distinguishing band at ~461 cm$^{-1}$ (possibly a constrained monolayer sulfur) prior to observance of bulk sulfur spectra at higher potentials. The ~461 cm$^{-1}$ band remains prominent over the potential region 0 V/Ag/AgCl to 650 V/Ag/AgCl. At lower sulfide concentrations, this band becomes less distinguishable and broadened. However, under such conditions, the $\nu$(AuS) band at ~310 cm$^{-1}$ becomes more evident. This may be difficult to distinguish on the gold-decorated chalcopyrite surfaces as it is found close to a chalcopyrite lattice mode ($E_{2}^{\text{TO}}$ ~322 cm$^{-1}$) even though it is evident on most enhanced chalcopyrite surfaces.

In addition, at low potentials (~0.35 V/Ag/AgCl) another $\nu$(AuS) mode at ~270 cm$^{-1}$ features prominently. This may be related to sulfide sorption on terrace sites, and would be readily distinguished on a reduced chalcopyrite surface. The $\nu$(AuS) modes did not coincide with $\nu$(SH) modes which indicates proposed mechanisms for sulfide underpotential deposition on gold in the literature may not be correct [61, 62]. At low sulfide concentrations (~1 mM H$_2$S) in 0.1 M HCl, it was observed that chloride competition became significant at potentials >0.9 V/Ag/AgCl and, in such systems, the formation and reduction of tetrachloroaurate and dichloroaurous species was readily identified, both voltammetrically and spectroscopically.

Raman investigations of the binary copper sulfide system showed that the electrochemical behaviour of covellite was in no way like that of the oxidation product layer formed on chalcopyrite. In the chalcopyrite system, the pre-wave product can be decomposed at potentials >0.8 V/AgCl, while much higher overpotentials are required for covellite decomposition (>1.1 V/Ag/AgCl).

The SERS studies indicated that a metal-deficient overlayer was formed during Cu$_2$S oxidation, simultaneously with a covellite-like phase, which was reduced at ~0.2 V/Ag/AgCl, before the onset of CuS reduction to chalcocite. This metal-deficient sulfide product displayed a distinct Raman band at ~420 cm$^{-1}$, which was not similar to the Raman band formed on chalcopyrite during SERS experiments.
5.5. References


6. Investigations using *ex situ* techniques
6.1. Preamble

The spectroelectrochemical studies presented in this thesis provided detailed information on kinetics and molecular species at the corroding interface. However, Raman Spectroscopy may lack sensitivity to structures in which ionic bonding is prevalent and elemental concentrations are not issued, except in regards to effects on crystal and molecular structures.

Various \textit{ex situ} techniques have been utilised in this investigation to provide this supporting information. A brief introduction to these techniques, their uses and limitations was presented in Chapter 2.

Environmental Scanning Electron Microscopy (ESEM) was used in secondary electron and back-scattered electron modes to provide topographical and phase information respectively on the corroding mineral faces, including gold-decorated samples.

Dynamic Secondary Ion Mass Spectrometry (SIMS) was used to determine the depth distributions of key elements on the corroding mineral and compare the various systems studied. While a good estimate of the corrosion depth can be obtained from the charge passed during potentiostatic oxidation experiments, SIMS is able to add information on the elemental stoichiometry of the corroded layer with much greater accuracy than could be gleaned from solution analyses.

X-ray photoelectron Spectroscopy (XPS) has been used to determine valence state information of the various elements on the corroding surface, which can then be combined with the Raman information to determine the species present and their stoichiometries. It was also used to examine the interaction between vapour-deposited gold and the sulfide mineral surface used in SERS experiments.

These techniques, being \textit{ex situ}, could possibly be measuring surfaces that have “aged” somewhat from those formed in solution, particularly using such a sensitive technique as XPS. The initial oxidation layer formed on chalcopyrite is known to decompose rapidly at elevated temperatures [1, 2], and it is unknown how long it is stable at room temperature, although studies suggest up to 17 hours in solution [3].

Unfortunately, stable synthetic chalcopyrite thin films could not be created for neutron reflectometry experiments, so binary CuS thin films were used as a model. Neutron reflectometry gives information about the depth distribution of phases. The
data is more difficult to model if the interfaces are not sharp. The technique is suited for *in situ* investigations but was used, in this case, for *ex situ* studies. None of these techniques is a spot analysis technique, so surface variations and inclusion phases of the natural specimens used would contribute to the observed signal.

### 6.2. ESEM investigations of oxidised chalcopyrite

BSE micrographs of chalcopyrite reference samples and the surface coatings formed during circumneutral leaching were presented in Chapter 3. Generally, this technique was not sensitive enough to yield useful information on samples leached in acidic solutions.

#### 6.2.1. Acid leached samples

BSE micrographs of a Mt Isa sample that had been ground and leached for two weeks in ferric sulfate are displayed in Figure 6.1 and Figure 6.2. Polishing was not undertaken to prevent thermal alteration of the surface. The leached surface exhibited grinding tracks with a few minor inclusion phases. There was little evidence of reaction products, though minor pitting of the surfaces was evident in places. Figure 6.1 shows an area which is darker than the surrounding chalcopyrite. Energy-dispersive X-ray (EDX) analysis revealed it was sulfur enriched. It appears as if this depression was created by removal of an inclusion phase during grinding, and that this area has reacted preferentially. EDX analysis of the surface indicated an otherwise uniform composition with comparable concentrations of copper and iron, except at one slightly darker inclusion phase, where pyrite was found.
Figure 6.1: BSE micrograph of Mt Isa chalcopyrite leached two weeks in 0.015 M Fe$_2$(SO$_4$)$_3$/0.1 M H$_2$SO$_4$.

Figure 6.2: BSE micrograph of Mt Isa chalcopyrite leached two weeks in 0.015 M Fe$_2$(SO$_4$)$_3$/0.1 M H$_2$SO$_4$. A polishing pit is evident adjacent to the inclusion phase.
In contrast, Figure 6.3 presents a topographical image from a Messina sample that has been leached in ferric chloride, and subsequently examined under vacuum. The sample had a visible sulfur layer over the surface prior to vacuum submission. Some particles remain on the surface, with evidence of leaching particularly around grinding lines. EDX analysis yielded a standard chalcopyrite composition.

![Figure 6.3: Scanning electron micrograph of Messina chalcopyrite leached 1 day in 0.03M ferric chloride/0.1 M HCl and kept under vacuum.](image)

**6.2.2. Circumneutral leaching**

ESEM micrographs of peroxide leached samples were presented previously. An iron oxide overlayer was observable with underlying crystal structures and variations evident when the electron beam energy was varied. Lowering the accelerating voltage can reduce the depth penetration provided that the accelerating voltage
remains above the critical-excitation energy. The EDX analyses at 12 kV indicated that the iron oxide layer was thicker in the darker region with the copper to sulfur ratio being similar in both the dark region and surrounding region (1:7 and 1:10 atoms, respectively) as was the iron to oxygen ratio (1:3 atoms). At beam energies of 15 kV, the EDX analysis still indicated an excess of iron oxide although the iron to oxygen ratio was less (1:4 atoms) in the dark area. The light area showed a much reduced iron oxide signal. The copper to sulfur ratio increased (3:7 atoms) in both areas at 15 kV. This indicates the underlying matrix in both areas is chalcopyrite, but in the darker area a thicker layer of iron oxide and sulfur has formed due to preferential crystal orientation.

![Figure 6.4: BSE micrographs of Messina chalcopyrite leached overnight in 1% H$_2$O$_2$, at beam energies 15 kV (left) and 12 kV (right).](image)

6.2.3. **Gold-decorated samples**

Gold-decorated samples were examined using ESEM. A Messina chalcopyrite sample that had been leached in 1% H$_2$O$_2$ then treated with 0.1M HCl to remove the overlying iron oxide layers before sputter coating with gold (~50 nm) clearly demonstrated SERS facilitation. Micrographs of the sample are displayed in Figure 6.5. The topography is extremely porous due to a thick sulfur layer present over the entire surface. Higher magnification reveals the globular nature of these sulfur structures. The BSE image displays a primarily uniform composition with some darker spots distributed across the surface, probably undissolved iron oxide or carbon contamination. The SERS spectra that were gathered from this sample showed
rhombohedral sulfur so, clearly, the energetic sputtering process did not lead to decomposition of the reacted layer.

As noted in Chapter 4, sputter coating was not desirable for less reacted samples where the “passivating” layer is known to be thermally unstable [1, 3] and, hence, likely to be unstable with regards to energetic atom bombardment. Application of colloidal suspensions was also not desirable due to the potential for electroless plating reactions with the surface (e.g. gold colloid suspensions typically contain halides, being produced from the reduction HAuCl$_4$ with a reducing agent such as citrate, borohydride or alcohols and various stabilising agents). Gold vapour evaporation was used for these more fragile samples. Again, due to product films being sensitive to temperature, the substrate was not heated and films were deposited at room temperature with a 15 cm source-to-sample distance. Heating a gold island film or depositing onto a warm substrate yields larger islands with separation distances that better facilitate SERS; however, room temperature deposition under specific conditions can yield SERS-active surfaces [4-7]. Generally, slower evaporation rates, higher substrate temperatures, and thinner films favour surface-plasmon resonance in the red region [5, 7].

It may be that the chalcopyrite surface itself possesses a nanoscale topographical roughness that facilitates SERS. Indeed, in most experiments, the chalcopyrite surface was leached prior to gold deposition. Figure 6.6 and Figure 6.7 display electron micrographs of gold-coated chalcopyrite surfaces that have been subjected to different oxidative procedures. While the surface features are far less rough than those of extensively oxidised samples (Figure 6.5), roughened areas are nevertheless apparent even though the resolution is too poor to distinguish their nature. It is clear that, in many cases, the surface enhancement achieved is not optimal; in some figures of the enhanced minerals chapter, the chalcopyrite lattice mode ~290 cm$^{-1}$ band was still clearly evident indicating that the bulk lattice anions in the beam are contributing as strong a signal as the surface groups.
Figure 6.5: Micrographs of gold-sputtered peroxide leached sample: (a), (c) and (d) show topographical structure and (b) shows a BSE image of part of the region displayed in (a).

Figure 6.6: Topographical micrographs of gold evapo-coated Messina chalcopyrite, which was subsequently electrochemically cycled.
6.3. Dynamic SIMS investigations of oxidised chalcopyrite

Dynamic SIMS investigations were undertaken in an attempt to determine the depth to which the non-stoichiometry of different ionic species extended. Non-stoichiometry of iron and copper species are typically observed in kinetics, XPS and Auger studies [8-10], although leach studies at elevated temperatures demonstrate the long-term stoichiometric release of iron and copper [9, 11, 12]. However, in such studies generally pre-oxidised (i.e. air oxidised during recovery and milling) concentrate samples were used and stringent control of $E_H$ and/or pH was not maintained.

All sputtering profiles in this section were collected using a Cs$^+$ ion beam. Resulting anions are likely to have undergone preferential sputtering [13, 14]. To prevent sample charging, a ~50 nm gold layer was sputtered onto the sample surface prior to profiling.

Polycrystalline samples tend to sputter unevenly, and “single crystal” chalcopyrite was obtained to alleviate this. However, the single crystal chalcopyrite contained galena and sphalerite intergrowths that would impact galvanic behaviour during leaching; hence, the polycrystalline samples were used.
6.3.1. Acid leached

Samples (from Ward’s and Messina chalcopyrite) were leached in ferric sulfate and ferric chloride solutions over periods of 1 day, 3 days and 5 weeks. While few inclusion phases were evident in the samples, a significant degree of microtopographical variation was unavoidable on a number of the samples due to scouring of quartz inclusions and chalcopyrite crystallites throughout the matrix (Figure 6.8 and Figure 6.9).

![Figure 6.8: Optical micrographs of samples surfaces leached 3 days in ferric chloride (a) and 3 days in ferric sulfate (b).](image1)

![Figure 6.9: Secondary electron micrograph of SIMS sputter crater on Wards Scientific reference sample (a) and BSE micrograph of Messina reference sample surface (b).](image2)

Despite the less-than-ideal nature of these samples for dynamic SIMS analysis, some conclusions can be drawn from the samples analysed. Although variable currents were used for depth profiling, the data was analysed in a preliminary fashion by assuming that sputter depth could be normalised against current. Quantitative
conclusions cannot be drawn because it was not possible to develop calibration samples for such a complex system.

Entrained reactants and products in the leached layers of the ferric leached samples made iron depth profiles difficult to interpret. Figure 6.10 displays the variation of different elements, normalised against the sulfur signal for a sample leached in 0.1M HCl for 6 weeks. An oxidised layer is clearly evident, with the O/S ratio decreasing with profile depth as elemental sulfur/sulfur-enriched oxidation products decrease. The Cu/S correspondence is close, with little variation in copper concentration at the surface, which, on the other hand, is clearly iron-depleted. It is important to note that, based on kinetic evidence reviewed in Chapter 1, non-stoichiometry indicates an altered oxidation front only, not long-term incongruent dissolution. Profilometer measurements were not undertaken, but estimates from microscopic observation put the sputter crater at ~1 µm indicating the iron-depleted surface layer is a few hundred nm thick.

Figure 6.10: $^{16}$O, $^{56}$Fe and $^{63}$Cu counts normalised to the $^{34}$S signal for a Ward’s chalcopyrite sample that has been leached for 6 weeks in 0.1 M HCl.

The copper signal is also depleted near the surface, but its signal is close to the bulk signal within half the time required for the iron. Both the iron and copper signals continue to rise slightly relative to the sulfur signal as the profile continued. As the signals for the two elements correspond, it is probable that this is an instrumental effect (sample charging, preferential sputtering) rather than a bulk effect.
A general trend in oxidation layers was evident (Figure 6.11), with the O/S ratio highest for samples leached for shorter times. The O/S signal also decreased more rapidly with increased leach time, indicating either that the O surface concentrations decrease with leach time or that the sulfur surface signal increases with leach time. Since the first is unlikely (iron oxyhydroxide phases would be improbable in this scenario) the ratio indicates an increasingly oxidised sulfur-enriched layer forms with continued leaching.

Figure 6.12 displays the copper signal for samples leached in ferric chloride for different times. Not surprisingly, longer leach times led to decreased copper signal at the surface, and apparently deeper leaching profiles. This was not completely expected, since the altered overlayer in the chloride leaching system is expected to be elemental sulfur, which would volatilise under UHV environments. It may be that the gold sputtered overlayer prevented excessive elemental sulfur volatilisation during sample degassing, and that sputtering was sufficiently rapid that it surpassed the sulfur volatilisation rate. More likely, it may indeed be that this trend reflects increasingly deep layers of low-volatility amorphous sulfur, or an altered metal-deficient sulfide layer.

Figure 6.11: Variation of leached chalcopyrite normalised oxygen/sulfur ratio with leach time.
Direct comparison of the sulfate and chloride leached samples is not possible because entrained leachant ions will affect sputtering yields and efficiencies (for instance chloride is known to preferentially sputter in Cs$^+$ ion beams). The different matrix compositions on leaching of the two systems also affects interpretation. Attempts to normalise data against the sulfur signal yielded the profiles shown in Figure 6.13. It seems that, irrespective of leach time or leachant, the copper/sulfur ratio varies relatively consistently although the chloride leached samples seem to be a little more copper deficient at the surface and to greater depth.
6.3.2. **Circumneutral leached**

Polished chalcopyrite samples, analogous to those used in the acid leaching experiments, were leached in 1% H$_2$O$_2$ solutions over various timeframes. Thin interference films of ferric oxyhydroxides/sulfates became evident on the peroxide leached surfaces within 24 hours with longer timeframes leading to thick iron oxide layers. These ferric oxyhydroxide overlayers were then removed using dilute acid (0.1M HCl, <1 hour) leaving the underlying leached sulfide material exposed. As for the acid leached samples, microtopographical variation was significant, affecting the resolution of results.

Although variable currents were used for depth profiling, the data was analysed, as per the acid leached samples, by assuming that sputter depth could be normalised against current. The intensity data was normalised against sulfur even though sputtering efficiency may change with sulfur’s changing oxidation state and lattice packing through the leached layers. Elemental sulfur on the surface is expected to have volatilised under vacuum.

Figure 6.14 clearly displays a trend between the leaching time and iron (relative to sulfur) signal in the leached layers. The curvature of the signal for the sample leached for 5 weeks is much less, indicating iron depletion to greater depths and greater sulfur...
overlayers. In addition, the longer the sample was leached, the lower the ultimate iron to sulfur ratio became thereby indicating a change in the bulk iron content relative to the bulk sulfur concentration.

Figure 6.14: Variation of normalised iron to sulfur ratio in chalcopyrite with leach time and leachant strength.

Figure 6.15 demonstrates a similar trend for leached samples although distinctly different behaviour is observed for the reference (unleached) sample. This is possibly due to the production of a Cu$_2$S overlayers as a result of thermal alteration during polishing [15]. As per the previous figure, the metal to sulfur ratio at the surface is low and increases as the product layer is transgressed and the bulk is sputtered. The normalised time scale in Figure 6.15 is identical to that shown in Figure 6.14, so it can be observed that the copper to sulfur ratio varies less than the iron to sulfur ratio with leach time and sputter depth. Indeed, each sample seems to behave similarly with greater correspondence between copper and sulfur composition than between iron and sulfur composition.

Leached samples show a decreasing oxygen to sulfur ratio with leach time (Figure 6.16) probably due to excess sulfur (and indicating that the “bulk” signal arises from elemental sulfur and not the sulfide lattice). Unlike for the ferric leached samples, the O/S ratio does not decrease more rapidly with increased leach time. This is probably because iron oxide products remain in the product layer.
Figure 6.15: Variation of the copper to sulfur ratio in chalcopyrite leached with H$_2$O$_2$ for various times.

Figure 6.16: Variation of normalised O/S ratio in chalcopyrite leached with H$_2$O$_2$ for various times.
6.4. X-ray photoelectron spectroscopic studies

X-ray photoelectron spectroscopy has been used extensively to examine the products of chalcopyrite leaching. While some researchers claim to have observed polysulfide products [10, 11, 16] on leached chalcopyrite surfaces, others have been cautious against assigning S(2p) moderate binding energy (BE) components to polysulfides [8, 17-19]. Indeed, Smart [20] notes the reliable assignment of high binding energy S(2p) components to polysulfides requires evidence from other techniques. Klauber et al. [17] and Smart [20] note that reliable assignment of S(2p$_{3/2}$) components to elemental sulfur can be made based on evaporative loss at 295 K even though they differ slightly in binding energy (~163.5-164 eV). However, Buckley et al. [21] note evaporative loss of even lower binding energy S(2p) species (162.9 eV), albeit at significantly slower rate. They attributed this binding energy to monolayer sulfur on gold.

Table 6.1 displays published XPS binding energies and assignments of various sulfide and oxide minerals and also crystalline polysulfide phases. Table 6.2 displays the binding energies and assignments of S(2p$_{3/2}$) regional spectra for selected studies of oxidized sulfide minerals. There are many more published XPS studies of sulfide mineral oxidation but those displayed in Table 6.2 underwent relatively detailed interpretation of the spectra.

It is clear from Table 6.2 that the binding energy assignments to a particular sulfur entity vary widely amongst different researchers. This may be due, in some part, to the different binding energy referencing systems used in these studies. While most instruments are calibrated against Au(4f$_{7/2}$) and Ag (3d$_{5/2}$) binding energies, the regional spectra were referenced in a variety of ways. For instance, Klauber et al. [17, 18, 22] reference their S(2p) spectra by assuming the lowest binding energy component to be sulfide and assigning this a binding energy of 161.15 eV. Many authors use C(1s) to reference regional spectra and correct for charge, but their assignment of the adventitious carbon binding energy included 284.6 eV [23, 24], 248.8 eV [11], and 285.0 eV [10, 16]. Others did not find charge correction to be necessary [8, 25]. Add to this the variation in Au(4f$_{7/2}$) binding energy assignment (from 83.8 eV [8, 21, 26] to 83.98 eV [23]) and it is easily understood why such varied binding energies are reported. Furthermore, the doublet splitting for the S(2p) spectra also varied across different studies.
Table 6.1: XPS binding energies (and intensities where available) of various minerals and crystalline species.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ref</th>
<th>S(2p$_{3/2}$)</th>
<th>Cu(2p$_{3/2}$)</th>
<th>Fe(2p$_{3/2}$)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covellite (CuS)</td>
<td>[27]</td>
<td>161.8</td>
<td>931.4</td>
<td>-</td>
<td>Synthetic, RT, calibration details not given, S(2p) assym.</td>
</tr>
<tr>
<td></td>
<td>[28]</td>
<td>161.8</td>
<td>-932</td>
<td>-</td>
<td>Mineral- vac. fractured, 180K, S splitting 1.15 eV</td>
</tr>
<tr>
<td></td>
<td>[23]</td>
<td>161 (1)</td>
<td>161.8 (2)</td>
<td>-932</td>
<td>Mineral-ground under N$_2$, RT, S splitting 1.2 eV</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>[27]</td>
<td>161.77</td>
<td>932.0</td>
<td>-</td>
<td>Synthetic, RT, calibration details not given</td>
</tr>
<tr>
<td>(Cu$_2$S)</td>
<td>[29]</td>
<td>161.6</td>
<td>932.5</td>
<td>-</td>
<td>Mineral-vac. fractured, 180K, S(2p$_{3/2}$) FWHM 0.8 eV</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>[18]</td>
<td>S$^2-_S$: 161.15 (1)</td>
<td>931.92,</td>
<td>Not fit</td>
<td>Mineral-vac. fractured, 150 K, S splitting 1.19 eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S$^2-_S$: 161.93 (0.36)</td>
<td>933.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Loss: 163.74 (0.18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(FeS$_3$)</td>
<td>[30]</td>
<td>S$^2-_S$: 161.3</td>
<td>-</td>
<td>707-708</td>
<td>Mineral-vac. fractured, 180 K</td>
</tr>
<tr>
<td>CuS$_2$</td>
<td>[27]</td>
<td>161.5</td>
<td>931.3</td>
<td>-</td>
<td>Synthetic-high pressure phase, calibration details not given, S(2p) assym, pyritic structure.</td>
</tr>
<tr>
<td>S$_8$</td>
<td>[31]</td>
<td>163.5</td>
<td>-</td>
<td>-</td>
<td>180K, S splitting 1.15 eV</td>
</tr>
<tr>
<td></td>
<td>[25]</td>
<td>163.5-164.2</td>
<td>-</td>
<td>-</td>
<td>RT, Raman verification</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S$^2-_S$: 162.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S(0): 162.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>[32]</td>
<td>-</td>
<td>934.3</td>
<td>-</td>
<td>O(1s) BE: 531.5</td>
</tr>
<tr>
<td></td>
<td>[33]</td>
<td>-</td>
<td>935-936</td>
<td>-</td>
<td>O(1s) BE: 530.9</td>
</tr>
<tr>
<td>CuO</td>
<td>[33]</td>
<td>-</td>
<td>933.8</td>
<td>-</td>
<td>O(1s) BE: 529.6</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>[33]</td>
<td>-</td>
<td>932.5</td>
<td>-</td>
<td>O(1s) BE:530.5</td>
</tr>
<tr>
<td>FeO</td>
<td>[33, 34]</td>
<td>-</td>
<td>-</td>
<td>709.5-709.6</td>
<td>O(1s) BE: 530.0</td>
</tr>
</tbody>
</table>

Table 6.1 continued.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ref</th>
<th>S(2p&lt;sub&gt;3/2&lt;/sub&gt;)</th>
<th>Cu(2p&lt;sub&gt;3/2&lt;/sub&gt;)</th>
<th>Fe(2p&lt;sub&gt;3/2&lt;/sub&gt;)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOOH/Fe₂O₃</td>
<td>[33, 34]</td>
<td>-</td>
<td>-</td>
<td>711-</td>
<td>O(1s) O² BE: 529.8-529.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>711.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCu₃S₄</td>
<td>[27]</td>
<td>161.1</td>
<td>931.7</td>
<td>-</td>
<td>Synthetic, RT, calibration details not given, S(2p) asym.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>161.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuV₄S₄</td>
<td>[27]</td>
<td>160.6</td>
<td>931.4</td>
<td>-</td>
<td>Synthetic, RT, calibration details not given, S(2p) asym.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(0)</td>
<td>[35]</td>
<td></td>
<td>932.7</td>
<td></td>
<td>Multi-element calibration (Ag, Au, Cu).</td>
</tr>
<tr>
<td>(NH₄)₂[Pt(S₅)₃]</td>
<td>[31]</td>
<td>161.9 (2), 162.8</td>
<td>-</td>
<td>-</td>
<td>180K, S splitting 1.15 eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2), 163.2 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu₄(S₄)₃]&lt;sup&gt;+&lt;/sup&gt;</td>
<td>[31]</td>
<td>161.0 (1), 163.0</td>
<td>-</td>
<td>-</td>
<td>180K, S splitting 1.15 eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂[Rh(S₅)₃]</td>
<td>[26]</td>
<td>161.5 (6), 162.6</td>
<td>-</td>
<td>-</td>
<td>180 K, S splitting 1.19 eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(7), 163.2 (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂[PtS₁₇]</td>
<td>[26]</td>
<td>161.9 (6), 162.8</td>
<td>-</td>
<td>-</td>
<td>180 K, S splitting 1.19 eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6), 163.2 (5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂S₂</td>
<td>[22]</td>
<td>163.59, 162.05*</td>
<td>-</td>
<td>-</td>
<td>150 K, S splitting 1.19 eV, XRD/Raman verification.</td>
</tr>
<tr>
<td>Na₂S₄</td>
<td>[22]</td>
<td>163.18, 161.67*</td>
<td>-</td>
<td>-</td>
<td>150 K, S splitting 1.19 eV, XRD/Raman verification.</td>
</tr>
<tr>
<td>Na₂S₅</td>
<td>[22]</td>
<td>163.36, 161.76*</td>
<td>-</td>
<td>-</td>
<td>150 K, S splitting 1.19 eV, XRD/Raman verification.</td>
</tr>
<tr>
<td>K₂S₅</td>
<td>[22]</td>
<td>162.73, 161.28*</td>
<td>-</td>
<td>-</td>
<td>150 K, S splitting 1.19 eV, XRD/Raman verification.</td>
</tr>
<tr>
<td>K₂S₆</td>
<td>[22]</td>
<td>163.18, 161.49*</td>
<td>-</td>
<td>-</td>
<td>150 K, S splitting 1.19 eV, XRD/Raman verification.</td>
</tr>
</tbody>
</table>

RT = Room temperature.

* Intensity ratios not as expected, due to XPS not being a bulk technique.
Table 6.2: S(2p\textsubscript{3/2}) binding energies and assignments of product layers on oxidized sulfide minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ref</th>
<th>S(2p\textsubscript{3/2})</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CuFeS\textsubscript{2}</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buckley and Woods (1984)</td>
<td>[8]</td>
<td>S\textsuperscript{2-}: 160.7</td>
<td>Acetic acid oxidised. Analysed at 150 K. Air oxidation yielded Fe(2p\textsubscript{3/2}) fits at CuFeS\textsubscript{2}: 708 eV and FeOOH: 711 eV. S(2p\textsubscript{3/2}) spectrum could also be fit with CuS+S\textsubscript{0} components, but CuS doublet not 2:1 intensity, the ratio of the two components was not 1:1 and no loss of elemental sulfur on warming. No Cu(II) or Fe(II) shake-up satellites.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu\textsubscript{0.8}S\textsubscript{2}: 162.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{2-}: 160.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 164.3</td>
<td></td>
</tr>
<tr>
<td>Hackl et al. (1995)</td>
<td>[10]</td>
<td>S\textsuperscript{2-}: 161.7</td>
<td>Oxygen pressure leached in sulfuric acid at elevated temperature (110-200°C).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{2-} 2\textsuperscript{-}: 162.4</td>
<td>No Cu(II) or Fe(II) shake-up satellites. C(1s, ref) BE: 285.00 eV.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 163.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 164.3</td>
<td></td>
</tr>
<tr>
<td>Klauber et al. (2001)</td>
<td>[17]</td>
<td>S\textsuperscript{2-}: 161.15</td>
<td>Ferric chloride and sulfate leached at 50°C. Analysed at 150 K. Cu(2p\textsubscript{3/2}) BE: 932 eV (lower by 0.15 eV in unleached) and Fe(2p\textsubscript{3/2}) BE: 708 eV (Fe-S) and 711.5 eV (Fe-O). Discounted polysulfides based on volatility of S\textsubscript{0} component. No Cu(II) or Fe(II) shake-up satellites. C(1s, ref) BE: 285.00 eV.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{2-} 2\textsuperscript{-}: 162.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 163.5*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO\textsubscript{4} 2\textsuperscript{-}: 168.66</td>
<td></td>
</tr>
<tr>
<td>Mikhlin et al. (2004)</td>
<td>[16]</td>
<td>S\textsuperscript{2-}: 160.8</td>
<td>Potentiostatically leached (25°C) and ferric sulfate/chloride leached (50°C).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu(2p\textsubscript{3/2}) BE: 932.1 eV (unleached)-932.8 eV (leached) and Fe(2p\textsubscript{3/2}) BE: 708.0 eV (Fe-S) and 711.5-711.7 eV (Fe-O). No Cu(II) or Fe(II) shake-up satellites. C(1s, ref) BE: 284.6 eV.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{2-} 2\textsuperscript{-}/(S\textsubscript{0})S\textsubscript{-}: 162</td>
<td>Analyses undertaken at room temperature, so assumed all sulfur volatilised and thus polysulfide endchain components at ~162 eV, and mid-chain components at ~162.8-163.8 eV. Relativity intensities give chain lengths. Possibility of non-volatilisable monolayer S\textsubscript{8} and thermal damage not considered.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn(S\textsubscript{-}): 162.8-163.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{+}: 164.5</td>
<td></td>
</tr>
<tr>
<td>Farquhar et al. (2003)</td>
<td>[24]</td>
<td>S\textsuperscript{2-}: 160.74</td>
<td>Potentiostatic oxidation at pH 4. Pre-ox polishing and analysed at room temperature. O(1s) BE: 529.65 eV (O\textsuperscript{2-}), 531.45 eV (OH\textsuperscript{-}), 533.9 eV (H\textsubscript{2}O\textsubscript{ad}) [36]; Cu(2p\textsubscript{3/2}) BE: 931.44 eV; Fe(2p\textsubscript{3/2}) BE: 707.44 eV (Fe-S) and 708.4 eV (Fe-S leached), 711.5-711.7 eV (Fe-O). No Cu(II) or Fe(II) shake-up satellites. C(1s, ref) BE: 284.6 eV.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 163.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO\textsubscript{4} 2\textsuperscript{-}: 167.85</td>
<td></td>
</tr>
<tr>
<td>Harmer (2002)</td>
<td>[11]</td>
<td>S\textsuperscript{2-}: 161.3</td>
<td>Acid (H\textsubscript{2}SO\textsubscript{4}, HClO\textsubscript{4}) and ferric leached at 85°C. pH/Eh control not stringent.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{2-}: 162.4</td>
<td>Analysed at ~150 K. C(1s, ref) BE: 284.8 eV; O(1s) BE: 530 eV (G\textsuperscript{\delta}), 531.5 eV (OH), 533.9 eV (H\textsubscript{2}O\textsubscript{ad}) [36]; Cu(2p\textsubscript{3/2}) BE: 932.0-932.7 eV (Cu(I)-S), 933.6-933.8 eV (CuO), 934.4-934.6 eV (Cu(OH)\textsubscript{2}), 933.3 eV (Cu(II) satellite). Not calibrated against reference compounds for all these assignments.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{2-}: 163.0-163.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 163.6-164.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO\textsubscript{4} 2\textsuperscript{-}: 168.5</td>
<td></td>
</tr>
<tr>
<td><strong>FeS\textsubscript{2}</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mycroft et al. (1990)</td>
<td>[25]</td>
<td>S\textsuperscript{2-}: 161.8</td>
<td>Oxidised at pH 5 in 0.1 M KCl (pH 5). Room temperature analyses. Calibration against Au(4f\textsubscript{7/2}) at 83.90 eV. Surface fractured under vacuum.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{2-}: 162.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 163.3-163.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsubscript{0}: 164.0</td>
<td></td>
</tr>
<tr>
<td><strong>Cu\textsubscript{2}S</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buckley et al. (2003)</td>
<td>[29]</td>
<td>S\textsuperscript{2-}: 161.6</td>
<td>Air oxidised 24 hours. Analysed at 180K. Cu(2p\textsubscript{3/2}) BE: 932.5 eV (Cu(I)) 933.6 eV (Cu(II)), 935 eV (Cu(II)).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S\textsupscript{2-}: 162.5</td>
<td></td>
</tr>
<tr>
<td><strong>CuS</strong></td>
<td>[23]</td>
<td>161, 161.8 (CuS)</td>
<td>Oxidised potentiostatically in borate buffer. Cu(2p\textsubscript{3/2}) BE: 932 eV (E&lt;0.92)</td>
</tr>
</tbody>
</table>

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In this study regional spectra were referenced against the C(1s) binding energy at 285.00 eV.

6.4.1. Chalcopyrite oxidation

Acid leached

Preliminary fitting of the Fe(2p), Cu(2p) and S(2p) regional spectra were undertaken. It was not possible to sensibly fit the Fe(2p) spectra, though the first two peaks tended to distinguish Fe-S type species (at ~708 eV) from Fe-O type groups (at ~711 eV). The Cu(2p) spectra were fitted with a Gaussian-Lorenzian lineshape assuming a splitting of 19.85 eV, while the S(2p) spectra where fit assuming a splitting of 1.18 eV and intensity ratio 2:1. The results are summarised in Table 6.3.

It may be observed that the binding energy components amongst oxidised samples are largely similar. Lower binding energy S(2p) components are required to fit the ground sample and reduced sample, which was included for comparative purposes. Notably, the Fe(2p) binding energy component of the reduced sample indicated an Fe-O type species with the O(1s) binding energies indicating a hydroxide species rather than an oxide species. The reduction reaction is thought to produce aqueous Fe$^{2+}$ which has clearly been retained on the surface and oxidised during subsequent washing. This was the only sample from which sulfate was recorded, indicating that an unstable reduced phase was formed which oxidised on exposure to air to yield a sulfate/hydroxide species. It may also be noted in this sample that the surface is enriched in copper, indicating the formation of Cu$_2$S type phase and loss of sulfide from the surface as H$_2$S.

In all cases the Cu(2p) spectra were devoid of detail in the 940-950 eV region indicating that Cu(II) species were not present as the satellite peaks were absent. There was pronounced asymmetry in the Cu(2p) spectra which was also observed by Klauber et al. [17, 18] and which they related to a loss feature.
Table 6.3: XPS binding energies and relative intensities for chalcopyrite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S (2p)</th>
<th>Cu(2p)</th>
<th>Fe(2p)</th>
<th>Fe/S</th>
<th>Cu/S</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>BE (eV)</td>
<td>I(%)</td>
<td>BE (eV)</td>
<td>I(%)</td>
<td>BE (eV)</td>
</tr>
<tr>
<td>Ground in air</td>
<td>161.6</td>
<td>67</td>
<td>932.4</td>
<td>80</td>
<td>708.2</td>
</tr>
<tr>
<td></td>
<td>162.3</td>
<td>16</td>
<td>934.0</td>
<td>20</td>
<td>710.8</td>
</tr>
<tr>
<td></td>
<td>163.2</td>
<td>17</td>
<td>708.3</td>
<td>17</td>
<td>710.0</td>
</tr>
<tr>
<td>Ground in air</td>
<td>161.7</td>
<td>49</td>
<td>932.4</td>
<td>83</td>
<td>708.4</td>
</tr>
<tr>
<td></td>
<td>162.9</td>
<td>16</td>
<td>934.3</td>
<td>17</td>
<td>710.3</td>
</tr>
<tr>
<td></td>
<td>163.9</td>
<td>35</td>
<td>708.4</td>
<td>17</td>
<td>710.0</td>
</tr>
<tr>
<td>Oxidised 10 mins at 0.6V/Ag/AgCl in 0.1M HCl</td>
<td>161.9</td>
<td>56</td>
<td>932.6</td>
<td>100</td>
<td>708.4</td>
</tr>
<tr>
<td></td>
<td>162.9</td>
<td>13</td>
<td>934.3</td>
<td>17</td>
<td>710.3</td>
</tr>
<tr>
<td></td>
<td>163.9</td>
<td>31</td>
<td>708.4</td>
<td>17</td>
<td>710.0</td>
</tr>
<tr>
<td>Oxidised in 0.03 M FeCl₃ for 1 day</td>
<td>161.6</td>
<td>63</td>
<td>N/A</td>
<td>N/A</td>
<td>708.5</td>
</tr>
<tr>
<td></td>
<td>162.8</td>
<td>14</td>
<td>710.2</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>163.6</td>
<td>23</td>
<td>711.1</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Oxidised in 0.015 M Fe₃(SO₄)₃ for 8 days</td>
<td>~163.9</td>
<td>100</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>161.7</td>
<td>61</td>
<td>932.5</td>
<td>85</td>
<td>711.4</td>
</tr>
<tr>
<td></td>
<td>162.7</td>
<td>11</td>
<td>934.0</td>
<td>15</td>
<td>711.9</td>
</tr>
<tr>
<td></td>
<td>163.2</td>
<td>18</td>
<td>710.9</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>168.5</td>
<td>10</td>
<td>711.9</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Leached 1 day in 0.01M CuSO₄, 0.015 M Fe₂SO₄ for 10 minutes</td>
<td>161.5</td>
<td>55</td>
<td>932.3</td>
<td>77</td>
<td>708.3</td>
</tr>
<tr>
<td></td>
<td>164.1</td>
<td>17</td>
<td>933.9</td>
<td>23</td>
<td>710.9</td>
</tr>
</tbody>
</table>

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Figure 6.17: S(2p) spectra (left), Fe(2p) spectra (middle) and Cu(2p) spectra (right) of chalcopyrite: (a) ground in air; (b) oxidised 10 minutes in 0.1 M HCl at 0.60 V/Ag/AgCl; (c) oxidised 1 day in 0.03 M FeCl$_3$/0.1M HCl; (d) oxidised 8 days in 0.015 M Fe$_2$(SO$_4$)$_3$/0.1M H$_2$SO$_4$; (e) reduced 10 minutes in 0.1M HCl at –0.45 V/Ag/AgCl; and (f) leached 1 day in 0.01M CuSO$_4$, 0.015 M Fe$_2$SO$_4$, 0.5 M FeSO$_4$.

Elemental sulfur is indicated on the samples oxidised in HCl, even after only 10 minutes. It is difficult to know whether to assign the components in the sulfate leach, reduced, and ground sample surface to monolayer or sub-monolayer sulfur, or to
polysulfide, without further examination. The sulfate oxidised, air-ground and reduced sample also show a much higher proportion of sulfide than the chloride oxidised samples. The sample leached in ferrous solution shows a much higher component at ~162.5 eV (possible disulfide) than do the other samples. If distributed charge is assumed in polysulfide chains this may indicate shorter polysulfide chains for the ferrous leach.

It is also evident in the sample oxidised potentiostatically that the surface is slightly iron-deficient. The analysis undertaken by Mikhlin et al. [16], assigning binding energies of ~162 eV to polysulfide chain end atoms, and those at 162.8-163.8 eV to mid-chain atoms was not appropriate here as the components at 163.9 eV did not fit this categorisation. However, if the S^{2-} component was aligned at 161.15 eV, as per Klauber et al. [17], then this categorisation was possible. Further investigation indicated the high binding energy component represented elemental sulfur, at least in the case of chloride, despite Mikhlin et al.’s claims that said sulfur would have volatilised at room temperature. What can be deduced is that the higher S(2p) (~163 eV) binding energy component to mid (~162.5 eV) and low (~162 eV) binding energy components ratio is greater for chloride leached samples than for sulfate leached samples or reduced/air-ground samples.

Most recent XPS studies of sulfides are undertaken at ~150K-200K to prevent sulfur volatilisation. The instrumentation used in this study did not allow for this, so room temperature scans were undertaken. A main factor in radiation damage during XPS is the secondary electron flux but damage cross sections are unlikely to be temperature dependent [17, 18]. However, induced thermal effects may also be factor and cannot be dismissed in this study. The sample oxidised for 10 mins at ~0.6 V/Ag/AgCl in 0.1M HCl was re-scanned after a 1.5 hour interval under vacuum at room temperature, and the results are displayed in Figure 6.18. The X-ray beam was used to examine other samples in the interim, so it is possible that the spot sampled after 1.5 hours was not identical to that sampled initially although the Fe(2p) and Cu(2p) spectra changed little. The S(2p) spectrum shows a reduction in high BE components, with the binding energies and actual intensities (in counts per second) of the lower BE components remaining virtually identical between scans. Thus, some variability in the XPS spectra may be due to volatilisation and/or thermal changes; such studies must be interpreted cautiously.
Circumneutral leached

Samples leached in 1% H$_2$O$_2$, yielded an iron-rich surface layer, consistent with the formation of ferric oxyhydroxide and possibly a small amount of a jarositic type compound. Removal of the ferric oxyhydroxide overlayer with 0.1M HCl yielded a sulfur-rich surface layer, deficient in both copper and iron. Approximately 5% of the S(2p) signal derived from sulfate, with more than 50% due to sulfur for the acid-
washed sample. No satellite peaks associated with the presence of Cu(II) were evident in the acid washed sample. The Cu(2p$_{3/2}$) binding energy of the unwashed sample (934.6 eV) is consistent with the presence of Cu(II). A great deal more of the O(1s) spectrum in the unwashed sample is due to oxide and hydroxide components than in the washed sample. About 40% of the sulfur signal is due to sulfate (indicative of small amounts jarosite and/or copper sulfate), with a small amount (~20%) due to a high binding energy component at 164.8 eV, which may be indicative of a polythionate species.

![Figure 6.19: Chalcopyrite leached overnight in 1% H$_2$O$_2$: (a) acid-washed (At%: Cu 6.6, Fe 14.9, O 30.3, S 48.1); and (b) untreated (At%: Cu 3.9, Fe 30.9, O 60.0, S 7.2). Note that the scale of the S(2p) spectra are different.](image)

6.4.2. Gold and sulfur

The evaporative deposition of gold on chalcopyrite (after oxidation and prior to redox cycling) as well as onto sulfur was investigated using XPS techniques. The Au(4f) spectra are displayed below in Figure 6.20.

The Au(4f) spectra are of consistent appearance, with no significant asymmetry and narrow FWHM in all cases (0.7 eV in the (a) and (b) and 0.9 eV in (c)). The binding
energy of the Au\((4f_{7/2})\) peak was 84.6 eV to 84.9 eV in these spectra. Spectra gathered from bulk fine gold at this time yielded an Au\((4f_{7/2})\) peak at 84.4 eV, thus the binding energies in Figure 6.20 represent bulk gold. A spin-orbit splitting of 3.67 eV was used to fit the data with an Au\((4f_{7/2})\) to Au\((4f_{5/2})\) intensity ratio of 1.3, which is in good agreement with the literature [37]. Carefully calibrated bulk gold is found at ~84 eV, with “small particle gold” (<5 nm) up to 85.6 eV [38, 39], and Au\(^+\) at 85.8-86.0 eV [40]. Implementing these corrections and adding the extremely low FWHM (compared to published studies where values of 1.0 eV are reported) allows the conclusion that Au\(^+\) is not detectable on the following samples. However, it is must be considered that SERS is considerable more sensitive than XPS, and so the presence of minor Au\(^+\) cannot be discounted. The S(2p) spectra are largely similar to their uncoated counterparts although the S(2p) fitting on the rhombohedral sulfur spectrum is poor (splitting is 1.22 eV) and may indicate another species at higher binding energy is present in minor amount. This spectrum was quite difficult to collect due to volatilisation.

The O(1s) spectra, where available, yielded single fits indicative of adsorbed water. Cu(2p) was present as Cu\(^+\) and the Fe(2p) spectra showed a mixture of Fe-S and Fe-O type species.
Figure 6.20: Au(4f) (top) and S(2p) (bottom) spectra of various samples with an evaporated gold coating: (a) Messina chalcopyrite pre-oxidised 1 minute in 0.1M HCl then coated (At% Cu 1, O 3, C 35, S 6, Au 55); (b) Messina chalcopyrite coated with gold then cycled between –0.45 V/Ag/AgCl and 0.9 V/Ag/AgCl 20 times in 0.1M HCl (At% Cu 17, Fe 6, O 9, C 36, S 11, Au 20); and (c) Rhombohedral sulfur crystal (recrystallised from CCl4) coated with Au (At% O 26, C 52, S 15, Au 8).

6.5. Neutron reflectometry studies of copper sulfide thin films

6.5.1. Composition

Neutron reflectometry investigation of chemical bath deposited (CBD) copper sulfide was undertaken as a means to examine the interfacial processes of this model binary system. Freshly deposited films on glass were shown to consist of two layers, a dense layer next to the substrate, covered by a less dense layer [41]. The dense layer had
scattering length density (SLD) of $3.25 \times 10^{-6} \text{Å}^{-2}$, which is greater than the theoretical value for covellite, at $3.11 \times 10^{-6} \text{Å}^{-2}$, and significantly greater than the upper layer at $2.34 \times 10^{-6} \text{Å}^{-2}$. The dense layer SLD was, nevertheless, well below the SLD expected for copper-rich phases (Cu$_x$S, where $x>1.1$). The film was also quite rough, possibly indicating that the film initially deposits as a bulk phase based on nucleation sites on the substrate, and subsequent colloidal aggregation results in the upper less dense film. The Raman spectroscopic investigation of these films was presented in the previous chapter indicated a form inconsistent with crystalline covellite, showing extensive ν(SS) modes of lower frequency (and more amorphous) than those expected for covellite.

Annealing of the films at 150°C led to the production of single layer film with Raman spectrum typical of covellite [41] and a colour change in ~100 nm films on glass from gold to green. However, the SLD remain below the theoretical covellite value, at $2.86 \times 10^{-6} \text{Å}^{-2}$.

Acid leached

Acid leaching of annealed films for 30 minutes (0.005 M Fe$_2$(SO$_4$)$_3$/pH 2.5) yielded a structure with poor reflectivity characteristics (Figure 6.21). The films have been noted to be quite unstable in aqueous solutions (particularly when unannealed) and tend to flake off. Acid conditions appear to decrease stability, and so the acidity was maintained as low as possible to retain ferric ion in solution. This may be complicated should non-oxidative dissolution occur and acid consumed at the interface such that there may be local precipitation of ferric or cupric salts.

Two different models gave reasonably good fits of the data (see Figure 6.22): a one-layer model issued a ~300 Å layer of SLD $1.75 \times 10^{-6} \text{Å}^{-2}$, in keeping with a metal-deficient sulfide phase, cupric oxide phase (theoretical SLD $1.8 \times 10^{-6} \text{Å}^{-2}$) or chalcanthite (CuSO$_4$.5H$_2$O, theoretical SLD $1.35 \times 10^{-6} \text{Å}^{-2}$). The cupric oxide phase is not likely given the acidic conditions.

The second was a three-layer model fit which showed the film thickness decreased by ~30% during the leaching process with substantial impact on the film composition. The film yielded a SLD post-leach of $0.267 \times 10^{6} \text{Å}^{-2}$ in the upper 700 Å, a SLD of $1.08 \times 10^{6} \text{Å}^{-2}$ for a further 95 Å, with a SLD of $1.84 \times 10^{6} \text{Å}^{-2}$ in the lower ~300 Å. Thus, a very porous overlayer is indicated, under which a layer more in keeping with elemental sulfur is found (theoretical SLD $1.25 \times 10^{6} \text{Å}^{-2}$). Under this a metal-deficient sulfide layer is indicated. The top layer bears some resemblance to cupric
hydroxide, which has theoretical SLD $0.292 \times 10^{-7} \, \text{Å}^{-2}$, rather than cupric sulfate, ferric hydroxide or hydronium jarosite which have higher theoretical SLDs. This was unexpected, as ferric hydroxides are generally less soluble at low pH; they typically form amorphous masses of which density determinations would be difficult to undertake. Thus, it is more likely that a ferric overlayer is formed on the oxidising covellite thin film although some non-oxidative dissolution would have occurred to generate the pH rise necessary for this to occur.

Figure 6.21: Reflectivity profile of CuS thin film leached for 60 minutes in 0.005 M Fe$_2$(SO$_4$)$_3$/pH 2.5
Intriguingly, leaching in DDI water led to apparent phase segregation and possible oxidation. Again, two models yielded reasonable fits of the data. In the two-layer model an underlayer with SLD $3.40 \times 10^{-6}$ Å$^{-2}$ extended for 50 nm, overlain by a less-dense layer with SLD $2.00 \times 10^{-6}$ Å$^{-2}$ (see Figure 6.24). This underlayer approximates a metal-enriched species like djurleite ($\text{Cu}_{31}\text{S}_{16}$), while the overlayer is significantly less dense than covellite. The three-layer model is more sensible, showing a dense underlayer with SLD close to that expected of yarrowite ($\text{Cu}_9\text{S}_8$; theoretical SLD $3.28 \times 10^{-6}$ Å$^{-2}$), overlain by a thin metal-deficient layer and with a thick porous layer of elemental sulfur above.

Figure 6.23: Reflectivity profile of CuS thin film leached for 60 minutes in DDI water.
A series of copper sulfide thin films were leached in peroxide solutions (1% $\text{H}_2\text{O}_2$, 30% $\text{H}_2\text{O}_2$). As per the sample leached in DDI water, the weak peroxide solutions yielded an underlayer more dense than covellite ($\text{SLD} \sim 3.28 \times 10^{-6} \text{Å}^{-2}$), with a metal-deficient overlayer ($\text{SLD} \sim 2.56 \times 10^{-6} \text{Å}^{-2}$) and a thick copper oxide/hydroxide overlayer ($\text{SLD} \sim 2.0 \times 10^{-6} \text{Å}^{-2}$). Stronger solutions resulted in similar underlayer and mid-layer compositions and thicknesses, while the overlayer SLD ($1.46 \times 10^{-6} \text{Å}^{-2}$) approached the theoretical value for chalcanthite.

### 6.6. Conclusions

The ESEM results showed that surface attack was far more substantial for chloride-leached samples than sulfate-leached samples. In particular, circumneutral leaching demonstrated that preferential attack occurred at different crystal face orientations. Dynamic SIMS indicated that non-stoichiometry extended a reasonable distance (several hundred nanometres) into the sample for both chloride and sulfate leached systems, and, where non-ferric leaching was undertaken, that iron non-stoichiometry extended substantially further into the sample than copper non-stoichiometry. Thus, while congruent dissolution is reported in the long-term for chalcopyrite leaching [10, 11], the initial incongruent stoichiometry reported by some researchers [9, 42] clearly has a significant effect on long-term leaching and extends some way into the mineral.
These results were compounded by sulfur overlayers that did not seem to volatilise greatly under ultrahigh vacuum, possibly due to the gold sputter coating. ESEM and SERS investigations indicated that gold-sputtered peroxide leached samples (acid washed to remove ferric compounds) still showed an octasulfur product layer despite long-term degassing under UHV. The overlayer was highly porous but not highly crystalline in appearance. A porous overlayer would be expected on chalcopyrite given the volume differences alone: chalcopyrite has a density of 4.3 g cm$^{-3}$, compared to sulfur at 1.96 g cm$^{-3}$. The atomic radius varies from 1.84 Å for S$^{2-}$ (Pauling radius) to ~1.00 Å for elemental sulfur.

The XPS spectra did not show much sulfur speciation variation between the sulfate and chloride leached samples, though chloride leached samples contained higher stoichiometries of the high BE species. The highest BE S(2p) component occurred at 163.6 eV for sulfate leached and 163.9 eV for ferric chloride and potentiostatically leached samples, possibly indicating a thicker sulfur product layer for chloride leached sample. S(2p) doublet fitting indicated the presence of disulfide/polysulfide species on all acid leached samples. The sample ground in air displayed an iron-enriched surface with S(2p) spectra indicating disulfide and polysulfide species in agreement with published studies [8, 43]. The potentiostatically-leached sample had an iron-poor surface, also as expected. Copper was present as the monovalent species in all acid-leached samples.

None of the samples, excepting that which had undergone reductive scanning, yielded S(2p) binding energies characteristic of sulfate. It seems that during reductive scanning Cu$_2$S and Fe$^{2+}$ were formed which subsequently oxidised in air to yield a sulfate species. Jarosite was not indicated as a product on the oxidised samples. This is not to say that studies in which it was identified are incorrect. Such studies tended to be undertaken in much more concentrated solutions (0.1-0.2 M Fe$^{3+}$, pH 1.3-1.9) at elevated temperatures and hence solubility criteria may well have been exceeded. In this study, leachant concentrations were selected based on known kinetic information (e.g. in sulfate solutions, leaching is independent of ferric concentrations above 0.005 M [44]) and likely conditions of hydrometallurgical operations [45, 46]. Studies undertaken using high leachant concentrations or high temperatures do not represent conditions which are ever likely to be economically feasible for chalcopyrite leaching. Samples leached in hydrogen peroxide solutions did show some evidence of sulfate species, with high S(2p) binding energy components (~164.8 eV) possibly indicative
of polythionate species. Elemental sulfur was the primary sulfur species present on these samples. The sulfate salts tended to be highly soluble with acid washing and associated with cupric ion. Ferric oxide species were formed predominantly although with acid washing, Fe-S species were exposed. The major O(1s) species remaining on the surface after washing was adsorbed water.

ESEM studies of gold-decorated chalcopyrite surfaces revealed surface nanostructures consistent with the Raman enhancement observed (Chapter 4). XPS investigations also indicated “small particle gold” on gold-decorated surfaces, in conjunction with bulk gold. No Au$^+$ was observed, indicating that, if the gold condensation energy does lead to surface modification of the mineral, the polysulfide species so formed do not remain associated with the gold to any significant extent. Even after extensive post-decoration redox cycling, Au$^+$ species were not detected from the Au(4f) spectra.

Neutron reflectometry was used to investigate the model binary CuS thin film system. Ferric sulfate leaching resulted in a low-density product, not consistent with octasulfur, but rather a metal-deficient phase. Circumneutral leaching indicated a dense underlayer (Cu$_x$S, $x$$<$1.4) topped by a metal-deficient phase. Such systems are unlikely to produce sharp interfaces, but rather a gradual change in refractive index properties, hence may not be best suited to such means of investigation. However, these observations of metal-deficient overphases is in keeping with the SERS investigation of the thin films, in which anodic scanning produced a covellite-like phase and another phase containing sulfur bonds at a lower frequency shift. This phase would vanish on commencement of cathodic current during a negative-going scan, at higher potentials than chalcocite would form, indicating that the phase was metal-deficient, prevented further oxidation, and reformed CuS on negative-going scans. Uniqueness of fit of the neutron reflectometry data was an issue and further investigations are necessary to elucidate the product phases with greater certainty. Better characterisation of the pre-oxidised thin film would assist in this.

6.7. References


7. Conclusions
7.1. Concluding remarks

This thesis has described the results of a spectroelectrochemical investigation into chalcopyrite oxidation, providing a comparison of product development in both sulfate and chloride lixiviants. A range of samples were studied, including chalcopyrites from different locations with significantly different compositions. Other sulfide minerals were also examined as model systems and potential intermediates. Normal Raman spectroscopy proved well suited to investigating leached layers formed on chalcopyrite in chloride electrolytes. Thin layers (<300 nm, determined potentiostatically) of oxidative product formed at transpassive potentials on chalcopyrite in chloride solutions were observable. Under 514.5 nm, 632.8 nm and 785 nm irradiation, octasulfur was observed. Under 442 nm irradiation, a laser-induced phase was also observed even at very low irradiation densities. The laser-induced phase was observed, on occasion, in the absence of octasulfur and was not observed at surfaces on which significant oxidation had not occurred (e.g. fractured or air-oxidised samples). It consisted of a single intense sulfur-sulfur stretching band at ~452 cm$^{-1}$, with very weak modes at ~270 cm$^{-1}$ and 415 cm$^{-1}$ which were only rarely observed. The observance of broad bands at similar Raman shifts on pyrite has been reported in the literature and interpreted as polysulfides [1-4]. However, the bands are inconsistent with published spectra of inorganic polysulfides, showing no bending modes or splitting of stretching modes due to undistributed charge along the polysulfide chain. The laser-induced phase was also observed on oxidised pyrite and sphalerite under 442 nm irradiation but not on covellite. Inorganic polysulfides are known to have a high cationic electric field dependence [5, 6]; hence, the observation of the same polysulfide product across this range of minerals is unlikely. In addition, polysulfides are unstable in aqueous solutions, particularly acidic solutions and, hence, would be unlikely to survive to form a reasonably thick layer on the leached surface [7].

The laser-induced phase was not associated with any ν(SO) or ν(SH) modes. Studies of model compounds convincingly demonstrated that the laser-induced phase was polymeric sulfur. It decomposed at temperatures of ~70°C to octasulfur and was not observed on recrystallised rhombohedral sulfur crystals confirming that it was not due to S$\textsubscript{8}$ photodecomposition and thus agreeing with the literature. The parent phase
could not be positively identified but is probably an amorphous metal-deficient remnant lattice on the oxidised sulfide minerals that can be restructured, under ideal conditions, to polymeric sulfur.

Normal Raman investigations of product phase formed on chalcopyrite in sulfate solutions were difficult to undertake as, even after months of leaching, the product layers were very thin. A method was developed to precisely relocate surface sites on a sample after extensive leach periods. It was observed that the product distribution on chalcopyrite leached in sulfate was heterogeneous, occurring preferentially at cracks, fractures and phase boundaries. Where product was observed, \( \nu(\text{SS}) \) modes at wavenumbers downshifted from those of polymeric sulfur were observed, indicating longer sulfur bonds and possibly a lower sulfur valence state (more metal-deficiency). Elemental sulfur was only rarely detected utilising normal Raman techniques on sulfate-leached samples.

While polymeric sulfur was not generally observed under irradiation at wavelengths >442 nm, once chloride leached samples were subsequently kept under ultrahigh vacuum (UHV) conditions and the octasulfur volatilised, a broad \( \nu(\text{SS}) \) mode at ~454 cm\(^{-1}\) in the absence of bending modes or other stretching modes was observed under 632.8 nm irradiation. The signal had been overwhelmed by the elemental sulfur signal prior to UHV treatment. This phase is unlikely to be an octasulfur thin layer because non-bulk sulfur is known to have different properties to bulk octasulfur [8, 9] and it would not be detectable using normal Raman techniques. Hence, it is probably and amorphous phase consisting of sulfur chains or large ring structures.

Astoundingly, thiosulfate and tetrathionate were observed at a corroding pyrite surface using normal Raman Spectroscopy. A laser effect was noted under 514.5 nm irradiation, leading to octasulfur stimulation, probably arising from decomposition of the polythionate species. No polythionate species were observed from oxidised chalcopyrite or sphalerite, indicating that a different mechanism leads to octasulfur formation on pyrite.

Leaching of chalcopyrite in circumneutral pH solutions demonstrated similar sulfur product phases to those found in acid leaching. Optical and environmental scanning electron microscopy (ESEM) observations demonstrated that the iron oxyhydroxide product layer formed over the entire surface, and that the depth of the product layer varied with grain/crystal orientation. This illustrates that crystal orientation has an effect on the extent of leaching (kinetics) and product morphology.
No jarosite or ferric sulfate phases were observed on oxidised acid-leached samples, contrary to some reports in the literature [10, 11]. This was confirmed through X-ray Photoelectron Spectroscopic (XPS) studies. While sulfate signals were detected via XPS on circumneutral leached phases, quantification indicated that ferric oxyhydroxide was the primary phase present. Only rarely on aged samples leached under circumneutral conditions was Raman identification of a jarositic phase found. Generally, broad bands indicative of oxide species were observed. The published studies in which ferric sulfate phases were reported were conducted in significantly more concentrated leached solutions (0.1-0.2 M Fe³⁺, pH 1.3-1.9) and at higher temperatures in which the formation of such phases might be more prevalent. The sulfate phase formed on circumneutral leached samples was highly soluble and easily removed.

Dynamic Secondary Ion – Mass Spectrometry (SIMS) investigations demonstrated that the leached layers extended some way into the sample (several hundred nanometres), assuming most of the sulfur formed on the surface volatilised under UHV degassing. Iron deficiency extended further into the sample than copper deficiency, confirming published reports that chalcopyrite leaching commences incongruently and that the oxidative product is more deficient in iron than copper [12, 13]. XPS investigations of potentiostatically-oxidised samples confirmed that the surface was iron poor. This non-stoichiometry is obviously an important feature of leaching, being maintained at the oxidation front despite the long-term congruent dissolution kinetics reported.

Surface-enhanced Raman scattering (SERS) investigations of the initial oxidation products on chalcopyrite were undertaken by decorating the mineral surface with gold particles. Enhancement was achieved via electroless plating, sputtering and evaporative deposition of gold on the chalcopyrite surface. Most experiments were undertaken with vapour-deposited gold island films (<50 nm thick) as this was felt to be the least energetic of the deposition processes and therefore the least likely to impact on mineral oxidation. Both ex situ and in situ investigations were undertaken and showed an amorphous product with sulfur bonds at Raman shifts below the ν(SS) mode of octasulfur and in the absence of bending modes. The product spectrum was similar in sulfate and chloride solutions, in good agreement with electrochemical observations. Polythionate species were not detected at the surface.
ESEM investigation of the oxidised sample surfaces showed greater pitting and etching on chloride-leached samples, with etching particularly pronounced around grinding tracks. Nanostructures were evident on the gold-decorated surfaces, consistent with the enhancement observed in Raman spectroscopic studies.

The possibility of the gold condensation energy on the mineral surface leading to surface restructuring was considered. During in situ electrochemical experiments, the product evident after the sample was decorated with gold, reformed after reduction of the oxidative product indicating that gold condensation energy did not affect the oxidative layer. It was possible that non-oxidative dissolution products and reduction products (H$_2$S) from chalcopyrite were sorbed on the gold and that it was these products that were being observed during in situ SERS investigations while potential scanning. Some care was taken to examine model gold/sulfur systems in acid electrolytes and it was noted that the continued supply of H$_2$S from chalcopyrite to Au at potentials at which sulfur monolayers and multilayers formed on Au was unlikely to occur, particularly after repeated cycling. Diagnostic ν(AuS) modes, particularly evident at potentials <-0.35 V/Ag/AgCl in the model system, were not evident on the Au-decorated chalcopyrite. Model system investigations also indicated that chloride competition for Au sites is significant at low sulfide concentrations and gold-chloride interaction is readily distinguished voltammetrically and spectroscopically. XPS Au(4f) spectra indicated the presence of bulk gold and “small particle” gold on leached and unleached gold-decorated chalcopyrite surfaces with no detection of Au$^+$ species.

The model binary CuS system was investigated using normal Raman, SERS and neutron reflectometry techniques. It was demonstrated that CuS was not an intermediate in chalcopyrite oxidation, as has sometimes been suggested [14-16]. Neutron reflectometry proved useful in describing the properties of thin films such as those formed in corroding copper sulfide systems, but the technique was not adaptable to the corroding chalcopyrite surface.

XPS studies produced results similar to those in the literature, with surface speciation evident on sulfate and chloride leached samples. No sulfate species were detected and the S(2p) fitting suggested disulfide/polysulfide type species although without resolution into undistributed charge expected from such species. The chloride-leached samples yielded a greater proportion of higher S(2p) binding energy components.
Normal Raman and SERS investigations indicate that oxidation of chalcopyrite proceeds by a mechanism of cation removal and coincident oxidation of the remnant sulfide lattice. Bonding does not appear to commence immediately and, when it does occur, a somewhat amorphous structure is formed. This amorphous leached layer is stable for long periods of time at room temperature and extends deeply into the mineral, rather than being confined to a ~3 nm layer as had been proposed in the literature [12, 14]. In the case of chloride leaching, the leached layer ages to sulfur although of a somewhat amorphous nature that does not volatilise extensively under vacuum. The greater aging of the leached layer on chloride-leached samples is probably facilitated by the ability of copper to leave the lattice as a cuprous complex.

7.2. Future work

The facilitation of SERS through the formation of Au island films opens up the possibility of exploring a vast range of interactions at mineral surfaces at the submonolayer level. This technique could therefore be extended to other minerals with good effect. In particular, it would be well suited to studying the interaction of chalcopyrite surfaces with flotation reagents, since the binding of such reagents to model Cu, Au and Ag surfaces is well characterised and tends to be distinctive.

With respect to chalcopyrite oxidation, it would be prudent to further investigate non-oxidative dissolution mechanisms and kinetics in acid solutions, and examine the possibility of interaction of such products with the SERS substrates. Thus, detailed studies of the effect of $E_H$ on surface product formation are suggested. Some *ex situ* investigations using alternative SERS substrates would also be beneficial to provide further evidence that Au condensation is not affecting the mineral surface unduly.

Investigation of novel leach technologies and appropriate copper complexants on the leach product and kinetics of the system might yield alternative leach systems that don’t suffer the inherent drawbacks of chloride systems. Unfortunately, normal Raman techniques do not appear to be suited to the cupric/ferrous leaching system proposed by Hiroyoshi *et al.* [17-20] in which the intermediate compound is unlikely to be Raman active. However, other catalysts, such as Ag⁺, are probably well suited to investigation via Raman Spectroscopic techniques.

The effects of sulfur solvents on the surface during ferric chloride leaching and ferric sulfate leaching might be studied using spectroelectrochemical techniques and hence
assist with some of the controversy about whether sulfur solvents alter the leaching rate. In particular, the effect on the observance of the laser-induced phase would be interesting.

While galvanic effects of accessory minerals on chalcopyrite leach rate have been reported in the literature, spectroelectrochemical methods facilitate the observation of leach product distribution and morphology over the surface. In particular, SERS might be used to undertake spot analyses to study interactions in complex systems at different mineral faces.

Investigation of bioleaching systems, including their kinetics and surface products could be undertaken using spectroelectrochemical techniques. Specifically, the differing effects of thermophile versus mesophile bacterial populations on leaching would assist in designing and optimising such systems. Parallel detailed investigations of sterile leaching, and investigation of proposed hydrometallurgical methods via spectroelectrochemical techniques may provide fundamental information on these processes and their key differences.

7.3. References


